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INDUSTRIAL HYGIENE ANALYSIS MANUAL
NUCLEAR DIVISION INDUSTRIAL HYGIENE

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Oak Ridge K-25 Site
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INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

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*This radiochemical procedure is principally applied to samples and programs administrated by the Health Physics functions of UCC-ND; however, the analytical results are also of interest to industrial hygienists, as confirmation of potential chemical toxicological problems.

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*This radiochemical procedure is principally applied to samples and programs administered by the Health Physics functions of UCC-ND; however, the analytical results are also of interest to industrial hygienists, as confirmation of potential chemical toxicological problems.

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

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INTRODUCTION

This manual of analytical procedures is a compilation of methods used within the Nuclear Division of Union Carbide Corporation in support of the industrial hygiene programs of the four plants. The emphasis is on chemical analysis procedures conducted in the laboratory on samples collected by, or under the direction of, the Industrial Hygiene Departments.

Industrial hygiene programs within the chemicals industry have received increased attention in recent years. Enhanced awareness of toxic substances by industrial management, employees, government, and the public has brought forth a number of new federal regulations. Some of these are under the charge of the Environmental Protection Agency; those most concerned with the industrial workplace are promulgated and administered by the Occupational Safety and Health Administration (OSHA), often at the recommendation of the National Institute for Occupational Safety and Health (NIOSH).

The protection of employees from exposure to toxic chemicals has been a traditional concern of UCC-ND and has been regularly scrutinized by management, by Union Carbide Corporation, and by the Department of Energy and its predecessors. Accordingly, the methodology for monitoring the working environments has been quite well established for a variety of recognized hazards. Nevertheless, the four plants of UCC-ND, all dealing closely with a variety of chemicals, have reviewed their industrial hygiene programs with increased frequency and have generally increased the scope of workplace monitoring. The laboratories have therefore been challenged to keep pace, to try to anticipate new plant programs which may need area sampling, to modernize their methodology, and often to gear for increased workloads.

As the Table of Contents for this manual reveals, the samples associated with industrial hygiene are generally derived from the working air environments, collected by special traps, absorbers, or filters. Additionally, some toxics may be monitored by analyses of urine, feces, or blood samples. The chemical types include both inorganics and organics. Some of the toxics are also radioactive; a few of the analytical procedures therefore are radiochemical methods; and while the radiochemical procedures are principally applied to samples and programs administered by the Health Physics functions of UCC-ND, the analytical results are also of interest to industrial hygienists, as confirmation of potential chemical toxicological problems. A category of miscellaneous sample analysis has also been included in the manual, to cover such industrial hygiene interests as insulating materials, drinking water quality, and certain chemicals which can contaminate work surfaces.

APPROVED BY Y-12	LAB / IH	APPROVED BY ORGDP	LAB / IH	APPROVED BY UCCND-COORD'R C W Weber
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The resources employed in generating industrial hygiene analytical procedures for use in the laboratory are many. The laboratory procedures manuals of the four plants have documented a host of techniques, some developed within UCC-ND, and some adopted from analytical journals. Most of the procedures in this manual include a section for References, listing the literature resources related to the procedure. A relatively recent resource which has become useful to the industrial hygiene programs is the:

> NIOSH Manual of Analytical Methods: Second Edition, Volumes 1-5 (1977-1979); and Volume 6 (1980): U. S. Department of Health, Education, and Welfare, National Institute for Occupation Safety and Health.

Some of the methods presented in the NIOSH Manual are applicable directly to the UCC-ND programs and have been selected by the procedures committee for inclusion verbatim in this manual.

The procedures in the manual are assembled, reviewed, and approved by the Nuclear Division Four-Plant Committee on Industrial Hygiene Analysis Procedures. The present committee members are:

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INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

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QUALITY CONTROL, EXTERNAL PROGRAM

1.0 Scope and Application

1.1 Appropriate controls on each parameter are employed by each of the laboratories to ensure that the reported analytical data are valid and meet the needs of the Industrial Hygiene organizations at each plant in their monitoring requirements.

1.2 As part of the Quality Assurance program at each plant, the analytical services employed to support the Industrial Hygiene functions must ensure reliable data, available in a timely and cost-effective manner, to demonstrate that pollutants to which employees are exposed at each plant are adequately monitored and are in compliance with the limitations established by the U. S. Occupational Safety and Health Administration (OSHA) and the U. S. Department of Energy (DOE).

2.0 Summary of Program

2.1 In addition to the appropriate internal controls and calibration techniques applied by each laboratory to ensure correct results, an external program is employed to compare the proficiency of an individual laboratory with that of other laboratories and to detect problem areas.

2.2 Participation in this QA program, administered by the U. S. National Institute for Occupational Safety and Health (NIOSH), fulfills one of the basic requirements for becoming a "certified laboratory" for the analysis of air samples related to industrial hygiene monitoring.

2.3 This program also provides a proficiency rating for each participating laboratory on every type of analysis in the program. Each laboratory is identified by a code number and receives a statistical evaluation of its reported results which includes its relative performance compared to all the reported results.

3.0 Description of Program

3.1 The program evaluates the measurement of metals, silica dust and asbestos fibers collected on filter discs, and organic compounds absorbed on charcoal filters. The filter discs are identified as to the contaminants present, but the quantities are not indicated; the level of a contaminant usually varies with each set of samples.

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3.1.1 The metal contaminants are cadmium, lead, and zinc. There are five filter discs per set for the metals, a blank plus four discs with unspecified quantities of each of the three metallic elements.

3.1.2 The silica controls are "cycloned dust"-generated to provide an even distribution of the particles on the surface of the disc, which is a cellulose membrane, 0.8-micron pore size, 25-mm diameter Millipore filter.

3.1.3 The asbestos controls consist of fibers evenly distributed on the surface of the filter disc for determining the count per unit area.

3.1.4 The organic contaminants consist of one or two identified compounds absorbed on charcoal in sample tubes. There are four filters with varying quantities present, plus the blank charcoal filter.

3.2 The analytical results determined at each plant are reported through the Industrial Hygiene Departments to the NIOSH Robert A. Taft Laboratories in Cincinnati, Ohio for evaluation.

3.3 The NIOSH Cincinnati laboratory disseminates statistical evaluations to each participating laboratory on a regular basis.

4.0 Data Evaluation

4.1 This NIOSH program, known as the PAT (Proficiency Analytical Testing) program, provides quarterly data to each participant as follows:

a. Summary of statistics for a quarterly round of samples - Table 1

b. Mean ratio of reported results for six quarters - Figure 1

c. Error ratio for individual results for six quarters - Figure 1

d. Proficiency rating for a laboratory - Figure 2

e. Relative performance for six quarters - Table 2

4.2 PAT Summary Statistics

Summary data are presented in Table 1 to assist in understanding the calculation of mean ratios and residuals (error ratios) used to construct PAT data charts. The data charts present a laboratory's PAT performance over several rounds in a format similar to a control chart; the charts are printed by computer. Because PAT data appear to be log-normally distributed, the referenced mean values are all geometric rather than arithmetic; however, arithmetic means are of interest to some participants. The Geometric Mean listed in Table 1 is the grand geometric mean of all participants in the particular PAT round. The values listed in Table 1 are calculated with residual and mean outliers removed.

4.2.1 Laboratory Mean Ratio

The grand geometric mean (without residual and mean outliers, R&M) is used to calculate a laboratory's plotted mean ratio (Figure 1, upper) using the following formula:

$$\text{Mean Ratio} = \frac{\text{Laboratory Geometric Mean}}{\text{Grand Geo. Mean (w/o R\&M)}} = \frac{\sqrt[4]{X_1 \cdot X_2 \cdot X_3 \cdot X_4}}{\text{Grand Geo. Mean (w/o R\&M)}}$$

Where X_1 = A Laboratory's Result for Filter 1,

X_2 = A Laboratory's Result for Filter 2,

X_3 = A Laboratory's Result for Filter 3, and

X_4 = A Laboratory's Result for Filter 4.

The grand mean falls near the center of the PAT laboratory means histogram (a graphical form used by the NIOSH laboratory but not currently submitted to the participants). The means chart (Figure 1, upper) is centered at 1.00 corresponding to the approximate center of the histogram. The vertical axis of the chart is on a log scale. If, for example, a limit equals 2.00, a corresponding lower limit will equal the inverse of the upper limit (1 divided by 2.00), 0.50. The chart is a true graphical representation with upper and lower limits equidistant from the 1.00 center line.

PAT data charts (e.g. Figure 1) include tolerance limits based on the distribution after statistically different laboratories are removed. The limits (X_I, inner limit, and X_O, outer limit) divide the distribution of results into three groups:

1. The NIOSH laboratory is 99% confident that those values outside X_O are part of the outer 2% of the distribution. For this reason they are considered as an indication of unacceptable performance.

2. The NIOSH laboratory is 99% confident that those values inside X_I are part of the center 98% of the distribution. For this reason they are considered as an indication of acceptable performance.

3. Those values falling between X_I and X_O are suspect and it cannot be stated with a high degree of confidence that they are part of the inner 98% of the distribution. For this reason they are considered as an indication of questionable performance.

4.2.2 Laboratory Error Ratio (Residual Test)

The residual test measures the laboratory's ability to obtain consistent results, not a laboratory's ability to obtain accurate results. A laboratory's plotted residual (error ratio) can be calculated as follows, assuming that the results of four filter analyses have been submitted:

$$\text{Residual 1} = \frac{X_1}{\text{Predicted Value 1}} = \frac{X_1}{F_1} \cdot \frac{\sqrt[4]{F_1 \cdot F_2 \cdot F_3 \cdot F_4}}{\sqrt[4]{X_1 \cdot X_2 \cdot X_3 \cdot X_4}}$$

$$\text{Residual 2} = \frac{X_2}{\text{Predicted Value 2}} = \frac{X_2}{F_2} \cdot \quad '' \quad ''$$

$$\text{Residual 3} = \frac{X_3}{\text{Predicted Value 3}} = \frac{X_3}{F_3} \cdot \frac{\sqrt[4]{F_1 \cdot F_2 \cdot F_3 \cdot F_4}}{\sqrt[4]{X_1 \cdot X_2 \cdot X_3 \cdot X_4}}$$

$$\text{Residual 4} = \frac{X_4}{\text{Predicted Value 4}} = \frac{X_4}{F_4} \cdot \quad '' \quad ''$$

Where F_1 = Geometric Filter Mean 1 (without residual outliers),

F_2 = Geometric Filter Mean 2 (without residual outliers),

F_3 = Geometric Filter Mean 3 (without residual outliers), and

F_4 = Geometric Filter Mean 4 (without residual outliers).

If a laboratory has submitted less than four values for a particular parameter, the equations are modified accordingly.

A laboratory's error ratios are interrelated because the product of error ratios equals one. A single error ratio exceeding PAT limits indicates excessive intra-laboratory variation. The value plotted on the residuals chart is the error ratio (the ratio of the observed value to the predicted value). The predicted value is defined as the filter mean times the laboratory mean divided by the grand mean. The filter means and grand means used to calculate the residuals chart are calculated with residual, but not mean, outliers removed. Although the grand mean with residual outliers removed is not identical to the grand mean with residual

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and mean outliers removed, the two values are usually very close to each other and both fall near the center of the laboratory mean histogram. The ratio of laboratory mean to grand mean is included in the calculation of the predicted value. Only laboratories with identical laboratory means will have an identical set of predicted values. A laboratory which obtains consistent, high values will have high predicted values and, therefore, still have error ratios which are within PAT limits.

4.3 Proficiency Rating

4.3.1 Figure 2 shows a NIOSH PAT Proficiency Rating form filled out by the NIOSH Cincinnati laboratory for a specific participating laboratory. All participants strive for a continued rating of "proficient."

4.3.2 A laboratory's rating may change from round to round, for a particular type of analysis, or for "overall" performance. The rating criteria were modified in a letter from NIOSH to PAT participants on December 14, 1979. The new criteria are interpreted as follows:

4.3.2.1 For an <u>individual contaminant</u>, the laboratory is rated as follows:

a. "Proficient" if all results have been reported and none are classified as outliers on the last two consecutive rounds.

b. "Nonproficient" if all results have been reported and all are classified as outliers on the last two consecutive rounds.

c. "Nonproficient" in all other situations if more than one-third of the last six rounds are classified as outliers.

4.3.2.2 For <u>overall performance</u>, the laboratory is rated as follows:

a. "Proficient" if at least two-thirds of the individual PAT contaminant analyses are rated proficient for the most recent round. (Exception: see c. below.)

b. "Nonproficient" if more than one-third of the individual PAT contaminant analyses are rated nonproficient for the most recent round.

c. "Nonproficient" if any individual PAT contaminant analyses are rated nonproficient for more than six consecutive rounds.

4.4 Laboratory Relative Performance

Table 2 is a compilation by NIOSH submitted to each participating laboratory to reflect its comparative performance on the most recent six rounds of analyses on all measurements. The summary at the bottom is designed to show the key areas in which a laboratory should take corrective quality control action.

5.0 Use of Evaluated Data

5.1 Each laboratory uses the evaluated data for the quality assurance aspects of its routinely reported results.

5.2 There are no specific requirements for individual laboratory actions based on the evaluated data. Each laboratory assumes the responsibility for taking action if the data indicate its results do not conform to the requirements of the procedures and the needs of the organizations which submit samples for analysis.

5.3 The PAT proficiency rating and supporting statistical data are used by each participating laboratory to guide the corrective action needed to achieve or maintain a rating of "proficient" on all measurements rated.

6.0 References

6.1 NIOSH Proficiency Analytical Testing (PAT) Program, U. S. Dept. of Health, Education, and Welfare, DHEW (NIOSH) Publication No. 79-128 (1979).

6.2 PAT Statistics and Ratings for Round 54, Letter from Chemical Reference Laboratory (NIOSH), Cincinnati, OH to PAT Participants, June 11, 1979.

6.3 Explanation and Examples of PAT Statistics and Data Charts, Letter from Chemical Reference Laboratory (NIOSH), Cincinnati, OH, to PAT Participants, August, 1977.

6.4 PAT Statistics and Ratings for Round 57, Letter from Chemical Reference Laboratory (NIOSH), Cincinnati, OH, to PAT Participants, December 14, 1979.

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Table 1

P A T ROUND 54
JUNE 6, 1979
FILTER SUMMARY STATISTICS *

CONTAMINANT	LAB 37830/002 DATA	FILTER	GEOMETRIC MEAN	ARITHMETIC MEAN	STANDARD DEVIATION	COEFFICIENT OF VARIATION
LEAD	0.0120	1	0.0100	0.0100	0.0012	0.1177
	0.0607	2	0.0594	0.0593	0.0036	0.0600
	0.0555	3	0.0557	0.0556	0.0034	0.0619
	0.0345	4	0.0331	0.0330	0.0020	0.0593
CADMIUM	0.0139	1	0.0146	0.0145	0.0010	0.0713
	0.0164	2	0.0177	0.0176	0.0011	0.0601
	0.0074	3	0.0085	0.0085	0.0005	0.0622
	0.0083	4	0.0096	0.0095	0.0006	0.0591
ZINC	0.2043	1	0.2119	0.2101	0.0149	0.0707
	0.1014	2	0.1091	0.1080	0.0081	0.0750
	0.1513	3	0.1631	0.1612	0.0102	0.0634
	0.1925	4	0.2059	0.2035	0.0107	0.0524
SILICA		1	0.0979	0.1059	0.0498	0.4706
		2	0.0556	0.0608	0.0273	0.4483
		3	0.1137	0.1195	0.0373	0.3124
		4	0.0958	0.1009	0.0316	0.3133
ASBESTOS	419.0	1	530.2	607.2	275.7	0.4541
	250.0	2	344.5	388.4	152.8	0.3933
	624.0	3	655.6	751.0	318.9	0.4247
	403.0	4	361.1	413.0	175.3	0.4246
SOLVENT 1	0.0278	1	0.0301	0.0303	0.0042	0.1369
	0.0129	2	0.0135	0.0137	0.0028	0.2012
	0.0602	3	0.0611	0.0614	0.0079	0.1281
	0.0074	4	0.0075	0.0077	0.0018	0.2331

* ALL FILTER SUMMARY STATISTICS ARE COMPUTED AFTER RESIDUAL AND MEAN OUTLIERS REMOVED EXCEPT FILTER GEOMETRIC MEANS WHICH ARE CALCULATED WITH ONLY RESIDUAL OUTLIERS REMOVED.

NIOSH PROFICIENCY ANALYTICAL TESTING (P A T) PROGRAM
LAB 37830/002 ASBESTOS

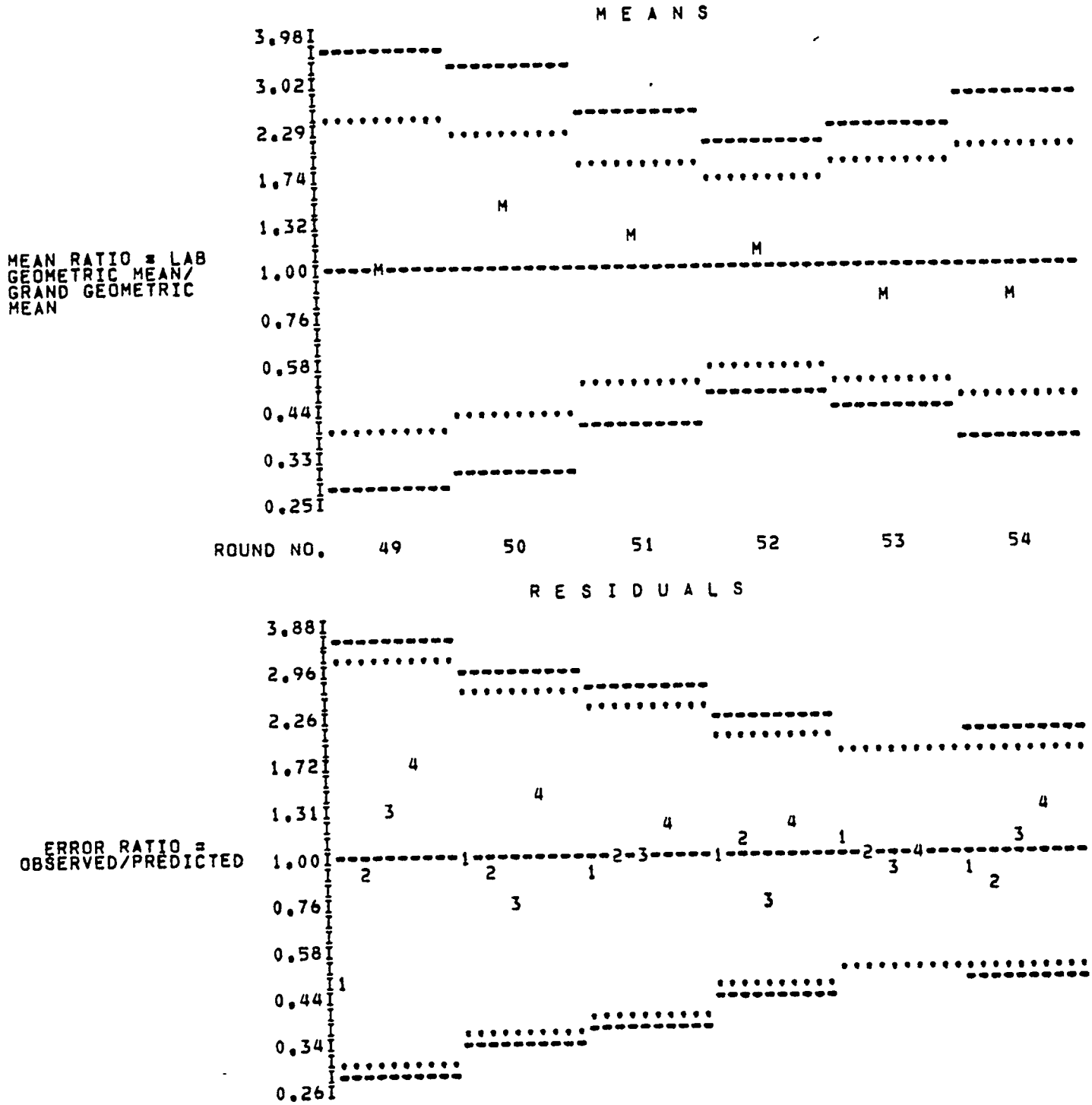

Figure 1. MEANS AND RESIDUALS CHARTS FOR A PARTICIPATING LABORATORY IN THE PAT PROGRAM

UCN-10766B (12 8-78)

DATE _____

ROUND 54

LAB I.D. 37830/002

NIOSH PAT PROFICIENCY RATING

Criteria Listed on Back of Form

	Proficient	NonProficient	Not Rated
New PAT Laboratories	___	___	___
All Other PAT Laboratories			
Lead	☑	☐	☐
Cadmium	☑	☐	☐
Zinc	☑	☐	☐
Silica	☐	☐	☑
Asbestos	☑	☐	☐
Organic Solvents	☑	☐	☐

Number of Analyses: 5 Proficient 0 NonProficient 1 Not Rated

OVERALL LABORATORY PERFORMANCE	☑	☐	☐

Figure 2. PROFICIENCY RATING FOR A PARTICIPATING LABORATORY IN THE PAT PROGRAM

Table 2

P A T ROUNDS 49 TO 54
JUNE 6, 1979
LABORATORY 37830/002 RELATIVE PERFORMANCE

CONTAMINANT	ROUNDS WITH AN OUTLIER	ROUNDS WITH A QUESTIONABLE RESULT	ROUNDS WITH NO PARTICI- PATION	LABS WITH HIGHER SCORE	LABS WITH EQUAL SCORE	LABS WITH LOWER SCORE	TOTAL LABS SCORED	LABS NOT SCORED
LEAD	0	1	0	72	14	86	172	65
CADMIUM	1	1	0	128	8	33	169	68
ZINC	1	0	0	70	32	64	166	71
SILICA	0	0	6	*	*	*	87	150
ASBESTOS	0	0	0	0	62	72	134	103
SOLVENTS	0	2	0	40	3	108	151	86

* INDICATES LABORATORY PARTICIPATED IN TOO FEW ROUNDS TO BE CONSIDERED IN SCORING

PERFORMANCE SUMMARY

	49	50	51	52	53	54
LEAD			um			
CADMIUM				R		lm
ZINC				R		
SILICA	*	*	*	*	*	*
ASBESTOS						
SOLVENT 1	lm		r			
SOLVENT 2			-	-		-

- ROUND DOES NOT HAVE SOLVENT 2
BLANK ANALYSIS RESULT ACCEPTABLE
* ANALYSIS NOT PERFORMED
R RESIDUAL OUTLIER
lm lower questionable mean
um upper questionable mean
r questionable residual

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-105
DATE	October 27, 1982
SUPERSEDES	
PAGE	1 OF 4

AMMONIA IN AIR, DIRECT NESSLER SPECTROPHOTOMETRIC METHOD

Analyte:	Ammonia, NH_3	Method No.:	IHA-105
Matrix:	Air	Range:	10-80 mg/m^3
Procedure:	Midget impinger; spectrophotometry	Precision:	RSD = 10% (Analytical)

1.0 Principle of the Method

1.1 Ammonia is collected in a dilute sulfuric acid solution in a midget impinger to form ammonium sulfate.

1.2 Nessler reagent is used to produce a yellow-brown complex.

1.3 The ammonia concentration is determined by reading the absorbance of the yellow-brown solution at 425 nm and comparing it with a standard curve.

2.0 Range and Sensitivity

2.1 The Nessler reagent is sensitive to as little as 0.002 mg of ammonia.

2.2 The range of application of this method is 0.10 mg to 0.80 mg of ammonia in a 10-liter air sample.

3.0 Interferences

3.1 Particulate ammonium salts will react with Nessler reagent to give a false high reading. These can be removed by filtration of the air before its passage into the midget impinger.

4.0 Precision and Accuracy

4.1 Precision and accuracy data are not available for the overall sampling and analysis procedure.

4.2 Precision of the analytical measurement is about 10% RSD.

APPROVED BY Y-12	LAB R. J. McElhaney	APPROVED BY ORGDP	LAB F. H. Frazier	APPROVED BY UCCND-COORD'R	C W Weber
	IH Gary L. Bear		IH David J. Dunn		
APPROVED BY PGDP	LAB R. E. Simmons	APPROVED BY ORNL	LAB J. R. Lawson	NUMBER	IHA-105
	IH C. H. Gurak		IH James A. Lake		

UCN-13234
(1235 1-79)

5.0 Advantages and Disadvantages of the Method

5.1 The method provides a sensitive measure of ammonia in air.

5.2 Entrained (particulate) ammonium salts can interfere.

6.0 Apparatus

6.1 Battery operated personal air sampling pump, capable of drawing 1 liter of air per minute through 10 mL of absorbing solution.

6.2 Impingers, standard midget, all-glass, calibrated.

6.3 Beckman Model B spectrophotometer, or equivalent.

6.4 Spectrophotometer cells, 1-cm.

6.5 Volumetric flasks, 50-mL, 100-mL, 200-mL, 1000-mL, glass-stoppered.

6.6 Pipettes, 0.5-mL, 1.0-mL, 5-mL, 10-mL, 20-mL.

6.7 Graduated cylinders, 25-mL, 50-mL, 100-mL.

7.0 Reagents

7.1 All reagents should be analytical reagent grade.

7.2 Double distilled water, free of ammonia.

7.3 Potassium iodide.

7.4 Mercuric chloride.

7.5 Potassium hydroxide.

7.6 Ammonium sulfate.

7.7 Nessler Reagent. Dissolve 35 grams of mercuric chloride in 500 mL of hot water. Filter and allow to cool. Dissolve 62.5 grams of potassium iodide in 260 mL of cold water. Gradually add the mercuric chloride solution to 250 mL of the iodide solution until a slight permanent red precipitate is formed. Dissolve the precipitate with the remaining iodide solution and again add mercuric chloride slowly until a slight permanent red precipitate forms.

Dissolve 150 grams of potassium hydroxide in 250 mL of distilled water. Add this solution to the potassium iodide-mercuric chloride solution and dilute to 1 liter with distilled water. Stir thoroughly and allow to stand a day or so, and decant the clear liquid.

Warning. The Nessler reagent should be handled with caution because of its toxicity and corrosive properties.

7.8 Standard Ammonium Sulfate Solution. Dissolve 77.6 mg of ammonium sulfate in distilled water and dilute to 1 liter. One mL of this solution contains 20 μg of ammonia. Discard solution after a week.

7.9 Absorbing Solution. Dilute 2.8 mL of concentrated sulfuric acid (18 M) to 1 liter with distilled water to form 0.1 N sulfuric acid.

8.0 Procedure

8.1 Sampling. Add 10 mL of absorbing solution to each midget impinger including one for the blank. Attach the bubbler to a personal air sampling pump and draw air through the bubbler at a rate of 1 liter/min for 10-15 min. Record the volume of air sampled.

8.2 Color Development. Dilute the sample to 50 mL with distilled water in a volumetric flask and shake well. Take 1 mL of this solution, dilute to 50 mL with distilled water in another volumetric flask and mix well. Add 2 mL of Nessler reagent to the latter flask and determine absorbance after 20 min at 425 nm in a spectrophotometer using a 1-cm cell. Treat the blank in the same manner as the sample.

NOTE: Some investigators use the wavelength of 440 nm with a 10-minute development time. Better precision is believed to be obtained with the more stable color measured at 425 nm after 20 minutes.

9.0 Calibration and Standards

Dilute samples of 0, 5, 10, 20, 30 and 40 mL of the standard ammonium sulfate solution and process in the same manner as described

UCN-10766B (12 8-78)

in Section 8.2. Measure the absorbance vs the reagent blank in a spectrophotometer at 425 nm. Prepare a standard curve of absorbance versus micrograms of ammonia.

10.0 Calculations

$$NH_3\ ,\ mg/m^3 = \frac{W}{V}$$

where:

W = μg of ammonia from the standard curve (corrected for the blank), and
V = Volume of air in liters, corrected to 25°C and 760 torr.

11.0 References

11.1 Goldman, F. H. and M. B. Jacobs, Chemical Methods of Industrial Hygiene, Interscience Publishers, New York, 1953.

11.2 Elkins, H. B., The Chemistry of Industrial Toxicology, 2nd Ed., John Wiley and Sons, New York, 1959.

11.3 NIOSH Manual of Analytical Methods, 2nd Ed., Vol. 1, Method 205; U. S. Department of Health, Education, and Welfare; Cincinnati, OH; April 1977.

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-110
DATE	Nov. 27, 1979
SUPERSEDES	
PAGE	1 OF 22

ASBESTOS FIBERS IN AIR, MICROSCOPIC COUNT METHOD

Analyte:	Asbestos fibers	Method No.:	IHA-110 (NIOSH 239)
Matrix:	Air	Range:	0.1 - 60 fibers/cm^3
Procedure:	Filter collection, slide preparation, fiber count using phase-contrast microscopy	Precision (CV_T):	0.24 to 0.38
		(or RSD):	24 to 38%

For this analysis, the undersigned committee has approved for inclusion in this manual an existing procedure, exactly as published. Accordingly, the following pages are taken verbatim from the NIOSH Manual of Analytical Methods, Second Edition, Vol. 1, U. S. Department of Health, Education, and Welfare, Method 239, 1977.

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APPROVED BY PGDP	LAB R. E. Simmons IH C. W. Turak	APPROVED BY ORNL	LAB W R Laing IH J. A. Ealy	NUMBER IHA-110

UCN-13234
(1235 1-79)

The following procedure is a photocopied excerpt from: NIOSH Manual of Analytical Methods, Second Edition, Vol. 1, U. S. Department of Health, Education, and Welfare, 1977.

ASBESTOS FIBERS IN AIR

National Institute for Occupational Safety and Health

Analytical Method

Analyte:	Asbestos fibers	**Method No.:**	P&CAM 239
Matrix:	Air	**Range:**	0.1-60 fibers/cm^3
Procedure:	Filter collection, microscopic count	**Precision (CV_T):**	0.24 to 0.38
Date Issued:	3/30/77	**Classification:**	D (Operational)
Date Revised:			

1. **Principle of the Method**

1.1 This method describes the equipment and procedures for collecting, mounting, and counting asbestos fibers on cellulose ester membrane filters in the evaluation of personal samples of airborne asbestos fibers. The purpose of the method is to determine an employee's index of exposure to airborne asbestos fibers. The method is primarily a personal monitoring technique, but can be used for area monitoring.

1.2 The sample is collected by drawing air through a membrane filter by means of a battery powered personal sampling pump. The filter is transformed from an opaque solid membrane to a transparent optically homogeneous gel. The fibers are sized and counted using a phase-contrast microscope at 400-450X magnification.

1.3 Definitions. Asbestos fiber, for counting purposes, means a particulate which has a physical dimension longer than 5 micrometers and with a length to diameter ratio of 3 to 1 or greater. Asbestos includes chrysotile, cummingtonite-grunerite (amosite), crocidolite, fibrous tremolite, fibrous anthophyllite, and fibrous actinolite.

1.4 Any laboratory attempting to use this procedure should have at least one counter attend a training course conducted by an experienced, proficient laboratory. Novice, untutored counters, using only published instructions, can easily obtain counts of half those performed by experienced, proficient counters. Large differences between laboratories can be caused by: 1) differences in technique and observing ability among counters and 2) small, but significant, differences between microscopes meeting the basic specifications of Section 6.2. The following procedures are recommended:

1.4.1 All microscopists who perform asbestos counting should meet together for an "asbestos counting workshop" at least quarterly. This is best accomplished with counters from several laboratories using their own microscopes.

1.4.2 Each microscopist should count the same series of slides and with the results being compared.

1.4.3 Differences between counters should be resolved with side-by-side counting of the fields by the different counters.

1.4.4 Individuals who are found to be persistent outliers over several sessions should be encouraged to seek other tasks in their respective laboratories.

2. **Range and Sensitivity**

2.1 The usable range is primarily a function of sample volume, microscope count field area, and background airborne particulates. The influence of these variables is discussed in 8.1.3. For a microscope count field area of 0.003 mm^2 (see Figure 1) and a pump flow rate of 1.7 lpm, the optimal fiber densities would be produced over the range of 0.4 fiber/cm^3 (8-hour sample) to about 60 fibers/cm^3 (15-minute sample). For a field area of 0.006 mm^2 (see Figure 2) and a pump flow rate of 1.7 lpm, the optimal range is 0.2 fiber/cm^3 (8-hour sample) to about 30 fibers/cm^3 (15-minute sample). In each case, the optimal detection limits are inversely proportional to pump flow rate.

The upper detection limit can be extended by using sample times less than 15 minutes or using lower flow rates. The lower detection limit can be extende[illegible] by increasing the flow rate up to about 2.5 lpm. Filter surface fiber densities less than o[illegible] (less than about 0.5 to 1.0 fiber per count field) are still adequate, but will lead to decr[illegible]d precision for the method (increased coefficient of variation, see Section 4).

The minimum total fiber count in 100 fields considered adequate for reliable quantitation is 10 fibers. Thus, the lower limit of reliable quantitation is 0.1 fiber cm^3 (100,000 fibers m^3). For this level, a flow rate of about 2.5 lpm is recommended. For a field area of 0.003 mm^2, the minimum sample time would be about 2 hours. For a field area of 0.006 mm^2, the minimum sample time would be about 1 hour.

2.2 This method considers only fibers with a length to diameter ratio of 3 to 1 or greater and a length greater than 5 micrometers.

3. **Interferences**

In an atmosphere known to contain asbestos, all particulates with a length to diameter ratio of 3 to 1 or greater, and a length greater than 5 micrometers should, in the absence of other information, be considered to be asbestos fibers and counted as such.

4. **Precision and Accuracy**

4.1 In the past decade, there have appeared a number of articles examining sources of variation in the asbestos sampling and counting procedure. These include: Lynch et al. (11.1), Weidner and Ayer (11.2), Conway and Holland (11.3), Leidel and Busch (11.4), Beckett and Attfield (11.5), and Rajhans and Bragg (11.6). The sources of variation will be discussed by stages in the membrane filter evaluation procedure.

4.2 **Sources of Variation in the Sampling Process.** These include variations in pump flow rate, proximity of the filter to the employee's body, and filter location (left to right) in the employee's breathing zone.

4.2.1 Section 9.1 requires that the personal sampling pump be calibrated with sufficient accuracy such that the 95% confidence limits on the flow rate are ± 10%. This is equivalent to a coefficient of variation (CV) of about 5%. However, this CV makes a negligible contribution to the total CV for the method due to the relatively large CV of the counting procedure.

4.2.2 Conway and Holland (11.3) concluded that positioning of the filter cassette on the wearer (regarding the angular portions of the filter and their proximity to the wearer) is not a significant factor in determining the fiber distribution on filters.

4.2.3 Weidner and Ayer (11.2) concluded that there is no appreciable difference between samples collected on either the right or left sides of a breathing zone or between samples collected side-by-side, especially for samples with concentrations less than 2.5 fibers/cm^3.

4.3 Sources of Variation in the Counting Procedure

4.3.1 Random variations exist in the fiber distribution on a filter wedge (intra-wedge variability). The industrial hygiene literature has seen considerable debate in the last 20 years concerning whether or not the distribution of mineral dust or asbestos fibers on a filter surface is adequately described by a Poisson distribution probability density function. Leidel and Busch (11.4) found excellent agreement between empirical error variance and theoretical variance calculated from the assumption of Poisson distributed true counts. They concluded that there was not excessive variation among count fields for a filter wedge and that clumping of fibers (non-random coalescence) did not occur.

4.3.2 Variations exist in the fiber distribution on the total filter surface (inter-wedge variability) due to the random or non-random distribution of fibers across the total surface of the filter. This type of variation is easily confused with intra-wedge variations. The count procedure does not require counting of multiple sectors of the filter. There may be significant differences between average counts for different wedges, or the fiber distribution variations for the total filter surface may be greater than the variations of the Poisson distribution. If either of these occur experimentally, one must use the experimental variations to estimate the minimum precision of the count procedure. The minimum precision is governed by the variations of the fiber distribution on the total surface of the filter.

Conway and Holland (11.3) concluded the distribution of fibers on filters is not uniform and the distribution of fiber counts is more disperse than Poisson. For their filters which had significant variations in fiber concentrations between sectors (as much as 50-60% of the total filter mean), they described the following relation for the standard deviation of the total number of fibers counted on a wedge (N)

$$\text{empirical } s(N) = 1.6\ (N)^{1/2}$$

where N is about 100. The Poisson standard deviation would be:

$$\text{Poisson } \sigma(N) = (N)^{1/2}$$

Rajhans and Bragg (11.6) in Series I of their study found significant variation between filter segments and rejected the Poisson distribution for the total filter surface. However, in Series II of their study, utilizing various experimental modifications, they found no significant variation between filter segments and no reason to reject the assumption of Poisson distributed fiber counts.

4.3.3 Systematic variations due to differences between microscopes were studied by Leidel and Busch (11.4). In their study using five different brands of microscopes, they found no significant differences among four, but the fifth gave counts approximately 45% higher on the average than the other four.

4.3.4 Variations due to differences between counters should be examined at three levels: experienced counters occasionally counting, experienced counters routinely counting, and inexperienced (new or untutored) counters. Leidel and Busch (11.4) studied five experienced counters, with one counting only occasionally. There were no significant differences among three of the counters, but a fourth was 16% lower than the first three. The fifth, who occasionally counted, averaged 27% higher than the first three. Conway and Holland (11.3) studied three experienced counters and three inexperienced counters. They found statistically significant differences between the means of both the experienced and inexperienced counters that typically were in the range plus or minus 5 to 15%. They concluded that experience as a fiber counter is not a significant parameter affecting intercounter variations.

Rajhans and Bragg (11.6) found no significant differences among means of five experienced counters in Series I of their study. But in their carefully controlled Series II, an analysis of variance showed significant variations between counters that were plus or minus 1 to 15%.

4.3.5 Variations between laboratories are most likely due to systematic biases and are not a significant additional source of random variations. Any additional variations are most likely due to differences in counting technique. Beckett and Attfield (11.5) observed that standard counters improved greatly after personal instruction; also new counters, after instruction, tended to overcompensate and get exceedingly high counts. Additionally, they found that counts from an experienced laboratory that had not had contact with other laboratories performing the same analysis were as far from the standard values as were the counts by new counters.

4.4 Sources of variations between samples taken at different times on one employee during one work shift can affect the exposure estimate for that employee. These are primarily due to a) differences in exposure concentrations during the day, b) differences in location of the employee within the plant, and c) differences in work operation performed by the employee during the day. These sources of variation can be controlled by proper choice of sampling strategy. Refer to Leidel and Busch (11.7) and Leidel, Busch, and Lynch (11.8) for an extended discussion of sampling strategies. Interday temporal variations can affect the exposure estimates obtained on different days. Refer to Leidel, Busch, and Crouse (11.9) for a discussion of this type of variation.

4.5 Until recently, the total coefficient of variation (CV_T) for the sampling and counting procedure was best estimated from the work of Conway and Holland (11.3). The conclusions of their study included:

4.5.1 The precision of their procedure for filters not containing an abundance of fine fibers can be estimated by a coefficient of variation of 16.2%. This value includes variation among counters and observed interaction effects.

4.5.2 The accuracy of the procedure for similar filters may be estimated for a 100-fiber count by a coefficient of variation of 21.4%. This assumes that the contribution of the overall variance from the nonuniform fiber distribution is additive.

4.5.3 A high percentage of very fine fibers on the filter can significantly affect the standard deviation and confidence limits for counts by different counters. After combining variations in fiber concentrations over the entire filter with those for different counters, it was concluded:

a. For filters with a low concentration of fine fibers, the coefficient of variation is estimated at 21% and the 95% confidence interval is ± 43%.

b. For filters with a high concentration of fine fibers, the coefficient of variation is estimated at 25% and the 95% confidence interval is ± 50%.

Lynch, Kronoveter, and Leidel (11.1) have also reported on variations of the method. Their intralaboratory study utilized the data from a large number of dust counts made by different methods by experienced counters over a period of years in an epidemiologic study of the asbestos products industry. They concluded that the standard deviation of counts of fibers longer than 5 micrometers on membrane filters could be estimated from the relation $\sigma = (N)^{0.501}$. Thus for counts of about 100 fibers, the coefficient of variation could be estimated at about 15.2% and the 95% confidence limits at ± 30.4%. These values are lower than the values reported by Conway and Holland (11.3).

Recently, the Johns-Manville Corporation conducted an in-house investigation of the asbestos count method (11.10). The study data contained total fiber counts for over

100 filters with each filter counted by two to five counters. From the Johns-Manville data, NIOSH calculated over 100 estimates of the count CV for the method (11.11). The NIOSH CV estimates included random intrafilter variations and intercounter variations, but did not include random pump flow rate variations. It was found that the count coefficient of variation (all random variations except for pump variations) was a function of the total fiber count. NIOSH then included a CV of 0.05 for random pump variations (see Section 9.1) in the CV-estimator equation to obtain a CV_T-estimator. The CV_T-estimator line is plotted on Figure 3 for total fiber counts in the range 10 to 100 fibers. Or the following equation can be used:

$$CV_T = [\text{antilog}_{10}(-0.215 - 0.203\,(\log_{10}FB)) + 0.0025]^{\frac{1}{2}}$$

where FB is total fiber count as discussed in Section 10.

Figure 3 demonstrates that for a total fiber count of 100, the best CV_T is attainable with the appropriate sampling times given in 8.1.3 and the count rules in 8.3.9. When making decisions regarding compliance with the OSHA asbestos exposure standards in 29 CFR 1910.1001, the statistical procedures given in Leidel et al. (11.11) should be followed. The procedures are based on statistical theory and assumptions given in References 11.12, 11.13.

Because of the possibility of systematic biases due to differences between microscopes, counters, and laboratories as discussed above, it is strongly recommended that any laboratory counting asbestos should participate in an interlaboratory quality control program that includes the counting of standard reference filters. These standard filters are available from NIOSH through the Proficiency Analytical Testing (PAT) Program. The PAT Program is used by the American Industrial Hygiene Association (AIHA) as part of its Laboratory Accreditation Program. Each laboratory's quality control program must include protocols for routinely adjusting and calibrating sampling and counting equipment plus training and evaluation programs for counters.

5. **Advantages and Disadvantages of the Method**

5.1 The method is intended to give an index of employee exposure to airborne asbestos fibers of specified dimensional characteristics.

5.2 It is not meant to count all asbestos fibers in all size ranges or to differentiate asbestos from other fibrous particulates.

6. **Apparatus**

6.1 Sampling Equipment

The personal sampling equipment train consists of 1) personal sampling pump, 2) tubing, 3) clothing spring clip, 4) tubing-to-field monitor metal adaptor, and 5) field monitor (filter and holder).

6.1.1 Personal Sampling Pump. The pump must be capable of sampling at 1.0 to 2.5 liters per minute (lpm) against a flow resistance of 7.5 inches of water (1.4 cm Hg) for 8 continuous hours on a fully charged battery.

6.1.2 Tubing. Laboratory tubing such as rubber or plastic with 6-mm bore and about 100 cm length.

6.1.3 Clothing Spring Clip. The clip attaches the rubber tubing to the lapel or shirt of the individual being monitored.

6.1.4 Tubing-to-field Monitor Adaptor. A short metal adaptor with ridges on one end to grip the inside of the tubing. The other end is designed for a pressure fit into the field monitor.

6.1.5 Field Monitor (Filter and Holder). The only field monitor currently considered acceptable by NIOSH is manufactured by the Millipore Corporation. The unit con-

sists of 1) a three section styrene plastic case designated Millipore Aerosol Monitor Case, 2) a 37-mm diameter plain white cellulose ester membrane filter designated Millipore AA (pore size of 0.8 micrometer), 3) a support pad, and 4) two plastic sealing caps. If a large number of samples are to be taken, it may be less expensive to reuse the plastic cases. Great care must be taken in the cleaning and reassembly process. The outside mating surfaces of the field monitors may be covered with a "shrink-fit" band to provide proper sealing and a writing surface for filter identification.

6.2 **Optical Equipment and Microscope Features**

6.2.1 Microscope body with binocular head.

6.2.2 10X Huygenian eyepieces are recommended. Other eyepieces can be substituted if necessary. Wide field eyepieces can be used; however, wide field eyepieces may yield a count field area less than 0.003 mm^2 with the Porton reticle. This is not always desirable from the standpoint of obtaining optimum sampling times (see Section 8.1.3). If wide field eyepieces are used, it is preferable to use the Patterson Globe and Circle reticle to obtain a larger count field area.

6.2.3 Koehler illumination (preferably built-in with provisions for adjusting light intensity).

6.2.4 A Porton reticle is recommended. Others such as the Patterson Globe and Circle can be substituted.

6.2.5 Mechanical stage.

6.2.6 Phase-Contrast condenser with a numerical aperture (N.A.) equal to or greater than the N.A. of the objective.

6.2.7 40-45X phase contrast achromatic objective (N.A. 0.65 to 0.75).

6.2.8 Phase-ring centering telescope or Bertrand lens.

6.2.9 Green or blue filter, if recommended by microscope manufacturer.

6.2.10 Stage micrometer with 0.01 mm subdivisions.

6.2.11 For general guidance on phase contrast microscopy, consult Needham (11.12), Clark (11.15) and McCrone (11.14).

6.3 **Filter Mounting Equipment.** Experience has shown that certain equipment is useful for efficient sample mounting. The following items are recommended for extracting and mounting a portion of the filter for counting.

6.3.1 Microscope slides. 2.5 by 7.5 cm glass slides are most commonly used. Sample number, data, initials, etc., can be conveniently written on a frosted end slide.

6.3.2 Cover Slips. Cover slips are a necessary part of the slide mount and optical system. The shape should be appropriate for the size of the filter wedge. The appropriate cover slip depends upon the objective to be used. Ordinarily, objectives are optically corrected for a #1½ (0.17 millimeter) thickness cover slip. Improper cover glass thickness will detract from the final image quality.

6.3.3 Scalpel. A scalpel is needed to cut out a portion of the filter to be examined. A number-ten curved blade scalpel is recommended.

6.3.4 Tweezers. A pair of fine-tipped tweezers is used to remove the membrane filter slice from the field monitor and place it upon the slide.

6.3.5 Lens Tissue. To insure cleanliness, a lint-free tissue is recommended. This tissue should also be used for wiping mounting tools and for cleaning slides and cover slips.

6.3.6 Glass Rod. A fire-polished glass rod may be used to spread the mounting solution on the slide.

6.3.7 Wheaton Balsam Bottle. This special glass container has a glass top which prevents contamination of the mounting solution. A glass rod is included for dispensing the solution.

7. **Reagents**

Chemicals should be reagent grade, free from particles and color, conforming to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

7.1 Dimethyl phthalate

7.2 Diethyl oxalate

Avoid getting the mounting solution on the skin. Wash skin promptly with soap and water if skin contact occurs.

8. **Procedure**

8.1 **Sampling**

8.1.1 General Information

Guidelines for the monitoring of employee exposures to industrial atmospheres are given in Reference 11.8. The Federal requirements for monitoring employee exposure to airborne asbestos are found in 29 CFR 1910.1001.

8.1.2 Mounting the Sampling Pump on the Worker

Fasten the sampling pump to the worker's belt and fasten the field monitor to the lapel or shirt front (as close to the breathing zone as is practical). Remove the top cover of the plastic monitor, then invert the monitor making certain the exposed filter is facing downward. Turn the pump on and adjust to the calibrated flow rate (1.0 to 2.5 lpm). Record the following information in a logbook.

1. Filter number
2. Pump start time and date
3. Flow rate
4. Subject's name and job title
5. Type of operation or process
6. Ventilation controls and is the worker wearing a respirator approved for asbestos?

The pump should be checked periodically during the sampling period for proper operation and flow rate.

8.1.3 Optimum Sampling Times

The requirement for the minimum count of 100 fibers or 20 fields in 8.3.9 was determined to be the best compromise to achieve adequate precision for the airborne fiber estimate and reasonable counting times. An optimum fiber density of about 1 to 5 fibers per microscope count field is recommended. To estimate appropriate sampling times for feasible counting and optimal counting, one must consider the following constraints:

1. microscope count field area (generally 0.003 to 0.006 mm^2)
2. pump flow rate (typically 2.5 lpm maximum)
3. average airborne fiber concentrations
4. counting rule range of 20 to 100 fields
5. adequate fiber density to obtain a minimum count of 10 fibers in 100 fields, which is the least total fiber count that yields an acceptable count precision
6. background airborne particulate levels that can reduce the count precision due to an obscuring of fibers on the filter surface

The preceding constraints were considered in drawing Figures 1 and 2. These figures were developed from the following relationship:

$$\text{sampling time} = \frac{(FB/FL)\ (ECA/MFA)}{(FR)\ (AC)\ (1000)} \quad \text{minutes}$$

where:

FB/FL = 1 to 5 fibers/field

ECA = effective collecting area of filters (855 mm^2 for 37-mm filter with effective diameter of 33 mm)

MFA = microscope field area (generally 0.003 to 0.006 mm^2)

FR = Pump flow rate (generally 1.0 to 2.5 lpm)

AC = Air concentration of fibers in fibers/cm^3.

Figure 1 (microscope field area = 0.003 mm^2) and Figure 2 (microscope field area = 0.006 mm^2) show optimum and feasible sampling times for a pump flow rate of 1.7 lpm. Each individual responsible for sampling asbestos should prepare a similar chart for his particular pump flow rate and microscope field area before sampling is performed to aid in estimating proper sampling times. On Figures 1 and 2, the areas with solid shading lines are generally the optimum conditions for counting. The broken shading lines are for conditions very close to optimal.

However, feasible counting conditions may extend down to about 0.1 fiber/field and and above 5 fibers/field. Recommended sampling times are most strongly influenced by background airborne particulate levels, once all the other constraints have been estimated. For heavy particulate levels, it may be necessary to limit each filter to about 60 to 180 minutes sampling duration. Each individual responsible for sampling should work closely with the microscopist to attain as high as possible filter surface fiber densities (up to about 5 fibers/field), while avoiding filter surface background particulate levels that create very difficult or impossible counting conditions. If one has very little idea of airborne fiber and particulate levels, the best procedure is to take several long samples (as one 8-hour or two consecutive 4-hour samples) in conjunction with several short samples (as four consecutive 2-hour or eight consecutive 1-hour samples). If the longer samples prove very difficult to count, the microscopist will have the shorter samples to fall back on.

From Figures 1 and 2, it can be seen that there are certain sampling times which will yield optimum fiber densities on the filter for almost all airborne fiber concentrations from 1 to 10 fibers/cm^3. These optimum times have been calculated and are presented in Figure 4. Note that the optimum times given by Figure 4 are approximate and can be varied by as much as ± 25%. The nomogram is intended as a guide to be used where no prior knowledge of the air concentration is available.

8.1.4 End of Sampling Period

Remove the field monitor, replace the plastic top cover and the small end caps, and store the monitor. Always shut off the pump when changing monitors to avoid contaminating or damaging the pump. Record the pump shutoff time and flow rate in the logbook.

8.1.5 Blanks

With each batch (25 to 50 filters) of samples sent for analysis, submit two unopened field monitors which have been subjected to the same treatment as the samples except that they were not exposed to the sampling environment. Label these as blanks. If the blanks yield fiber counts greater than 5 fibers/100 fields, then the entire sampling procedure should be examined carefully for the cause of contamination. The

mounting solution of Section 8.2.1 should also be examined for contamination and/or crystal growth.

8.1.6 Shipping

The field monitors in which the samples are collected should be shipped in a rigid container with sufficient packing material to prevent crushing.

8.1.7 Numbers of Samples

When sampling for the Federal ceiling standard of 10 fibers (>5μm)/cm³, [29 CFR 1910.1001(b) (3), effective July 7, 1972], only one sample (15 minutes maximum duration) is necessary, theoretically. However, several samples should be taken during expected periods of peak air concentrations to allow for detection of gross sampling or counting errors.

When sampling for determination of noncompliance with the Federal 8-hour TWA standard of 2 fibers (>5μm)/cm³, [29 CFR 1910.1001(b) (2)], one should continuously sample as large a portion of the work day as is feasible for airborne concentrations of about 2 to 10 fibers/cm³. However, for a lower airborne concentration such as 0.5 fiber/cm³, one sample might require 4 to 8 hours sampling time in order to get the proper filter fiber density (Section 8.1.3). For this situation, the 8-hour TWA exposure would be determined from one 8-hour or two 4-hour samples as appropriate.

8.2 Sample Preparation

8.2.1 Preparation of Mounting Solution

A very important part of the sample evaluation is the mounting process. This process involves a special mounting medium of prescribed viscosity. The proper viscosity is important in order to expedite filter dissolving and still minimize particle migration. After the sample has been mounted, an elapsed time of approximately sixty minutes is needed before the sample is ready for evaluation.

Combine the dimethyl phthalate and diethyl oxalate in a one to one ratio by volume and pour into a Wheaton balsam bottle. Add approximately 0.05 (± 0.005) grams of new membrane filter per milliliter of solution to reach the necessary viscosity. The mixture must be stirred periodically until the filters have dissolved and a homogeneous mixture is formed. The normal shelf life of the mounting solution is about three months. Twenty milliliters of mounting solution will prepare approximately 300 samples.

8.2.2 Sample Mounting

Cleanliness is important! A dirty working area may result in sample contamination and erroneous counts. The following steps should be followed when mounting a sample.

1. Clean the slides and cover slips with lens tissue. Lay each slide down on a clean surface with the frosted end up. It is a good practice to rest one edge of the cover slip on the slide and the other edge on the working surface. By doing this, you keep the bottom surface (the one which contacts the filter) from becoming contaminated.
2. Wipe all the mounting tools clean with lens tissue and place them on a clean surface (such as lens tissue). All tools should be wiped clean prior to mounting each sample.
3. Using the glass rod supplied with the Wheaton balsam bottle, apply a drop of mounting solution onto the center of the slide. It may be necessary to adjust the quantity of solution so that after the cover slip has been placed on top, the solution extends only slightly beyond the filter boundary. If the quantity is greater than this, particle migration may occur.

4. Using another glass rod, spread the mounting media into a triangular shape. The size of this triangle should coincide with the dimension of the filter wedge.
5. Separate the middle and bottom sections of the field monitor case to expose the filter. Cut a triangular wedge from the center to the edge of the filter using the scalpel. The size of the wedge should approximate one-eighth of the filter surface. The filter can be very carefully removed from the cassette for cutting, but this should only be done with great care.
6. Grasp the filter wedge with the tweezers on the perimeter of the filter which was clamped between the monitor case sections. Do not touch the filter with your fingers. Place the wedge, **sample side up,** upon the mounting medium.
7. Pick up a clean cover slip with tweezers and carefully place it on the filter wedge. Once this contact has been made, **do not reposition the cover slip.**
8. Label the slide with the sample number and current date before proceeding to the next filter. On the bottom (backside) of the slide, trace the perimeter of the filter wedge with a felt tip marking pen. This will enable the counter, after the filter has become transparent, to stay within the filter perimeter when counting.
9. The sample should become transparent within fifteen minutes. If the filter appears cloudy, it may be necessary to press very lightly on the cover slip. This is rarely necessary; however, counting should not be started until an hour after the mounting. This allows the microscopic texture of the filter to become invisible to microscope viewing.
10. Discard the sample mount after two days if it has not been counted. Crystals appearing similar to asbestos fibers may begin to grow at the mounting media/air interfaces. They seldom present any problems if the slide is examined before two days. In any case, stay away from the filter's edges when counting and sizing.

8.3 Counting of Fibers

8.3.1 Place the slide on the mechanical stage of the microscope and position the center of the wedge under the objective lens and focus upon the sample. Start counting from one end of the wedge and progress along a radial line to the other end (count in either direction from perimeter to wedge tip). Random fields are selected, without looking into the eyepieces, by slightly advancing the slide in one direction with the mechanical stage control.

8.3.2 It is essential to continually scan over a range of focal planes (generally the upper 10 to 15 micrometers of the filter surface) with the fine focus control during each field count. This is especially necessary for asbestos fibers due to their impaction into the filter matrix.

8.3.3 On most airborne samples, asbestos fibers will generally have fiber diameters less than one micrometer. Therefore, it is necessary to look carefully for faint fiber images.

8.3.4 Regularly check phase ring alignment.

8.3.5 When an agglomerate (mass of material) covers a significant portion of the field of view (approx 1/6 or greater) reject the field and select another. (Do not include it in the number of fields counted.) However, report the fact as it may have meaning on other data collection.

8.3.6 Bundles of fibers are counted as one fiber unless both ends of the fiber can be clearly resolved.

8.3.7 Count only fibers with a length to width ratio greater than or equal to 3:1.

8.3.8 Count only fibers greater than 5 micrometers in length. (Be as accurate as possible in accepting fibers near this length.) Measure curved fibers along the curve to estimate the total length.

8.3.9 Count as many fields as necessary to yield a total count of at least 100 fibers. Exceptions: a) count at least 20 fields even if you count more than 100 fibers, and b) stop at 100 fields even if you haven't reached 100 fibers.

8.3.10 For fibers that cross either one or two sides of the counting field, the following procedure is used to obtain a representative count.
COUNT any fiber greater than 5 micrometers in length, that lies entirely within the counting area. COUNT as "½ fiber" any fiber with only one end lying within the counting area. DO NOT COUNT any fiber crossing any two sides.
Reject and do not count all other fibers. Refer to Figures 5 through 10. Note that the fibers in Figures 5 through 10 **are not representative** of the appearance of most asbestos fibers. Most fibers have a very faint image.

9. Calibration and Standards

9.1 Sampling Train Calibration

The accurate calibration of the sampling pump is essential to the correct calculation of the air volume sampled. The frequency of calibration is dependent on the use, care, and handling to which the pump is subjected. Pumps must be recalibrated if they have just been repaired, misused, or received from the manufacturer. If the pump receives hard usage, more frequent calibration may be necessary. Ordinarily, pumps should be calibrated in the laboratory both before they are used in the field and after they have been used to collect a large number of field samples.

The accuracy of calibration is dependent upon the type of instrument used as a reference. The choice of a calibration instrument will depend largely on where the calibration is performed. For laboratory testing, a 1-liter buret used as a soap bubble flow meter or wet-test meter is recommended. Other standard calibrating instruments, such as a spirometer, Marriott's bottle, or dry gas meter can be used. The calibration should be of sufficient precision that the 95% confidence limits on the flow rate are ± 10% (95% of the flow rates will fall within ± 10% of the calibrated value).

Instructions for calibration with the soap bubble flow meter follow. The sampling train used (pump, hose, filter cassette) in the pump calibration should be the same as the one used in the field.

9.1.1 Check the voltage of the pump battery with a voltmeter both with the pump off and while it is operating to assure adequate voltage for calibration. If necessary, charge the battery to manufacturer's specifications.

9.1.2 Fill a beaker with 10 ml of soap solution.

9.1.3 Connect the filter cassette inlet to the top of the buret with a length of hose.

9.1.4 Turn the pump on and moisten the inside of the soap bubble meter by immersing the open end of the buret into the soap solution and drawing bubbles up the inside of the buret. Perform this task until the bubbles are able to travel the entire length of the buret without breaking.

9.1.5 Adjust the pump rotameter to provide a flow between 1.5 to 2.5 lpm.

9.1.6 With a water manometer, check that the pressure drop across the filter is less than 13 inches of water (about 1 inch of mercury).

9.1.7 Start a soap bubble up the buret and measure the time it takes for the bubble to travel a minimum volume of 1 liter.

9.1.8 Repeat the procedure in 9.1.7 at least three times, average the results, and calculate the calibrated flow rate by dividing the volume traveled by the soap bubble by the elapsed time. If the range between the highest and lowest of the three flow rates is greater than about 0.33 lpm, then the calibration should be repeated since it is likely that the precision is not adequate.

9.1.9 Data required for the calibration include the volume measured, elapsed time, pressure drop, air temperature, atmospheric pressure (or elevation), pump serial number, date, and name of person performing the calibration.

9.1.10 Corrections to the flow rate for pumps with rotameters may be necessary if the pressure (elevation) or temperature where the samples are collected (actual flow rate) differs significantly from that where the calibration was performed (indicated flow rate). Actual flow rates at time of sampling may be calculated for a linear scale rotameter by using the following correction formula:

$$Q_{actual} = Q_{indicated} \sqrt{\frac{P_{cal}}{P_{actual}} \cdot \frac{T_{actual}}{T_{cal}}}$$

where both pressure (P) and temperature (T) are in absolute units such as:

psia = psig + 14.7
deg Rankin = deg Fahrenheit + 460
deg Kelvin = deg Celsius + 273

9.2 **Microscope Setup**

9.2.1 Porton Reticle and the Counting Field
The asbestos fiber count procedure consists of comparing fiber length to the diameters of calibrated circles of a Porton reticle, and counting all fibers greater than 5 micrometers in length lying within a given counting field area. The Porton reticle is a glass plate inscribed with a series of circles and rectangles. The left half of the reticle is divided into six rectangles constituting the counting field. The counting field is illustrated in Figures 5 through 10.

9.2.2 Placement in Eyepiece
The Porton reticle is placed inside the Huygenian eyepiece where it rests on the field-limiting diaphragm. If other types of eyepieces are used, it may be necessary to insert a counting collar for retaining the reticle. The reticle should always be kept clean, since dirt on the reticle is in focus and could complicate the counting and sizing process.

9.2.3 Stage Micrometer
The Porton reticle cannot be used for counting until it has been properly calibrated with a stage micrometer. Most stage micrometer scales are approximately two millimeters long and are divided into units of one-hundredth of a millimeter (ten micrometers).

9.2.4 Microscope Adjustment
When adjusting the microscope, follow the manufacturer's instructions while observing the following guidelines.

1. The light source image must be in focus and centered on the condenser iris or annular diaphragm.
2. The particulate material to be examined must be in focus.
3. The illuminator field iris must be in focus, centered on the sample, and opened only to the point where the field of view is illuminated.
4. The phase rings (annular diaphragm and phase-shifting elements) must be concentric.

9.2.5 Porton Reticle Calibration Procedure
Each eyepiece-objective-reticle combination on the microscope must be calibrated. Should any of the three be changed (disassembly, replacement, zoom adjustment, etc.), the combination must be recalibrated. Calibration may change if interpupillary dis-

tance is changed. For proper calibration, the following procedure should be followed closely.

With a 10X objective in place, place the stage micrometer on the mechanical stage, focus the millimeter scale, and center the image. Change to the 40-45X objective and adjust the first millimeter scale division to coincide with the left boundary of the Porton rectangle. Measure the distance between the left and extreme right boundaries of the Porton rectangle, estimating any portion of the final division. This measurement represents 200 L units. The rectangle is 100 L units on the short vertical dimension. The calculated "L" is inserted into the formula $D = L(2^N)^{1/2}$ where "N" is the circle number (indicated on the reticle) and "D" is the circle diameter. Since the circle diameters vary logarithmically, every other circle doubles in diameter. For example, circle number three is twice the diameter of number one; number four is twice the diameter of number two. When the circle sizes have been determined, the counting field area which consists of the left six smaller rectangles can be calculated from the relation $10{,}000\ L^2$. This completes the reticle calibration for this specific objective-eyepiece-reticle combination.

Example for Porton Reticle

The following calibration was obtained for a pair of 10X Huygenian eyepieces and a 43X objective:

200 L = 0.148 mm = 148 micrometers
100 L = 0.074 mm = 74 micrometers
One L-unit = 0.74 micrometers

Thus Circle #1 has a diameter $D = L(2^N)^{1/2} = 0.74(2^1)^{1/2} = 0.74\ (1.414) = 1.05$ micrometers.

Then our circle diameter calibration table looks like:

Diameter of Circle #1 = 1.05 micrometers
#2 = 1.48
#3 = 2.09
#4 = 2.96
#5 = 4.19
#6 = 5.92

Field area = $(10{,}000)\ (L^2) = (100\ L)\ (100\ L) = (0.074)\ (0.074) = 0.0055\ mm^2$

Thus fibers with a length greater than a distance halfway between the diameters of the #5 and #6 circles would be counted.

If a Patterson Globe and Circle reticle is used, a different calculation procedure is required. The circle diameters are related as follows. The #25 circle diameter is (0.1) (reticle length).

The circle diameters are proportional to the ratio of their numbers. Thus the #20 circle diameter is (20/25) or 0.8 times the #25 circle diameter.

10. **Calculations**

10.1 The average airborne asbestos fiber concentration estimated by the filter sample may be calculated from the following formula:

$$AC = \frac{[(FB/FL) - (BFB/BFL)]\ (ECA)}{(1000)\ (FR)\ (T)\ (MFA)}$$

where:

AC = Airborne fiber concentration in (fibers > 5 μm)/cm^3.
BFB = Total number of fibers counted in the BFL fields of the blank or control filters in fibers > 5 μm.
BFL = Total number of fields counted on the blank or control filters.
ECA = Effective collecting area of filter (855 mm^2 for a 37-mm filter with effective diameter of 33 mm).
FR = Pump flow rate in liters/min (lpm).
FB = Total number of fibers counted in the FL fields in fibers > 5 μm.
FL = Total number of fields counted on the filter.
MFA = Microscope count field area in mm^2 (generally 0.003 to 0.006).
T = Sample collection time in minutes.

10.2 Recount criteria. It is very desirable for a counter to conduct a "blind recount" for about 1 in every 10 filter wedges (slides) counted. Alternatively, a second counter could perform the blind recount. In training sessions for novice counters, the trainee should conduct a blind recount for filter wedges counted by an experienced, proficient counter. In all cases, we will observe differences between the first and second counts of the same filter wedge. Most of these differences will be due to chance alone, that is, due to the random variability (precision) of the count method. Statistical recount criteria enable us to decide whether observed differences can reasonably be explained due to chance alone or are probably due to systematic differences between counters or microscopes or due to some other biasing factor.
The following recount criterion is for a pair of counts that estimate some airborne fiber concentration (AC) in fibers/cm^3. The criterion is given at the type-I error level. That is, there is a 5% maximum risk that we will reject a pair of counts for the reason that one might be biased, when the large observed difference is really due to chance.
Reject a pair of counts because one might be biased if:

$$(AC_2 - AC_1) \text{ exceeds } 2.77(\overline{AC})(CV_{FB})$$

where:

AC_1 = lower estimated airborne fiber concentration
AC_2 = higher estimated airborne fiber concentration
$\overline{AC}$ = average of the two airborne concentration estimates
CV_{FB} = average CV for the two concentration estimates which are a function of the total fiber count (FB) in each case. Use the relation in Section 4 or Figure 3.

For a pair of counts on the same filter, reject the pair because one might be biased if

$$(FB_2 - FB_1) \text{ exceeds } 2.77(\overline{FB})(CV_{\overline{FB}})$$

where:

FB_1 = lower fiber count on the filter (total fibers)
FB_2 = higher fiber count on the filter (total fibers)
$\overline{FB}$ = average of the two total fiber counts
$CV_{\overline{FB}}$ = CV_F for the value FB. Use the relation in Section 4 or Figure 3.

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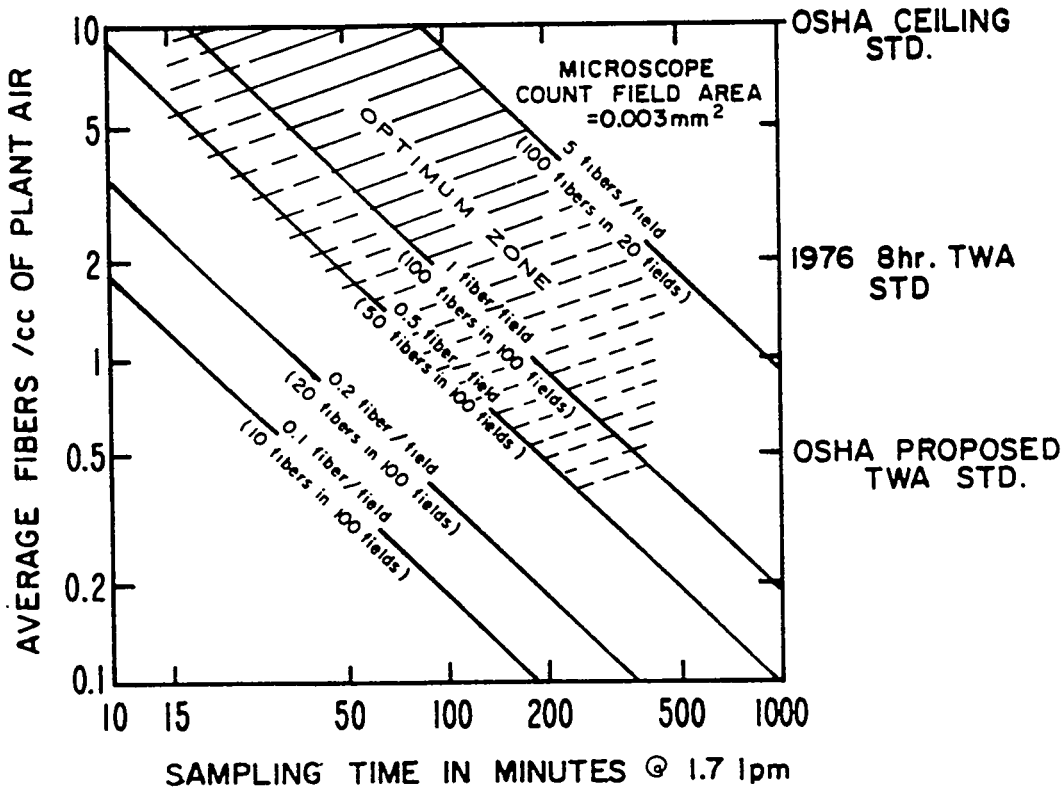

FIGURE 1. Optimum Sampling Times for airborne asbestos where microscopic field area = 0.003 mm²

UCN-1076B (12 8-78)

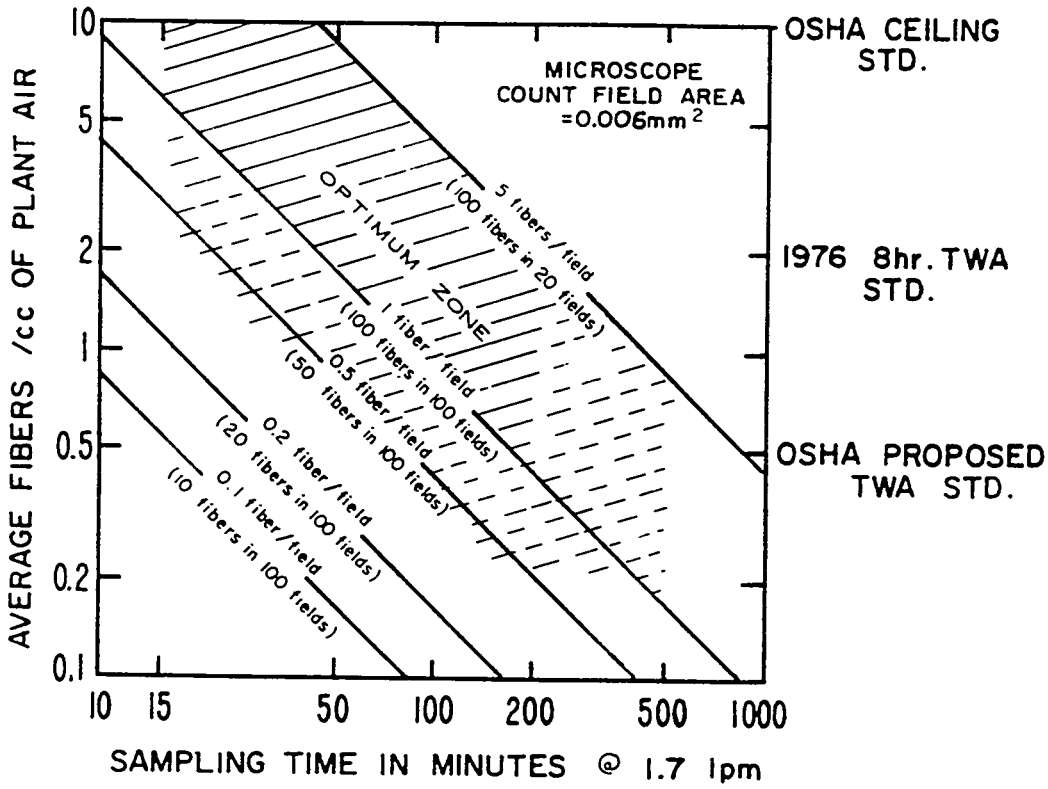

FIGURE 2. Optimum sampling times for airborne asbestos where microscopic field area = 0.006 mm^2

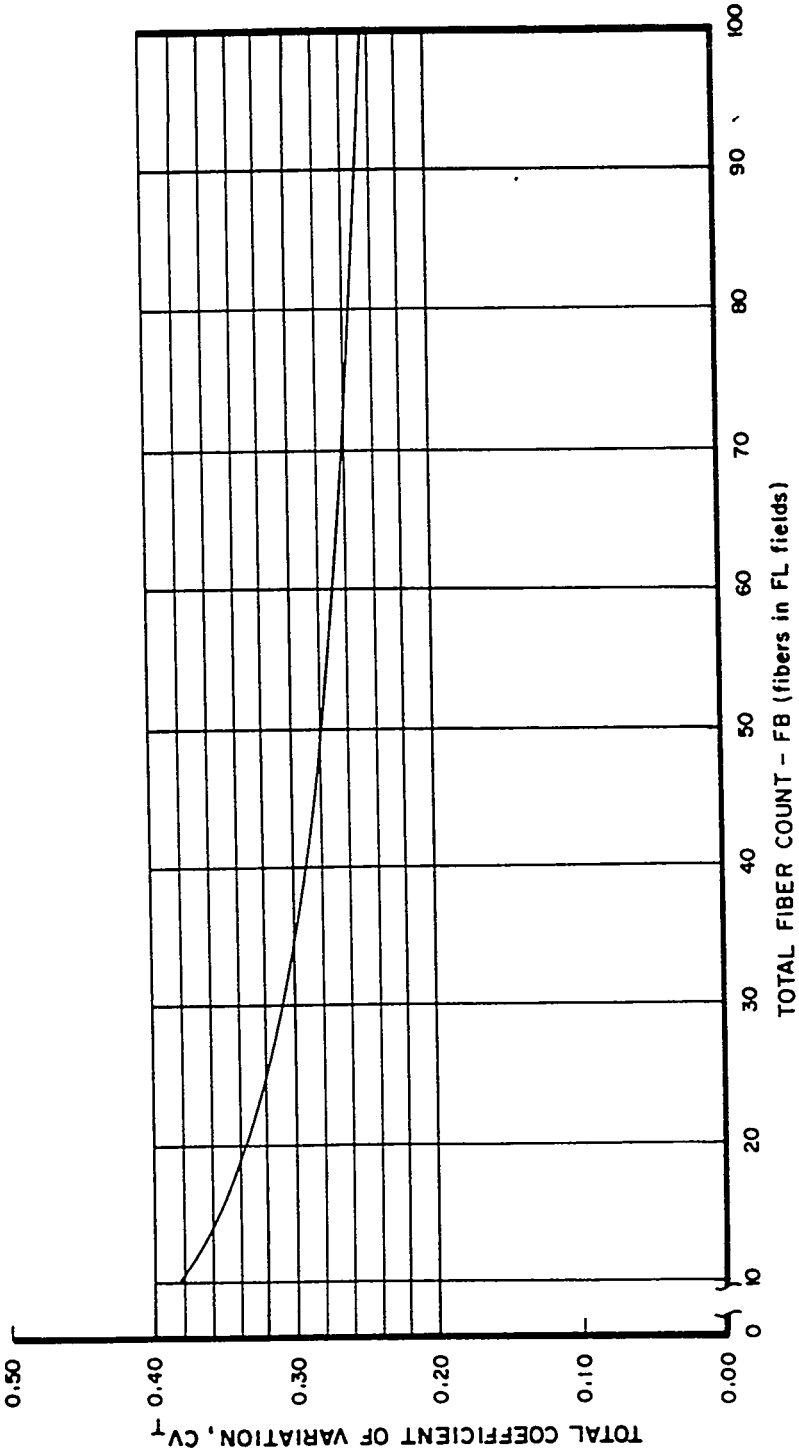

FIGURE 3. Total coefficient of variation as a function of total fiber count

UCN-10766B (12 8-78)

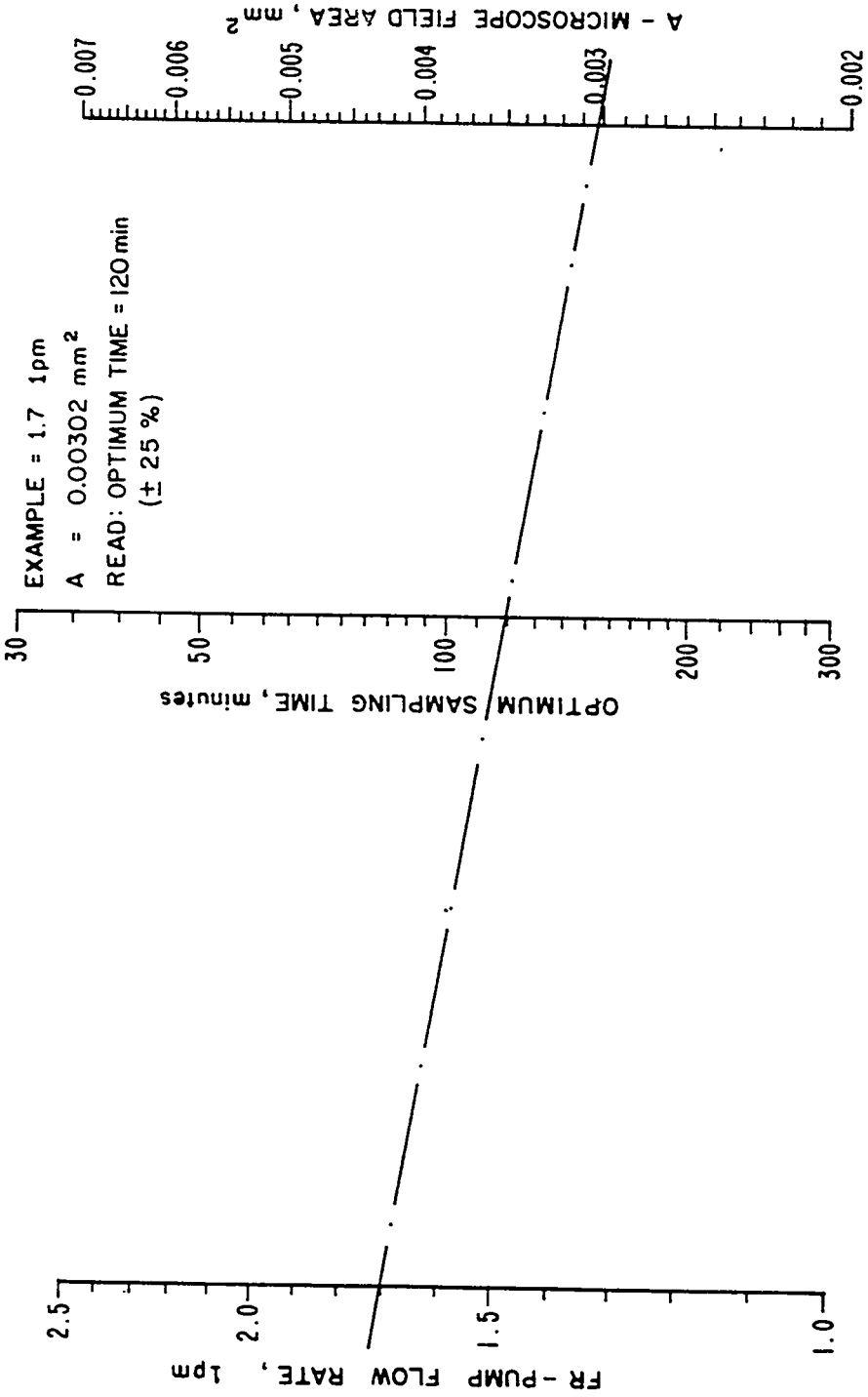

FIGURE 4. Nomogram of optimum sampling times for airborne asbestos fibers in concentrations of 1 to 10 fibers/cm³

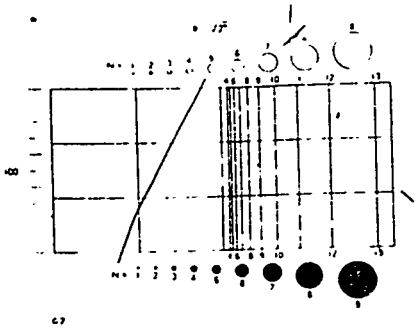

FIGURE 5

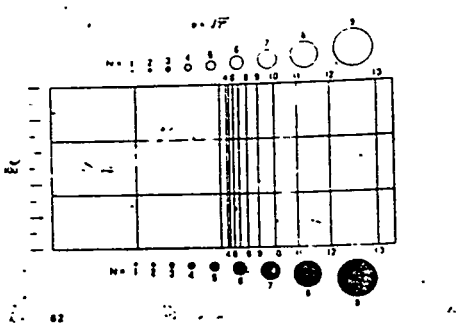

FIGURE 6

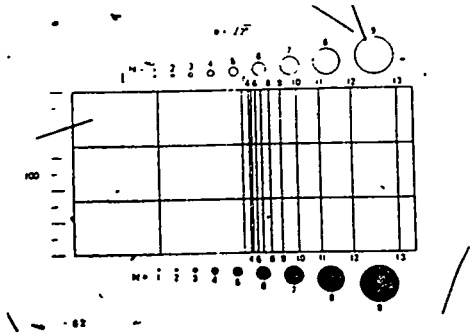

FIGURE 7

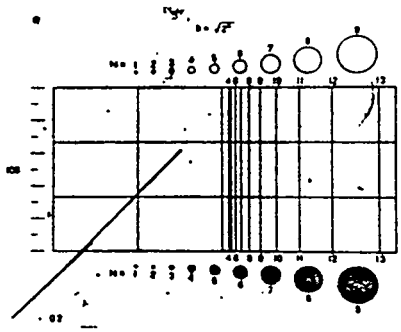

FIGURE 8

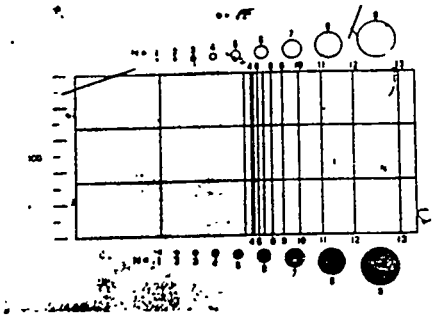

FIGURE 9

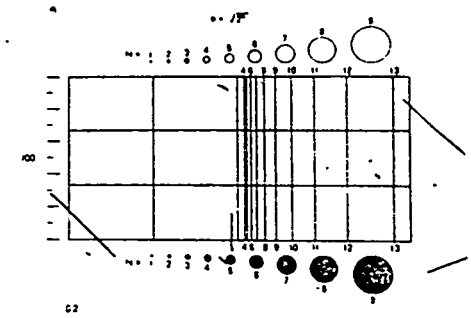

FIGURE 10

LIST OF FIGURES

(5 through 10)

FIGURE 5. DO NOT COUNT. Fiber crosses top and bottom sides.

FIGURE 6. COUNT. One fiber.

FIGURE 7. COUNT. One-half fiber. Fiber crosses left side and one end lies within count area.

FIGURE 8. COUNT. One-half fiber. Fiber crosses bottom side and one end lies within count area.

FIGURE 9. DO NOT COUNT. Fiber crosses two sides.

FIGURE 10. DO NOT COUNT. Fiber crosses two sides (bottom left corner).
COUNT. One-half fiber. Fiber crosses bottom side and one end lies within count area.
COUNT. One fiber (top right corner).

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-115
DATE	Nov. 27, 1979
SUPERSEDES	
PAGE	1 OF 5

BERYLLIUM IN AIR AND SMEAR SAMPLES, EMISSION SPECTROGRAPHIC METHOD

Analyte:	Beryllium	Method No.:	IHA-115
Matrix:	Air, smears	Range:	0.5 to 500 μg Be
Procedure:	Optical emission spectroscopy	Precision:	25% at the 95% confidence level
		Accuracy:	-10% to +10%

1.0 Principle of the Method

1.1 This procedure applies to specialized equipment and techniques at the Y-12 Plant.

1.2 Air and smear samples are collected on filter paper (32-mm diameter).

1.3 The filter paper containing the sample is compacted and placed in the crater of a graphite electrode and ashed in a muffle furnace.

1.4 The sample electrode is excited in a direct current arc until the sample is consumed. Light from the arc enters the optical emission spectrometer where the intensity of a beryllium spectral line is measured.

1.5 On the beryllium spectrograph at Y-12, the instrument computes the quantity of beryllium present in the sample electrode from the measured intensity, and prints the results in micrograms Be.

2.0 Sensitivity

2.1 The lower reporting limit is 0.5 microgram.

3.0 Interference

3.1 The exit slit is centered on the 265.06 nm Be line. There are no serious interferences when a spectral bandpass of less than 0.06 nm is used.

4.0 Precision

4.1 In the routine quality control program, precisions of 25% at the

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UCN 13234

95% confidence level are normally achieved for Be levels from 10 to 100 μg. At beryllium levels above 100 μg, the precision becomes worse, evidently due to photoelectric "saturation" in the spectrometer phototube.

5.0 Accuracy

5.1 In the routine quality control program, biases range randomly from -10% to +10% of the values in the range from 10 to 100 μg.

6.0 Advantages and Disadvantages of the Method

6.1 The average analyst time per sample is approximately 3.5 minutes.

6.2 The method has a minimum turnaround (results-reporting) time of approximately 15 minutes when an ashing temperature of 800°C is used.

6.3 The spectrograph employed at Y-12 for this measurement is not portable; therefore, all samples must be sent to the Plant Laboratory for analysis.

7.0 Apparatus

7.1 Optical emission spectrometer with a beryllium channel and associated equipment, to convert spectral intensity to micrograms of beryllium by an appropriate linear calibration and subsequently print the result on cards or paper.

7.2 Pellet press for compacting the 32-mm-diameter filter paper sample into a cylinder 4 mm in diameter. (UCC-ND, Y-12 Plant Engineering Drawing E-28585)

7.3 Muffle furnace for igniting samples to 800°C.

7.4 Mixer-mill.

7.5 Block for holding electrodes, lava.

7.6 Scoop for measuring approximately 20 mg of graphite powder.

7.7 Analytical balance, 0.0005-g precision.

7.8 Tool for rolling filter disc for pelletizing.

7.9 Plastic vial, 1/2 x 2 inches (12.7 x 50.8 mm)

7.10 Plastic balls, 3/8-inch diameter. (9.5 mm)

7.11 Graphite tamping tool.

7.12 Electrodes, counter, Y-12 Material Purchase Specification 15-AC-12g, Figure F.

7.13 Electrodes, sample, Y-12 Material Purchase Specification 15-AC-12g, Figure N.

8.0 Reagents

8.1 BeO, reagent grade.

8.2 Graphite powder, 20-mesh, Specpure, Ultra Carbon Co., or equivalent.

9.0 Procedure

9.1 Sample Preparation

9.1.1 Roll the filter paper containing the sample onto the special tool and insert it into the pellet press. An air-actuated plunger compacts the sample into a cylindrical pellet.

9.1.2 Place the pellet into the appropriate electrode in the electrode holder block.

9.1.3 Heat the block of electrodes in the muffle furnace at 600°C for 20 minutes or until sample is thoroughly ashed. (If sample is not sufficiently ashed, the pellets will be ejected from the electrode when the arc is ignited.)

NOTE

A furnace temperature of 800°C may be used to reduce the time required for ashing the samples. However, electrodes must be observed frequently to prevent burning away of the crater rim.

9.1.4 Add a scoop of graphite to the crater of each electrode.

9.1.5 Tamp charge in crater with graphite tamping tool.

9.2 Instrument Calibration

9.2.1 Arc a blank (empty) electrode at 30 amps D.C. for 60 seconds to obtain the zero reading.

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9.2.2 Arc a second electrode to confirm the reading.

9.2.3 Using the same conditions, arc a 50-μg Be standard to calibrate the instrument.

9.2.4 Arc a second standard to confirm the reading.

9.2.5 Recalibrate if confirmation readings are not within limits--blanks, 0 ± 0.3 μg; and standards, 50 ± 4 μg.

9.3 Analyzing Samples

9.3.1 Load sample electrodes into the automatic electrode changer. Insert, alternately, a blank or standard every tenth electrode.

9.3.2 Load an equal number of counter electrodes into the carousel of the upper changer.

9.3.3 Place sample identification cards in the card punch in the order in which the samples, blanks, and standards are to be run.

9.3.4 Switch to "Automatic." The electrodes will be sequentially arced and the results in μg Be will be punched onto the cards.

10.0 Standards

10.1 Standard Mix, 5000 μg Be/g

10.1.1 Weigh 0.1388 g BeO and 0.8612 g graphite powder into a plastic vial.

10.1.2 Add a plastic ball to the vial and mix 5 minutes on a mixer-mill.

10.1.3 Weigh 0.1000 g of the above mix and 0.9000 g of graphite powder into a plastic vial with a plastic ball and mix similarly, to obtain the 5000-μg Be/g standard mix.

10.2 Standard Electrode Charging

10.2.1 Weigh 0.010 g of the 5000-μg/g standard mix into an electrode crater to obtain the 50-μg Be calibration standard.

11.0 References

11.1 Pipes, E. W.; *Automatic Beryllium Analyzer*; Maintenance Training Manual MTM-11; Union Carbide Corporation-Nuclear Division, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee, June 14, 1962.

11.2 *Spectrographic Analysis of Industrial Hygiene Samples for Beryllium Using the Automatic Beryllium Analyzer*; Plant Laboratory Instrumental Manual-Spectrographic, Document No. Y/P65-223051 (Revision A); Union Carbide Corporation-Nuclear Division, Oak Ridge, Tennessee, June 10, 1971.

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-117
DATE	May 28, 1980
SUPERSEDES	
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CHLORINE IN AIR, SPECTROPHOTOMETRIC METHOD

Analyte:	Chlorine	Method No.:	IHA-117 (NIOSH 209)
Matrix:	Air	Range:	0.05 - 1.0 ppm (145 - 2900 $\mu g/m^3$)
Procedure:	Fritted bubbler; methyl orange bleaching; spectrophotometric measurement	Precision:	±5% (analytical)

For this analysis, the undersigned committee has approved for inclusion in this manual an existing procedure, exactly as published. Accordingly, the following pages are taken verbatim from the NIOSH Manual of Analytical Methods, Second Edition, Vol. 1, U. S. Department of Health, Education, and Welfare, Method 209, 1977.

The following exceptions to NIOSH 209 should be understood:

A. Free fluorine will interfere in a positive direction, and should be included in Section 3. Interferences.

B. There is an error under 10. Calculations. The equation should be:

$$\text{ppm } Cl_2 = \frac{\mu g\ Cl_2 \text{ found}}{\text{liters of air sampled}} \times \frac{24.450}{71} .$$

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UCN-13234
(1235 1-79)

The following procedure is a photocopied excerpt from: NIOSH Manual of Analytical Methods, Second Edition, Vol. 1, U. S. Department of Health, Education, and Welfare, 1977.

FREE CHLORINE IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Chlorine	**Method No.:**	P&CAM 209
Matrix:	Air	**Range:**	0.05-1.0 ppm
Procedure:	Fritted bubbler for sampling colorimetric methyl orange	**Precision:**	± 5% (Analytical)
Date Issued:	1/1/75		
Date Revised:		**Classification:**	C (Tentative)

1. **Principle of the Method**

   1.1 Sampling is performed by passing a measured volume of air through a fritted bubbler containing 100 ml of dilute methyl orange.

   1.2 Near a pH of 3.0, the color of a methyl orange solution ceases to vary with acidity. The dye is quantitatively bleached by free chlorine, and the extent of bleaching can be determined colorimetrically (11.1, 11.6). The optimum concentration range is 0.05-1.0 ppm in ambient air (145 μg to 2900 μg per m^3 at 25°C and 760 Torr).

2. **Range and Sensitivity**

   2.1 The procedure given is designed to cover the range of 5-100 micrograms of free chlorine/100 ml of sampling solution. For a 30-liter air sample, this corresponds to approximately 0.05-1.0 ppm in air, which is the optimum range.

   2.2 Increasing the volume of air sampled will extend the range at the lower end, but only within limits, since 50 liters of chlorine-free air produce the same effect as about 0.01 ppm of chlorine.

   2.3 By using a sampling solution more dilute in methyl orange, a concentration of 1 μg/100 ml of solution may be measured. But beyond this, problems are encountered because of the absorption of ammonia and other gases from the air and by the presence of minute amounts of chlorine-consuming materials even in distilled water.

3. **Interferences**

   Free bromine, which gives the same reaction, interferes in a positive direction (11.4). Manganese (III, IV) in concentrations of 0.1 ppm or above also interferes positively (11.3). In the gaseous state, interference from SO_2 is minimal, but in solution, negative interference from SO_2 is significant. Nitrites impart an off-color orange to the methyl orange reagent. NO_2 interferes positively, reacting as 20% chlorine. SO_2 interferes negatively, decreasing the chlorine by an amount equal to one-third the SO_2 concentration. Ozone may also interfere positively (11.2).

4. **Precision and Accuracy**

   The data available (11.5) indicate that 26 chlorine concentrations produced by two different methods (flowmeter calibrated by KI absorption, and gas-tight syringe) were measured by this procedure with an average error of less than ± 5% of the amount present.

5. **Advantages and Disadvantages of the Method**

5.1 The method is relatively simple with direct bleaching of the methyl orange reagent.

5.2 Interfering substances in the air sample may affect the accuracy of the method. The sampled solutions must be protected from direct sunlight if the color is to be preserved for 24 hr.

6. **Apparatus**

6.1 Spectrophotometer. Suitable for measurement at 505 nm, preferably accommodating 5-cm cells.

6.2 Fritted bubbler. Coarse porosity, of 250-350 ml capacity. A small bubbler of 50-60 ml capacity may be more convenient for industrial hygiene sampling; volumes of reagents are then reduced proportionally.

7. **Reagents**

Reagents must be ACS analytical grade quality. Distilled water should conform to ASTM Standard for Referee Reagent Water.

7.1 Chlorine-demand-free water. Add sufficient chlorine to distilled water to destroy the ammonia. The amount of chlorine required will be about ten times the amount of ammoniacal nitrogen present. In no case should the initial residual be less than 1.0 mg/l free chlorine. Allow the chlorinated distilled water to stand overnight or longer, then expose to direct sunlight for one day or until all residual chlorine is discharged. A UV lamp may also be used to discharge the chlorine.

7.2 Methyl orange stock solution, 0.05%. Dissolve 0.500 g reagent grade methyl orange in distilled water and dilute to 1 liter. This solution is stable indefinitely if freshly boiled and cooled distilled water is used.

7.3 Methyl orange reagent, 0.005%. Dilute 100 ml of stock solution to 1 liter with distilled water. Prepare fresh for use.

7.4 Sampling solution. 6 ml of 0.005% methyl orange reagent is diluted to 100 ml with distilled water and 3 drops (0.15-0.20 ml) of 5.0 N HCl added. One drop of butanol may be added to induce foaming and increase collection efficiency.

7.5 Acidified water. To 100 ml of distilled water, add 3 drops (0.15-0.20 ml) of 5 N HCl.

7.6 Potassium dichromate solution, 0.1000 N. Dissolve 4.904 g anhydrous $K_2Cr_2O_7$, primary standard grade, in distilled water and dilute to 1 liter.

7.7 Starch indicator solution. Prepare a thin paste of 1 g of soluble starch in a few ml of distilled water. Bring 200 ml of distilled water to a boil, remove from heat, and stir in the starch paste. Prepare fresh before use.

7.8 Potassium iodide, reagent grade.

7.9 Sodium thiosulfate solution, 0.1 N. Dissolve 25 g of $Na_2S_2O_3 \cdot 5H_2O$ in freshly boiled and cooled distilled water and dilute to 1 liter. Add 5 ml chloroform as preservative and allow to age for 2 weeks before standardizing as follows: To 80 ml of distilled water, add, with constant stirring, 1 ml conc. H_2SO_4, 10.00 ml 0.1000 N $K_2Cr_2O_7$, and approximately 1 g of KI. Allow to stand in the dark for 6 minutes. Titrate with 0.1 N thiosulfate solution. Upon approaching the end-point (brown color changing to yellowish green), add 1 ml of starch indicator solution and continue titrating to the end-point (blue to light green).

$$\text{Normality } Na_2S_2O_3 = \frac{1.000}{\text{mls of } Na_2S_2O_3 \text{ used}}$$

7.10 Sodium thiosulfate solution, 0.01 N. Dilute 100 ml of the aged and standardized 0.1 N $Na_2S_2O_3$ solution to 1 liter with freshly boiled and cooled distilled water. Add 5 ml chloroform as preservative and store in a glass-stoppered bottle. Standardize frequently with 0.0100 N $K_2Cr_2O_7$.

7.11 Chlorine solution, approximately 10 ppm. Prepare by serial dilution of household bleach (approx. 50,000 ppm), or by dilution of strong chlorine water made by bubbling chlorine gas through cold distilled water. The diluted solution should contain approximately 10 ppm of free (available) chlorine. Prepare 1 liter.

8. **Procedure**

8.1 Place 100 ml of sampling solution in the fritted bubbler. A measured volume of air is drawn through at a rate of 1-2 l/min for a period of time appropriate to the estimated chlorine concentration. Transfer the solution to a 100-ml volumetric flask and make to volume, if necessary, with acidified water. Measure absorbance at 505 nm in 5-cm cells against distilled water as reference.

8.2 The volume of sampling solution, the concentration of methyl orange in the sampling solution, the amount of air sampled, the size of the absorbing vessel and the length of the photometer cell can be varied to suit the needs of the situation as long as proper attention is paid to the corresponding changes necessary in the calibration procedure.

9. **Calibration and Standards**

9.1 Prepare a series of six 100-ml volumetric flasks containing 6 ml of 0.005% methyl orange reagent, 75 ml distilled water, and 3 drops (0.15-0.20 ml) of 5.0 N HCl. Carefully and accurately pipet 0, 0.5, 1.0, 5.0 and 9.0 ml of chlorine solution (approximately 10 ppm) into the respective flasks, holding the pipet tip beneath the surface. Quickly mix and make to volume with distilled water.

9.2 Immediately standardize the 10 ppm chlorine solution as follows: To a flask containing 1 gm KI and 5 ml glacial acetic acid, add 400 ml of chlorine solution, swirling to mix. Titrate with 0.01 N $Na_2S_2O_3$ until the iodine color becomes a faint yellow. Add 1 ml of starch indicator solution and continue the titration to the end-point (blue to colorless). One ml of 0.0100 N $Na_2S_2O_3$ = 0.3546 mg of free chlorine. Compute the amounts of free chlorine added to each flask in 9.1.

9.3 Transfer the standards prepared in 9.1 to absorption cells and measure absorbance vs. micrograms of chlorine to draw the standard curve.

10. **Calculations**

$$\text{ppm } Cl_2 = \frac{\text{mg } Cl_2 \text{ found}}{\text{liters of air sampled}} \times \frac{24{,}450}{71}$$

For different temperatures and atmospheric pressures, proper correction for air volume should be made to standard conditions of 25°C and 760 Torr.

11. **References**

11.1 Taras, M., "Colorimetric Determination of Free Chlorine with Methyl Orange", Anal Chem 19:3-12, 1947.

11.2 Boltz, D. F., Colorimetric Determination of Nonmetals, p. 163, Interscience Publishers, New York, 1958.

11.3 Standard Methods for the Examination of Water and Waste Water, 12th Ed., p. 9, American Public Health Association, New York, 1965.

11.4 Traylor, P. A. and S. A. Shrader, Determination of Small Amounts of Free Bromine in Air, Dow Chemical Company, Main Laboratory Reference MR4N, Midland, Michigan.

11.5 Thomas, M. D. and R. Amtower, Unpublished work.

11.6 Intersociety Committee, Methods of Air Sampling and Analysis, Analysis for Free Chlorine Content of the Atmosphere, (42215-01-70T), pp. 282-284, American Public Health Association, Washington, D. C., 1972.

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-120
DATE	May 28, 1980
SUPERSEDES	
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DUST PARTICULATES IN AIR, PARTICLE SIZE AND ELEMENTAL ANALYSIS

Analyte:	Particle size and elemental analysis	Method No.:	IHA-120
Matrix:	Dust	Range:	0.1 to 100 μm
Procedure:	Scanning Electron Microscope	Precision:	5% absolute reproducibility (particle size)

1.0 Principle of the Method

1.1 The Scanning Electron Microscope (SEM) is used to take magnified photographs of dust particles that have been collected by passing air through a filter.

1.2 These particulates, on representative photographs, are then measured and counted to obtain a particle size distribution.

1.3 A semiquantitative elemental analysis of representative particles of the sample is made, using the energy-dispersive analyzer coupled with the SEM.

2.0 Range and Sensitivity

2.1 Particles in the size range of 0.1 to 100 μm are easily measured.

2.2 Determination of an element in a single particle requires a concentration in the particle of ~10% or more.

2.3 Only elements with an atomic number of ten or more are detected by this method.

3.0 Interferences

3.1 If the deposit of particles obtained on the filter material is too dense, then some particles may be covered by other particles. In this case the size and elemental analyses of the covered particles are not possible by this method.

4.0 Precision and Accuracy

4.1 SEM accuracy (magnification) is confirmed by use of the SEM Master Calibration Sample No. SRM-484A.

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4.2 Table 1 shows the results of a particle size analysis by two different operators. The weighted mean particle diameter ($\Sigma nd/N$) obtained from two different operators agrees within 7.5%. Figure 1 shows the data for the two operators plotted on logarithmic probability graph paper. For any given particle size, the percentage agreement is within ±5% absolute.

4.3 The elemental analysis (semiquantitative) will be only as reliable as the homogeneity of the filtered sample and of each particle. Therefore, the more particles analyzed, the greater the reliability. Since elemental standards are used, the positive identification of a given element in a particle is ensured if it is present in sufficient concentration ($\geq \sim 10\%$). The population precision of the elemental analysis summary data is equal to 1/N where N is the total number of particles analyzed; in the example of Table 2 (40 particles), it would be ±1/40, or ±2.5%.

5.0 Advantages and Disadvantages of the Method

5.1 Advantages include relative simplicity; systematic methodology; and ability to measure and analyze extremely small particles.

5.2 Disadvantages include inability to analyze particles for any element under atomic number 10; inability to accurately analyze dense collections of particles; and relatively long sample turnaround time.

6.0 Apparatus

6.1 Scanning Electron Microscope (SEM), Materials Analysis Corporation Model 700-S, or equivalent.

6.2 Particle Size Analyzer, Zeiss, or equivalent.

6.3 Energy Dispersive Analyzer (EDS), Princeton Gamma-Tech (PGT), or equivalent.

6.4 Dish, glass, with cover, large enough to hold the dust filter.

6.5 Scissors.

6.6 SEM sample mounts.

6.7 Adhesive, Television Tube Koat (2-fl-oz bottle), or equivalent.

6.8 Calculator - any model or type.

6.9 Logarithmic probability graph paper.

6.10 Sputter Coating Unit, Polaron Model 5000HS, or equivalent.

7.0 Reagents

None used for this procedure.

8.0 Procedure

8.1 Sample Handling Procedure

8.1.1 Dust particulates may be collected on different size filters. It is important to cut out different areas of the filter if the original sample is larger than 1 in. in diameter. One inch is as large a sample as may be used for an examination in the SEM. The cut samples should be taken (1) near the center, (2) near the outer edge, and (3) about halfway between the center and the edge.

8.1.2 It is important that the original sample, and the smaller cut samples to be used for the examination, be protected in a covered glass container to prevent contamination from particles in the air where the sample is being handled.

8.2 Operating Procedure

8.2.1 Record the receipt of the dust filter sample in the SEM Logbook, which gives the sample a specific log number. This SEM log number will always be used on the pictures and on other data in reference to this sample.

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8.2.2 Place the sample in a glass dish, cover it with a glass cover, and put the SEM log number on the cover top. Leave the sample covered until ready to examine it in the SEM.

8.2.3 If the sample is 1 in. in diameter or smaller, place it on top of an SEM sample mount, with the particles on the top--not touching the mount.

8.2.4 If the sample is greater than 1 in. in diameter, it must be subsampled, with no section larger than 1 in. in diameter. Care must be taken when cutting the sample to minimize loss of any particles and to take representative subsamples. In cutting a larger sample, at least 3 subsamples should be taken, in accord with Section 8.1.1.

8.2.5 Bind the sample or samples in the proper position on the sample mount, centered, by use of the adhesive (6.7). This adhesive is placed on the outer edge and should not touch any of the particles.

8.2.6 After the adhesive has dried, place each sample in the Sputter Coating Unit to apply a thin conductive metallic film over all the samples. This will ensure that all of the samples are electrically conductive, which is necessary for good SEM analysis.

8.2.7 Protect the mounted samples from contamination until ready to be examined in the SEM.

8.3 Picture-Taking Procedure

8.3.1 Complete details for operation of the SEM are assumed to be known by anyone performing this procedure (Reference 11.1).

8.3.2 Using low magnification scans (50X to 200X), make a survey of the sample from center to the outer edge to determine the uniformity of the particles on the filter. If the particle distribution is not uniform, then a decision must be made as to the various areas to be examined to obtain a true representation of the particle population on the filter.

8.3.3 Take at least three SEM pictures of different areas on the sample.

8.3.4 If subsamples have been made of the original sample (Section 8.2.4), then take at least one representative picture of each subsample, to provide a good representation of the various cut sections of the original sample.

8.3.5 All of the SEM pictures should be taken at 1000X. This makes it possible to obtain a good distribution of the particles in the range of 1 to 30 μm in diameter, which covers the sizes most often of interest.

8.3.6 These three (or more) SEM pictures will be used for the dust particle size analysis on the Particle Size Analyzer.

8.4 Analysis of Samples

8.4.1 It is assumed that the operator is familiar with the necessary conditions for elemental analysis of particles by use of the SEM (Section 11.2).

8.4.2 Having obtained, from Section 8.3.2, an idea of the homogeneity of the particles on the filter, select areas as in Section 8.3.3 and take at least three 5000X SEM pictures.

8.4.3 After each picture is taken, number each particle on the SEM photograph.

8.4.4 Enough 5000X SEM pictures should be taken to cover at least 30 to 100 particles.

8.4.5 Obtain an elemental analysis on each of these particles, using the Energy Dispersive Analyzer coupled to the SEM.

8.4.6 Keep good records of each particle and its elemental composition, tabulated as in Table 2.

9.0 Calibration and Standards

9.1 Using the SEM Master Calibration Sample No. SRM-484A, check the 1000X photograph obtained on the SEM to be assured that it is operating correctly.

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10.0 Calculations

10.1 Particle Size

10.1.1 Figure 2 shows a particle size analysis form. The numerical data obtained from the particle size analyses in Section 8.3.6 are recorded in the appropriate column for the SEM picture area.

10.1.2 Continue recording the numbers obtained from the different counters on the Particle Size Analyzer until all of the SEM pictures that were counted have been recorded. This should include at least three pictures.

10.1.3 Obtain the sum for Areas 1, 2, and 3 for each line in Figure 2.

10.1.4 Add all of the numbers in the "Sum" column to obtain a total of all the particles counted.

10.1.5 Divide the sum on each line by the total to obtain the percent of each size. Record each of these percent figures in the proper column.

10.1.6 Add the sum of the size percent cumulatively for each line, to obtain a "% Less Than" to be recorded in the last column. That is, on line 2 will be the sum of the % from lines 1 and 2; on line 3 will be the sum of the % from lines 1, 2, and 3; etc. Continue adding until all of the lines have been added and recorded.

10.1.7 Figure 1 shows the logarithmic probability graph. On this graph is plotted the size listed in Column 2 of Figure 2 versus the "% Less Than" that would be listed in Column 8. This graph will cover sizes from 1 to 100 μm.

10.1.8 From this graph one can readily obtain (1) the percent less than any given size for the sample examined, and (2) the percentage of a given size dust particle on the filter, by recognizing that the plotted %'s are cumulative from the small particle sizes to the large.

10.2 Elemental Analysis

10.2.1 A record of the elemental composition of the particles on three SEM photographs has already been obtained, tabulated as in Table 2.

10.2.2 By use of a calculator, compute the "Particle Analysis" summary as given at the bottom of Table [illegible].

11.0 References

11.1 Wells, Oliver C.; *Scanning Electron Microscopy*; McGraw-Hill Book Company (1974).

11.2 Armstrong, John Thomas; *Quantitative Electron Microprobe Analysis of Airborne Particulate Material*; PhD Dissertation, Arizona State University, 766 pp.(1978).

Table 1
PARTICLE SIZE ANALYSIS

Measurement No.	d, Particle Size, µm	No. of Particles, n: Operator 1	% Each Size	% Less Than	No. of Particles, n: Operator 2	% Each Size	% Less Than
1	1.49						
2	2.04	1	0.2				
3	2.59	10	2.3	2.5	7	1.8	
4	3.14	26	3.9	8.4	22	5.6	7.4
5	3.69	34	7.7	16.1	39	9.9	17.3
6	4.25	49	11.1	27.2	48	12.2	29.5
7	4.80	58	13.1	40.3	31	7.9	37.4
8	5.35	37	8.4	48.7	29	7.4	44.8
9	5.90	28	6.3	55.0	16	4.1	48.9
10	6.45	29	6.5	61.5	21	5.3	54.2
11	7.01	20	4.5	66.0	23	5.8	60.0
12	7.56	15	3.4	69.4	20	5.1	65.1
13	8.11	20	4.5	73.9	14	3.6	68.7
14	8.66	18	4.1	78.0	15	3.8	72.5
15	9.22	4	0.9	78.9	9	2.3	74.8
16	9.77	13	2.9	81.8	9	2.3	77.1
17	10.32	9	2.0	83.8	9	2.3	79.4
18	10.87	16	3.6	87.4	7	1.8	81.2
19	11.42	6	1.4	88.8	8	2.0	83.2
20	11.98	6	1.4	90.2	9	2.3	85.5
21	12.53	7	1.6	91.8	6	1.5	87.0
22	13.08	3	0.7	92.5	5	1.3	88.3
23	13.63	4	0.9	93.4	5	1.3	89.6
24	14.18	5	1.1	94.5	13	3.3	92.9
25	14.74	1	0.2	94.7	1	0.3	93.2
26	15.29	2	0.5	95.2	3	0.8	94.0
27	15.84	3	0.7	95.9	2		
28	16.39	2	0.5	96.4	3	0.8	94.8
29	16.94	1	0.2	96.6	1	0.3	95.1
30	17.50	3	0.7	97.3	3	0.8	95.9
31	18.05	1	0.2	97.5	1	0.3	96.2
32	18.60	1	0.2	97.7	1	0.3	96.5
33	19.15	4	0.9	98.6	3	0.8	97.3
34	19.70						
35	20.26	1	0.2	98.8	6	1.5	98.8
36	20.81						
37	21.36	2	0.5	99.3	1	0.3	99.1
38	21.91						
39	22.47						
40	23.02						
41	23.57	1	0.2	99.5	1	0.3	99.4
42	24.12	1	0.2	99.7	1	0.3	99.7
43	24.67						
44	25.26						
45	25.78						
46	26.33	1	0.2	99.9			
47	26.88						
48	27.43	1	0.2	>100	1	0.3	
	Σnd/N	7.09			7.63		
	Σn = N	443			394		

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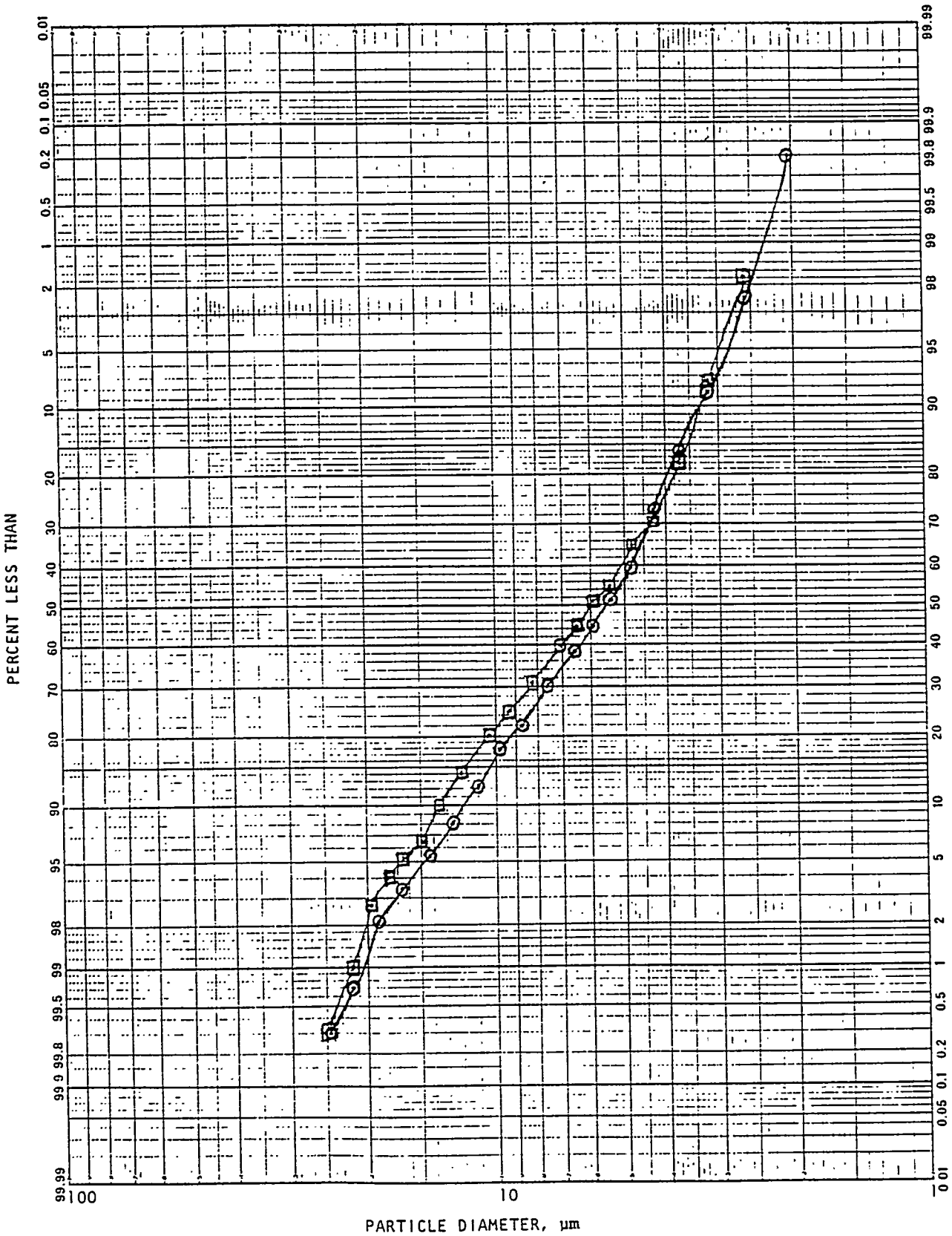

Figure 1. DUPLICATE SIZE DISTRIBUTION MEASUREMENTS

NUMBER	IHA-120

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Table 2

PARTICLE NUMBER VS. ELEMENTAL COMPOSITION

Particle No.	U	Organic	Mg	Si	Al	Ca	K	Fe	Other
1	VS								
2	VS								
3			W	S				VW	
4		X							
5			Tr	S		W		S	Ti W
6			Tr	S		W		S	Ti W
7	VS							Tr	
8				S	W		W	W	
9				W		VS	W	W	Cl W
10	Tr	X							
11	Tr			Tr		VS	Tr	Tr	
12				VS				Tr	
13						W	S	Tr	Cl S
14		X		Tr		Tr		Tr	
15		X						Tr	
16			W	Tr		VS		Tr	
17			W	Tr		VS		Tr	
18				VS	Tr			Tr	
19	Tr	X						Tr	
20	S				S				
21	VS								
22	VS							Tr	
23				VS	Tr	Tr		Tr	
24	Tr			Tr		VS		Tr	Cl Tr
25		X						Tr	
26	VS								
27	Tr	X						Tr	
28		X		Tr		Tr	Tr	Tr	Cl Tr
29	Tr	X						Tr	
30				Tr	Tr	VS		Tr	
31				Tr	Tr	VS		Tr	
32	Tr		Tr		VS			Tr	
33	VS								
34	Tr		Tr		VS			Tr	
35				Tr	Tr	S	Tr	Tr	
36	Tr	X						Tr	
37		X							
38	Tr		Tr	S	W			Tr	
39		X				Tr	Tr	Tr	Cl Tr
40			Tr	VS	W			Tr	

Definitions: Estim. % (of Signals)

VS (Very Strong)	>60
S (Strong)	40-60
W (Weak)	20-40
VW (Very Weak)	10-20
Tr (Trace)	<10

X = organic assumed because no other elements were detected (@ atomic no. $\geq$ 10). May be totally organic or contain complexes of carbon, such as $CO_3^{=}$.

Particle Analysis*: % of particles in which the constituent is a major component (VS or S).

Uranium major element	20%	Aluminum major element	7.5%
Organic major constit.	30%	Calcium major element	20 %
Silicon major element	22.5%	Others (Potassium, iron, chlorine)	10 %

*Some particles contain more than 1 major element. Thus, the total may equal > 100%.

Measurement No.	Particle Size, µm	Area 1	Area 2	Area 3	Sum 1 + 2 + 3	% Each Size	% Less Than		
1	1.49								
2	2.04								
3	2.59								
4	3.14								
5	3.69								
6	4.25								
7	4.80								
8	5.35								
9	5.90								
10	6.45								
11	7.01								
12	7.56								
13	8.11								
14	8.66								
15	9.22								
16	9.77								
17	10.32								
18	10.87								
19	11.42								
20	11.98								
21	12.53								
22	13.08								
23	13.63								
24	14.18								
25	14.74								
26	15.29								
27	15.84								
28	16.39								
29	16.94								
30	17.50								
31	18.05								
32	18.60								
33	19.15								
34	19.70								
35	20.26								
36	20.81								
37	21.36								
38	21.91								
39	22.47								
40	23.02								
41	23.57								
42	24.12								
43	24.67								
44	25.26								
45	25.78								
46	26.33								
47	26.88								
48	27.43								
				Total					
	Σn = N								

Figure 2. PARTICLE SIZE ANALYSIS (FORM)

UCN-10766P (12 8-78)

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-130
DATE	Nov. 27, 1979
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FLUORIDE, GASEOUS AND WATER-SOLUBLE PARTICULATE IN AIR, SELECTIVE ION ELECTRODE METHOD

Analyte: Fluoride, gaseous and water-soluble particulate

Matrix: Air

Procedure: Adsorption on alkaline-treated filter paper; leach with water; and selective ion electrode measurement

Method No.: IHA-130

Range: 5 μg to 1500 μg per sample

Precision: 10% RSD

1.0 Principle of the Method

1.1 A known volume of air is drawn through a sampling train.

1.2 Atmospheric fluoride is collected by absorbing the fluoride on a filter treated with potassium carbonate. Gaseous fluoride may be differentiated from water-soluble particulate fluoride (if desirable) by preceding the treated filter with an untreated filter in the sampling train.

1.3 Fluoride is removed from the filters by leaching them in water. The fluoride is then determined potentiometrically using an ion-selective electrode in conjunction with a standard single junction sleeve-type reference electrode and an expanded millivolt scale electrometer, or a selective ion meter with a direct scale for fluoride.

2.0 Range and Sensitivity

2.1 The lowest amount of fluoride reported is 5 micrograms per sample.

2.2 The upper range is limited only by the capacity of the filter paper used for collecting the gaseous fluoride sample. As much as 1500 micrograms has been collected on two back-to-back 50-mm diameter filters without significant fluoride loss.

3.0 Interferences

3.1 The presence of acid gases or fumes in the sample collection area may bias results low by depleting the potassium carbonate in the filter.

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APPROVED BY PGDP	LAB R. E. Simmons IH C. W. Turak	APPROVED BY ORNL	LAB W R Laing IH J. A. Ely	NUMBER IHA-130

UCN 13234
(1-35 1-79)

3.2 Potential interferences of OH^-, Si^{+4}, Fe^{+3}, and Al^{+3} are eliminated by addition of a pH buffer containing a cation complexing agent prior to measuring the fluoride in the sample solution.

4.0 Precision and Accuracy

4.1 The relative standard deviation of the analysis is estimated to be 10% or better when greater than 10 micrograms of fluoride is present on the filter.

4.2 Field tests conducted at the Paducah Gaseous Diffusion Plant indicated the treated filters were greater than 95% efficient for absorbing atmospheric fluoride in the range of 1 to 20 $\mu g/m^3$ when air was passed through two back-to-back 50-mm filters at a flow rate of 0.3 cfm.

5.0 Advantages and Disadvantages of the Method

5.1 Sampling using filter papers is much more desirable than the use of wet scrubbers and impingers, from the viewpoint of handling and sample preparation. Samples are easily retrieved and new filters can be installed at the same time.

5.2 One moderate disadvantage of the method is that the amount of sample which can be taken is limited by the capacity of the filter paper for absorbing gaseous fluoride. However, as much as 1500 μg of fluoride has been collected on two back-to-back filters.

5.3 Using a conventional sampling train, the precision and accuracy of the method is limited by the reproducibility of the pressure drop across the filter papers. With extended periods of sampling the paper tends to plug somewhat, thus affecting the pressure drop. This drop will affect the flow rate and cause the air volume to be imprecise. Regular adjustment of the flow rate reduces this problem.

6.0 Apparatus

6.1 Air sampling system: the area can be sampled with a combination of a vacuum pump, flow throttle, and air flowmeter, with which flow can be accurately determined at 0.3 cfm or less. To minimize analyte losses in the system, the fluoride filters must be placed at the air entry.

6.2 Electrometer (pH), with expanded mv scale, such as the Orion Model 801 digital pH/mv meter, or equivalent.

6.3 Fluoride ion activity electrode, such as the Orion No. 94-09.

6.4 Reference electrode, single junction, sleeve type, such as Orion No. 90-01, Beckman No. 40454, or Corning No. 476010.

6.5 Magnetic mixer, Teflon-coated stirring bar.

6.6 Membrane filters, 47-mm dia, 0.8-μ pore, Gelman GA-4. These filters have proven to be satisfactory; whereas, similar filters from Millipore have been found to crack during extended periods (several days) of service.

6.7 Filter holders for use with above filters.

6.8 Laboratory oven capable of controlling at 40°C.

6.9 Stainless steel screen wire to support treated filters and fit in oven.

7.0 Reagents

7.1 Buffer solution, pH 5.0-5.5: To approximately 500 ml of distilled water in a 1-liter beaker add 57 ml of glacial acetic acid, 59 g of sodium chloride and 2 g of CDTA (1,2-cyclohexylene dinitrilotetraacetic acid or cyclohexane diaminetetraacetic acid). Stir to dissolve and cool to room temperature. Adjust pH of solution to between 5.0 and 5.5 with 5 N sodium hydroxide (about 150 ml will be required). Transfer to a 1-liter volumetric flask and dilute to volume with distilled water.

7.2 Potassium carbonate, 5% w/v solution. Dissolve 50 g of K_2CO_3 in distilled water and dilute to 1 liter.

7.3 Sodium fluoride standard stock solution: 1 ml = 0.1 mg F. Dissolve 0.2210 g of anhydrous NaF in distilled water and dilute to 1 liter with distilled water. Dilute aliquots of this solution to provide standard solutions as needed.

8.0 Procedure

8.1 Preparation of Filters for Sampling

8.1.1 Pour about 50 ml of 5% K_2CO_3 solution into a disposable weighing dish or other shallow container.

8.1.2 Immerse the membrane filters in the K_2CO_3 solution and allow them to soak about 30 seconds.

8.1.3 Remove each filter with a spatula, allowing the excess solution to drain off, and place the filters on a stainless steel wire screen.

8.1.4 Place the screen in an oven and dry at 40°C. Overheating may discolor the filter paper.

8.1.5 After the filters dry, place two filters in each filter holder. If it is desirable to preclude water-soluble particulate fluoride from the sample, assemble a holder with a single untreated filter to precede the treated filters in the sampling train. Any metal parts of a filter holder exposed to the air sample should be coated with clear acrylic lacquer to prevent losses of fluoride by chemisorption on the metal surfaces.

8.2 Collection and Shipping of Samples

8.2.1 After attachment of the filter holder to the sampling pump, the flow rate is adjusted to an indicated level of 0.3 cfm or less to attain the total sample volume required over a fixed period of time.

8.2.2 After sampling, the filter holders are returned to the laboratory for quantitative fluoride analysis.

8.2.3 No special handling techniques are required after the sample is collected.

8.3 Analysis of Samples

8.3.1 Place the filter paper containing the trapped fluoride into an appropriate beaker and add 25 ml of distilled water. Allow approximately 5 minutes with occasional stirring for the fluoride to solubilize.

8.3.2 Transfer a suitable aliquot into a 100-ml beaker, dilute to 25 ml with distilled water and add 25 ml of buffer solution. Obtain the mv reading by measuring on the selective ion meter as in 9.2.

8.3.3 Determine the amount of fluoride in the sample aliquot from the standard calibration curve prepared in accordance with 9.0.

9.0 Calibration and Standards

9.1 Transfer to 100-ml beakers several 25-ml aliquots of standard sodium fluoride solutions prepared with concentrations sufficient to cover the expected concentration range of the samples. Add 25 ml of buffer solution to each beaker.

9.2 Place each standard on a magnetic stirrer and mix. Immerse the fluoride and reference electrodes in the solution and observe the meter reading while mixing. After the meter reading has stabilized, record the mv reading.

9.3 Prepare a calibration curve by plotting μg F/ml in the standard vs mv reading, using semilogarithmic graph paper. Plot the concentration of fluoride (based on the 25-ml volume of the standards) on the log axis vs the electrode potential developed by the standard on the linear axis, starting with the lowest concentration at the bottom of the scale.

9.4 For calibration of a direct-reading selective ion meter, follow the directions of the manufacturer.

10.0 Calculations

10.1 Fluoride on filter, μg $= \frac{A \times 625}{V}$

where:

A = μg fluoride/ml from calibration curve,

V = sample aliquot, ml, and

625 = 25 ml · 25 ml = dilution factor.

10.2 Fluoride in air, mg/m^3 $= \frac{\text{fluoride on filter, } \mu g}{1000 \times \text{air volume, } m^3}$.

UCN-10766B (12 8-78)

11.0 References

11.1 Chumbler, D. L., Horntrop, J. O., and Simmons, R. E.; "Treated Filter Paper for Collecting Fluoride from the Atmosphere"; Paducah Plant Development Progress Report, 1973, KYL-646, Part 12.

11.2 Technical Procedures Manual, Technical Services Division, Paducah Gaseous Diffusion Plant, Procedure No. SA-F-2, (1974).

11.3 Manual of Methods for Chemical Analysis of Water and Wastes, U. S. Environmental Protection Agency, p. 65 (1976).

11.4 Standard Methods for the Examination of Water and Wastewater, 14th Edition, p. 391 (1975).

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-140
DATE	August 26, 1981
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HYDROGEN CHLORIDE IN AIR, SELECTIVE ION ELECTRODE METHOD

Analyte: Hydrogen Chloride

Matrix: Air

Procedure: Bubbler collection in 0.5M sodium acetate; measurement with selective ion electrode

Method No.: IHA-140 (NIOSH S246)

Range: 3.5 to 14 mg/m^3 in a 15-L air sample

Precision: 0.064 (CV_T)
6.4% (RSD)

Accuracy: No bias established

For this analysis, the undersigned committee has approved for inclusion in this manual an existing procedure, exactly as published. Accordingly, the following pages are taken verbatim from the NIOSH Manual of Analytical Methods, Second Edition, Vol. 3, U. S. Department of Health, Education, and Welfare, Method S246, 1977.

The following comment on NIOSH S246 should aid understanding:

A. The calculation in Section 10.5 expresses ppm on a volume/volume basis, as normally employed by the American Conference of Governmental Industrial Hygienists (ACGIH).

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APPROVED BY PGDP	LAB R. E. Simmons IH C. H. Turak	APPROVED BY ORNL	LAB W R Laing IH James A. Ealy	NUMBER IHA-140

The following procedure is a photocopied excerpt from: NIOSH Manual of Analytical Methods, Second Edition, Vol. 3, U. S. Department of Health, Education, and Welfare, 1977.

Hydrogen Chloride

Analyte:	Hydrogen Chloride	Method No.:	S246
Matrix:	Air	Range:	3.5-14 mg/cu m
OSHA Standard:	5 ppm (7 mg/cu m) - Ceiling	Precision ($\overline{CV}_T$):	0.064
Procedure:	Bubbler collection in 0.5 M sodium acetate, ion specific electrode	Validation Date:	1/30/76

1. Principle of the Method (Reference 11.1)

1.1 A known volume of air is drawn through a midget bubbler containing 10 ml of sodium acetate solution.

1.2 The resulting solution is diluted to 25 ml with distilled water.

1.3 The diluted samples are analyzed using a chloride ion specific electrode.

2. Range and Sensitivity

2.1 This method was validated over the range of 3.5-14 mg/cu m at an atmospheric temperature and pressure of 22°C and 764 mm Hg, using a 15-liter sample. The probable useful range of this method is 1-20 mg/cu m for 15-liter samples.

2.2 The upper limit of the range of the method is dependent on the capacity of the midget bubbler. If higher concentrations than those tested are to be sampled, smaller sample volumes should be used. The collection efficiency for hydrogen chloride was determined to be 0.981, standard deviation of 0.005 (essentially 1.00), when sampled for 15 minutes at 0.94 liter per minute from a test atmosphere containing 70 mg/cu m. Therefore, no correction for collection efficiency is necessary.

3. Interferences

3.1 This method is not specific for hydrogen chloride since any chloride ion which is trapped in the bubbler will be measured and give a positive interference.

3.2 Sulfide ion must be absent because it poisons the chloride ion electrode. Touch a drop of the sample to a piece of lead acetate paper to check for sulfide ion.

If sulfide is present, it is removed by addition of a small amount of powdered cadmium carbonate to the sample. Swirl to disperse the solid and recheck a drop of the sample with lead acetate paper. Avoid a large excess of cadmium carbonate and long contact time with the solution. Filter the sample through a small plug of glass wool and proceed with the analysis.

3.3 Other common interfering ions are bromide ion, iodide ion, and cyanide ion. For interference-free operation, the chloride ion level must be at least 3×10^2 times the bromide ion level, 2×10^6 the iodide ion level, and 5×10^6 the cyanide ion level.

3.4 Sufficient high concentrations of species which form extremely stable complexes with silver ion (such as ammonia and thiosulfate) will also interfere and will result in reading of higher chloride ion activity than actually exists. For less than a 1% error, the maximum ratio of ammonia to chloride concentration should be 0.12 and the maximum ratio of thiosulfate ion to chloride ion concentration should be 0.01.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 3.5-14 mg/cu m was 0.064. This value corresponds to a standard deviation of 0.45 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 A collection efficiency of 0.981 was determined for the collecting medium. On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 2.7% higher than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result in Section 10.4.

5. Advantages and Disadvantages of the Method

5.1 Collected samples are analyzed by means of a quick, instrumental method.

5.2 A disadvantage of the method is the awkwardness in using midget bubblers for collecting personal samples. If the worker's job performance requires much body movement, loss of the collection solution during sampling may occur which would invalidate the sample. If more than 5% of the sample volume is lost, the sample should be discarded.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the bubbler collection method consists of the following components:

6.1.1 A glass "midget bubbler" containing the collection medium (Section 7.2).

6.1.2 A pump suitable for delivering at least 1.0 liter per minute for 15 minutes. The sampling pump is protected from splashover or solvent condensation by a 5-cm long by 6-mm I.D. glass tube loosely packed with a plug of glass wool and inserted between the exit arm of the bubbler and the pump.

6.1.3 An integrating volume meter such as a dry gas or wet test meter.

6.1.4 Thermometer.

6.1.5 Manometer.

6.1.6 Stopwatch.

6.2 Pipets: 1, 2, 3, 5, and 10 ml.

6.3 Orion Model 94-17A chloride specific ion electrode, or equivalent.

6.4 Reference electrode, Orion 90-02 double junction, or equivalent.

6.5 Expanded scale millivolt-pH meter, capable of measuring to within 0.5 millivolt.

6.6 Polyethylene beakers, 50-ml capacity. Premark the beakers by pipetting 25 ml of distilled water into each beaker and mark the liquid level. Pregraduated polyethylene beakers may be used. However, they should be checked as described above. Discard the water and dry the beakers.

6.7 Magnetic stirrer and stirring bars for 50-ml beakers.

6.8 Polyethylene containers. These containers should be used to store diluted sodium chloride standards and also for shipping of air samples.

6.9 100-ml volumetric flasks.

7. Reagents

All chemicals must be ACS reagent grade or equivalent.

7.1 Doubly distilled water.

7.2 Collection Medium: 0.5 M sodium acetate solution. Dissolve 82 g of sodium acetate in doubly distilled water and dilute to 2 liters.

7.3 Sodium chloride, for preparation of standards.

7.4 Standard Chloride Solution.

7.4.1 Dissolve 0.584 g of sodium chloride in double distilled water and dilute to 1 liter for 10^{-2} M (Cl^-) or 354 µg Cl^-/ml. Adjust the pH to 5 with glacial acetic acid. This solution is stable for about two months. The following more dilute standards should be prepared fresh weekly and kept in polyethylene containers.

7.4.2 Dilute 10 ml 10^{-2} M (Cl^-) to 100 ml with 0.5 M sodium acetate for 10^{-3} M (Cl^-) or 35.4 µg Cl^-/ml.

7.4.3 Dilute 5 ml 10^{-2} M (Cl^-) to 100 ml with 0.5 M sodium acetate for 5 x 10^{-4} M (Cl^-) or 17.7 µg Cl^-/ml.

7.4.4 Dilute 3 ml 10^{-2} M (Cl^-) to 100 ml with 0.5 M sodium acetate for 3 x 10^{-4} M (Cl^-) or 10.6 µg Cl^-/ml.

7.4.5 Dilute 2 ml 10^{-2} M (Cl^-) to 100 ml with 0.5 M sodium acetate for 2 X 10^{-4} M (Cl^-) or 7.1 µg Cl^-/ml.

7.4.6 Dilute 1 ml 10^{-2} M (Cl^-) to 100 ml with 0.5 M sodium acetate for 10^{-4} M (Cl^-) or 3.5 µg Cl^-/ml.

8. Procedure

8.1 Cleaning of Equipment. All glassware and plastic ware are washed in detergent solution, rinsed in tap water, and then rinsed with doubly distilled water.

8.2 Calibration of Personal Sampling Pumps. Each pump should be calibrated by using an integrating volume meter (Section 6.1.3) or other means.

8.3 Collection and Shipping of Samples

8.3.1 Pour 10 ml of the collection medium (Section 7.2) into the midget bubbler, using a graduated cylinder to measure the volume.

8.3.2 Connect the bubbler (via the splashover tube) to the vacuum pump with a short piece of flexible tubing. The air being sampled should not pass through any other tubing or other equipment before entering the bubbler.

8.3.3 Turn the pump on to begin sample collection. Care should be taken to measure the flow rate, time and/or the volume as accurately as possible. Record the atmospheric pressure and the temperature. If the pressure reading is not available, record the elevation. The sample should be taken at a flow rate of 1.0 liter per minute for 15 minutes. The flow rate should be known with an accuracy of ± 5%.

8.3.4 The pump rotameter should be observed frequently, and sampling should be terminated at any evidence of a problem.

8.3.5 Terminate sampling at the predetermined time and note sample flow rate and collection time.

8.3.6 After sampling remove the bubbler stem and transfer the contents of the bubbler to a polyethylene container. Rinse the bubbler and bubbler stem with 3-5 ml of collection medium, adding the rinse to the polyethylene container. Seal the polyethylene container with the associated caps just prior to shipment.

8.3.7 Care should be taken to minimize spillage or loss by evaporation at all times. Refrigerate samples if analysis cannot be done within a day.

8.3.8 Whenever possible, hand delivery of the samples is recommended. Otherwise, special shipping cases designed by NIOSH should be used to ship the samples.

8.3.9 A "blank" bubbler should be handled in the same manner as the bubblers containing samples (fill, seal, and transport) except that no air is sampled through this bubbler.

8.4 Analysis of Samples

8.4.1 The sample in each polyethylene container is analyzed separately.

8.4.2 Quantitatively transfer the contents of each polyethylene container to a 50-ml polyethylene beaker which has been pre-marked at 25 ml. Rinse the polyethylene container with 2-3 ml of distilled water and add rinse to the beaker. Adjust the pH to 5 with acetic acid and check the pH with pH paper. Dilute each sample to 25 ml with distilled water and stir the samples with a magnetic stirrer.

8.4.3 Lower the chloride ion specific electrode and reference electrode into the stirred solution and record the resulting millivolt reading (to the nearest 0.5 mv) after it has stabilized (drift less than 0.5 mv/min).

9. Calibration and Standards

9.1 Prepare a series of chloride standard solutions in the pre-marked 50-ml beakers by diluting 10 ml of each of the chloride standards prepared in Section 7.4.2-7.4.6, to a volume of 25 ml with double distilled water, starting with the most dilute standard. Place the chloride ion electrode and the double reference electrode in the stirred solution. Record the resultant millivolt readings to the nearest 0.5 millivolt.

9.2 Plot the millivolt readings vs. the chloride ion concentrations of the standards on semi-log paper. The chloride ion concentration in µg/25 ml is plotted on the logarithmic axis.

10. Calculations

10.1 Read the weight in µg corresponding to each millivolt reading from the standard curve. No volume corrections are needed, because the standard curve is based on µg/25 ml volume, and the volume of the samples is identical to the volume of the standards.

10.2 Corrections for the blank must be made for each sample.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

µg sample = µg found in sample container
µg blank = µg found in blank container

10.3 Calculate the µg of hydrogen chloride by multiplying the µg chloride ion found (Section 10.2) by 1.028, which is the conversion factor to convert µg chloride ion to µg hydrogen chloride.

10.4 The concentration of the analyte in air sampled can be expressed in mg/cu m (mg/cu m = µg/liter).

$$\text{mg/cu m} = \frac{\mu g \text{ (Section 10.3)}}{\text{Air volume sampled (liter)}}$$

10.5 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \cdot X \frac{24.45}{M.W.} X \frac{760}{P} X \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
M.W. = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 "Analytical Method for Chloride in Air," Health Laboratory Science, Vol. 12, No. 3, (July 1975), 253-258.

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-150
DATE	Nov. 27, 1979
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MERCURY IN AIR, FLAMELESS AA METHOD

Analyte:	Mercury	Method No.:	IHA-150
Matrix:	Air	Range:	0.05 - 1.0 total µg
Procedure:	Adsorption on treated charcoal, acid desorption, digestion; measured by flameless atomic absorption	Precision:	∿5% RSD (estimated, not evaluated)
		Bias:	-3%

1.0 Principle of the Method

1.1 Air is drawn through a sampling tube containing activated charcoal impregnated with iodine and potassium iodide. The flow rate and sampling time are chosen to provide a representative workplace air sample.

1.2 The charcoal is digested in an acid-permanganate-persulfate solution at 95°C for 2 hours. Elemental mercury is then liberated by reduction with $SnSO_4$, and measured by flameless atomic absorption.

1.3 All forms of mercury--elemental, inorganic, organic--are determined by this method.

2.0 Range and Sensitivity

2.1 The normal working range is up to 1.0 µg of mercury. The lowest concentration reported is 0.05 µg.

2.2 Provision is made for extending the range to 10 µg.

3.0 Interferences

3.1 Organic compounds interfere by absorption at the 253.7 nm wavelength. This interference is minimized by the digestion step.

4.0 Precision and Accuracy

4.1 No precision studies have been made; however, specific amounts of mercury vapor were loaded on sampling tubes and analyzed by this method with the following results:

APPROVED BY Y-12	LAB A. J. McGlamery	APPROVED BY ORGDP	LAB T. Kwamoshi	APPROVED BY UCCND COORD'R	C W Weber
	IH W. S. Everett, Jr.		IH R. J. Duncan		
APPROVED BY PGDP	LAB P. E. Simmons	APPROVED BY ORNL	LAB W R Laing	NUMBER	IHA-150
	IH C. W. Turoke		IH J. A. Ealy		

UCN 13234
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µg Hg added	µg Hg found	Recovery, %
50	50.9	101.8
40	35.8	89.5
30	26.9	89.7
5	4.7	94.0
4	4.0	100.0
3	3.2	106.7

The average recovery was 97%.

5.0 Apparatus

5.1 Atomic absorption spectrophotometer, with an absorption cell at least 10-cm long x 2-cm I.D. with quartz endwindows.

5.2 Mercury hollow cathode lamp.

5.3 Strip-chart recorder.

5.4 Reagent bottles, 250-ml.

5.5 Gas supply: air, N_2, or argon.

5.6 Flowmeter, to deliver gas at 1 liter per minute.

5.7 Aerating tube: fitted with a straight cylindrical flat-end glass frit of coarse porosity.

5.8 Drying tube: a 15-cm x 19-mm O.D. tube packed with magnesium perchlorate desiccant. The apparatus is assembled as shown in Figure 1.

5.9 Water bath, capable of maintaining 95 ± 2°C.

5.10 Charcoal tubes: glass tube with both ends flame-sealed, 7 cm long with 6-mm O.D. and 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C and impregnated with 0.3% I_2 and 0.6% KI prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section.

These tubes, as described, are commercially available.

6.0 Reagents

All reagents are reagent grade and water is double-distilled or deionized.

6.1 Sulfuric acid, conc.

6.2 Sulfuric acid, 0.5 N: Add 14.0 ml of conc sulfuric acid to about 900 ml of water and dilute to 1 liter.

6.3 Nitric acid, conc: Reagent grade of low mercury content. TRANSISTAR grade (Mallinckrodt) is suitable. If this grade is not used, and a reagent blank of >0.05 μg is obtained, it will be necessary to distill the nitric acid.

6.4 Stannous sulfate suspension: Add 25 g of stannous sulfate to 250 ml of 0.5 N sulfuric acid. This mixture should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

6.5 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in water and dilute to 100 ml. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

6.6 Potassium permanganate, 5% solution (W/V): Dissolve 5 g of potassium permanganate in 100 ml of water.

6.7 Potassium persulfate, 5% solution (W/V): Dissolve 5 g of potassium persulfate in 100 ml of water.

6.8 Stock mercury solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of water, add 10 ml of conc nitric acid, and dilute to 100 ml. 1 ml = 1 mg Hg.

6.9 Working mercury solution: Add 1 ml of the stock mercury solution to 1.5 ml of conc nitric acid and dilute to 1000 ml with water. 1 ml = 1 μg Hg. This solution is stable for several months.

7.0 Procedure

7.1 Cleaning of Equipment: Acid-clean all glassware by soaking in 1:1 HNO_3 for 30 minutes and rinsing with water.

7.2 Collection and shipping of samples

7.2.1 Open both ends of the sample tube and connect to a sampling pump. Collect a sample at a given flow rate for a given time period. A flow rate of 0.2 L/min for 6 hrs is typical.

7.2.2 At the end of the sampling period, remove the tube from the pump, cap both ends, and transport to the laboratory.

UCN-10766B (12 8-78)

7.3 Sample Preparation

7.3.1 Remove the end caps and add the two sections of charcoal to separate 250-ml bottles.

7.3.2 Add to each bottle in succession: 50 ml of water, 5 ml of H_2SO_4, 2.5 ml of HNO_3, 15 ml of $KMnO_4$ solution (6.6), and 8 ml of $K_2S_2O_8$ solution (6.7).

7.3.3 Place the bottles in a water bath at 95°C for 2 hours.

7.3.4 Cool and add 6 ml of sodium chloride-hydroxylamine sulfate solution (6.5) to each bottle to reduce the excess permanganate.

7.3.5 Transfer the contents of each bottle to a 100-ml volumetric flask and dilute to volume.

7.4 Analysis of Sample

7.4.1 Transfer 10 ml of each sample to a 250-ml bottle and dilute to ∿100 ml with water.

7.4.2 Add 5 ml of the stannous sulfate suspension to a bottle and immediately attach the bottle to the aeration assembly (Figure 1).

7.4.3 Set the bypass valves to allow the gas (@ 1 liter/min) to sweep the elemental mercury from the bottle to the absorption cell. The absorbance will reach maximum within 30 seconds.

7.4.4 As soon as the absorbance begins to decrease, open the bypass valves and continue the aeration until the recorder returns to baseline.

7.4.5 Repeat 7.4.2 through 7.4.4 for each 10→100 dilution. If the level of mercury is too high in the 10→100 dilution, repeat 7.4.1 through 7.4.4 with a smaller aliquot (diluted to 100 ml) until the mercury level is within the range of the standards. If the 10→100 dilution is too low, repeat 7.4.1 through 7.4.4 with the remaining 90 ml of sample, diluted to ∿100 ml (See Note 1).

Note 1

After adding the 5 ml of stannous sulfate suspension to a 90→100 dilution, the bottle must be stoppered and a delay of 10 minutes observed before attaching the bottle to the aeration assembly. This delay is necessary to overcome the effects of interferences which are encountered only in the 90→100 dilution.

Note 2

If a dual-channel spectrophotometer is available, the entire 100-ml sample from 7.3.5 may be processed. (Observe the delay discussed in Note 1.) The scale expansion controls of each channel can be adjusted to record low levels on one channel and high levels on the other channel, thus eliminating the need to make multiple dilutions.

8.0 Calibration and Standards

8.1 Transfer 0, 100, 300, 500, and 1000-µl aliquots of the working mercury solution (6.9) to a series of 250-ml bottles. Note: Reagent blank values should not exceed 0.05 µg.

8.2 Dilute to 100 ml with water and treat as samples beginning with the H_2SO_4 addition in 7.3.2 and ending with 7.3.4.

8.3 Analyze the standards beginning with 7.4.2.

8.4 Plot peak heights versus µg mercury as a calibration curve.

9.0 Calculations

9.1 The total µg mercury found in each charcoal section is found using the following formula:

$$\text{Hg, } \mu g = (A-B) \times \frac{100}{V}$$

where A = Hg found from the calibration curve, µg,

B = Hg found in the reagent blank, µg, and

V = volume of aliquot taken in 7.4, ml.

9.2 The Hg content of each charcoal section is reported separately to allow evaluation of the efficiency of the sampling.

10.0 Reference

10.1 Procedure No. IHA-450, this manual.

UCN-10766B (12 8-78)

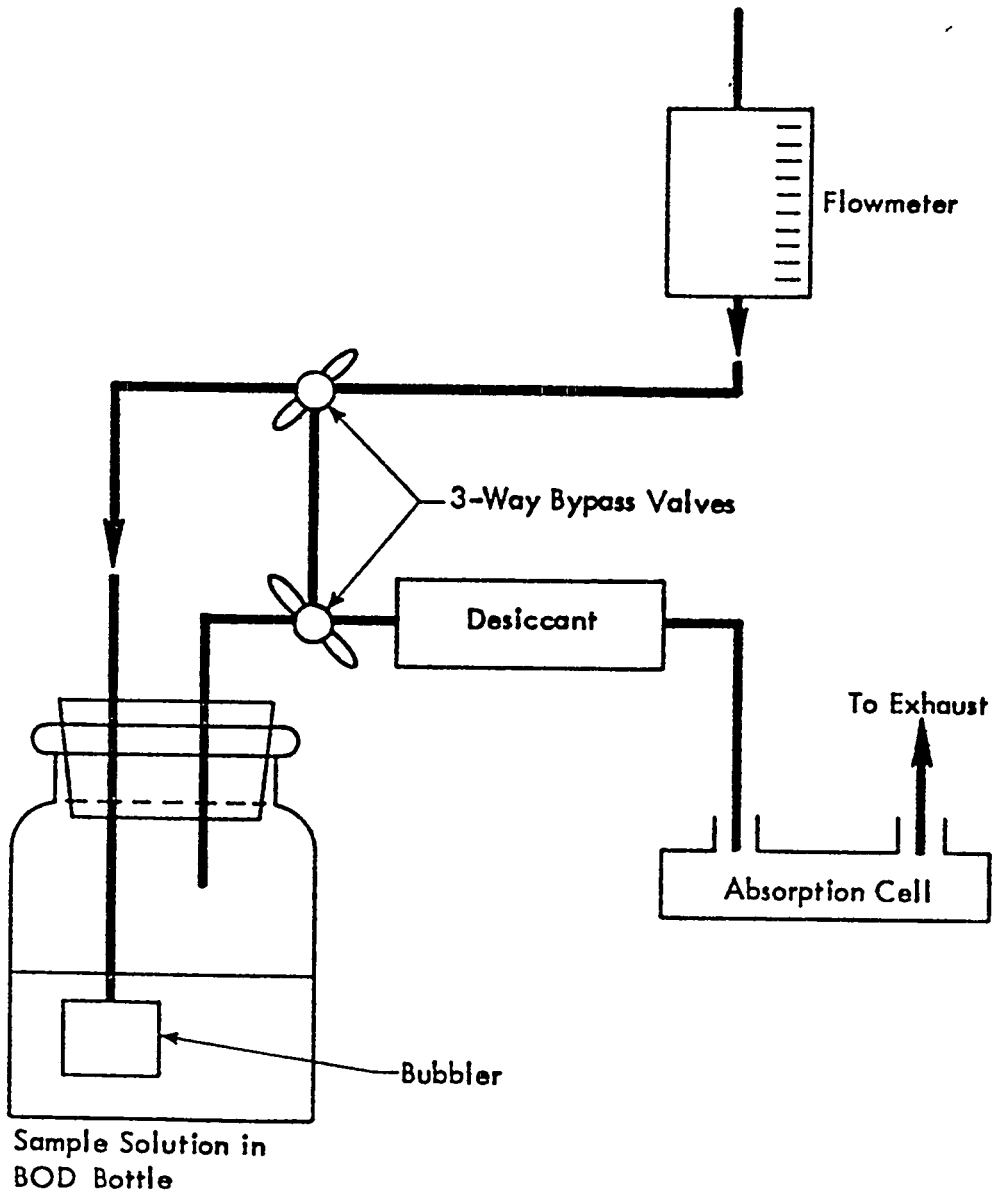

Figure 1. APPARATUS FOR FLAMELESS MERCURY DETERMINATION.

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-160
DATE	March 16, 1981
SUPERSEDES	November 27, 1979
PAGE	1 OF 9

METALS IN AIRBORNE PARTICULATES, EMISSION SPECTROGRAPHIC METHOD

Analyte:	48 trace metals, Table 1	Method No.:	IHA-160
Matrix:	Air	Sensitivity:	See Table 1
Procedure:	Sample collected on membrane filter; optical emission spectrograph	Precision:	35% LE_x, by densitometry

1.0 Principle of the Method

1.1 A known volume of air is sampled by drawing it through a membrane filter using a low-volume air sampler at a known flow rate for a fixed time.

1.2 The membrane filter containing the air particulates is ashed in a furnace at 450°C.

1.3 Graphite and buffer powders are added to obtain a final graphite-residue weight of 100 mg.

1.4 Ten-milligram charges are burned using the D.C. arc in an argon-oxygen atmosphere. Forty-eight elements are determined by visual comparison with graphite matrix standards, and densitometric measurements are used for Cu, Fe, and Ni.

1.5 An alternate technique, which does not use the buffer and argon-oxygen excitation, is also included.

2.0 Sensitivity

2.1 The lowest concentrations reported are given in Table 1 for 48 elements.

3.0 Interference

3.1 The suggested wavelengths are given in Table 1 for 48 elements. The spectroscopist applies judgment in using the emission lines to minimize interferences and to confirm elemental identity.

APPROVED BY Y-12	LAB R J McElhaney IH G. L. Dean	APPROVED BY ORGDP	LAB T. Kwasnoski IH D. J. Duncan	APPROVED BY UCCND-COORD R C W Weber
APPROVED BY PGDP	LAB R. E. Simmons IH C. W. Turak	APPROVED BY ORNL	LAB W. R. Laing IH James A. Ealy	NUMBER IHA-160

3.2 Contamination is a continual potential source of interference, and may arise from laboratory environment dust, reagent impurities, unclean apparatus, or sample containers. Such problems must be under constant control.

4.0 Precision and Accuracy

4.1 It is estimated that a precision range of +100% to -50% is obtainable, at the 95% confidence level, for visual analytical results.

4.2 It is estimated that the precision of the densitometric procedure for Cu, Fe, and Ni at the 95% confidence level is 35% at the 75-microgram level.

4.3 Bias in the results is generally of no more importance than the precision of the technique; accuracy has not been statistically examined. However, it is recognized that contamination and ignition losses can lead to positive and negative errors, respectively, for some elements (see 5.7).

5.0 Advantages and Disadvantages of the Method

5.1 This method is applicable to a large number of metals found in airborne particulates in the workroom environment.

5.2 A large number of metals are determined simultaneously, requiring much less analyst time than multiple single analysis methods.

5.3 A large air sample is not needed for measurements of low concentrations.

5.4 The method is not as precise as atomic absorption spectrophotometry.

5.5 A relatively large capital outlay is required for instrumentation.

5.6 Competent technical personnel are needed for its operation.

5.7 Contamination and ignition loss are of prime concern for the determination of some trace metals. Furnace ashing of the membrane filter sample at 450°C may result in poor recovery for several elements such as As, Cd, Pb, Tl, and Zn. If these five elements are critical, wet ashing should be used at 200°C.

6.0 Apparatus

6.1 Spectrograph capable of a reciprocal linear dispersion of < 0.6 nm/mm in the first-order.

6.2 Power source, D.C. arc, capable of delivering 15 amperes D.C.

6.3 Photographic plate processing and drying unit.

6.4 Comparator-microdensitometer.

6.5 Calculating board, Baird-Atomic Model RB-1, or equivalent.

6.6 Wig-L-Bug sample shaker.

6.7 Analytical balance, Mettler Type H10T, or equivalent.

6.8 Weighing paper.

6.9 Electrode holder block, graphite.

6.10 Electrode holder block, plastic.

6.11 Electrode funnel, plastic.

6.12 Platinum spatula.

6.13 Plastic polystyrene vials, 1/2-in. diameter x 1-in. long, with caps.

6.14 Plexiglas grinding balls, 3/8-in. diameter.

6.15 Membrane Filters: 37-mm diameter, 0.5- or 0.8-micrometer pore size, PVC or mixed cellulose esters, supported by a cellulose backup pad.

6.16 Lindberg box furnace, Model 51848, or equivalent.

6.17 Low-volume air sampler, M.S.A. Model G personnel sampling pump, or equivalent.

6.18 Argon-oxygen excitation apparatus, Stallwood Jet (commercially available).

6.19 Platinum crucible, 15- to 30-ml.

6.20 Filter holder, 37-mm three-piece cassette.

6.21 Mortar and pestle.

6.22 Mixer-mill.

7.0 Reagents

7.1 Metal oxides or carbonates, spectrographically pure.

7.2 Graphite electrodes.

7.2.1 Sample-Ultra Carbon 4880, or equivalent.

7.2.2 Counter-National L3752, or equivalent. For alternate procedure, use ASTM E 130 Type C-1.

7.2.3 Sample-ASTM E 130, Type S-2.

7.2.4 Sample - National SP9077, or equivalent.

7.3 Graphite powder, National Carbon SP-2X, 100-mesh, or equivalent.

7.4 Graphite powder, Ultra Carbon, UCP 2-200, or equivalent.

7.5 Photographic plates, Eastman Kodak Spectrum Analysis No. 1 and Eastman Kodak Type 1-N.

7.6 Developer, Eastman Kodak D-19.

7.7 Acid short stop, 5% acetic acid solution.

7.8 Photographic fixer, Eastman Kodak Rapid Liquid Fixer with Hardener.

7.9 Fluorographite $(CF_x)_n$, x = 1.1, Ozark Mahoning; used as a buffer/carrier.

7.10 Silver chloride, spectrographic grade; used as a buffer/carrier.

7.11 Argon:oxygen gas mixture, 80:20 (by vol); made up of 99.995%-minimum-purity argon and 99.5%-minimum-purity oxygen.

8.0 Procedure

8.1 Sample Preparation

8.1.1 Airborne particulate matter is collected on a membrane filter (6.15) placed on a low-volume sampler (6.17), through which the air is passed at about 1.5 LPM (liter per minute) for a fixed time. (Reference 11.3)

8.1.2 Fold the membrane filter sample tightly and place in the crater of a Type 9077 sample electrode (see 7.2.4); and place the electrode in the graphite holder block (6.9). NOTE: See 5.7.

8.1.3 Place the electrode in a cold laboratory furnace (6.16) and set the temperature for 450°C. Remove the electrode and the sample residue from the furnace after ignition is complete, usually within 10 minutes after reaching maximum temperature.

8.1.4 Transfer the ignited residue to weighing paper. If the residue weight is < 5 mg, the entire residue can be combined with a known weight of graphite (7.3), plus 5% (5 mg) of fluorographite (7.9) or 17% (17 mg) of silver chloride (7.10), to yield a final mix of 100 mg. This mixture is blended on a Wig-L-Bug before aliquoting.

NOTE 1

Silver chloride buffer is used whenever a 0.2-μg nickel detection limit is needed in evaluating a very low threshold limit value for nickel.

8.1.5 If the residue weight exceeds 5 mg, the entire residue is blended and a known portion is combined with graphite plus buffer (7.9 or 7.10) to yield a blended aliquot suitable for excitation (see Section 8.1.4).

8.1.6 Transfer 10 mg of the blended mixture to a Type 4880 sample electrode.

8.1.7 Prepare three electrodes for replicate spectrographic exposures.

8.2 Alternate Sample Preparation

8.2.1 Fold the filter sample tightly and place in a tared platinum crucible (6.19).

8.2.2 Place the platinum crucible in a cold furnace. Set temperature for 450°C and ignite until all the paper has oxidized and only the residue remains.

8.2.3 Weigh the cooled platinum crucible and determine the weight of the residue.

8.2.4 Add enough graphite (7.4) so the final mix will contain 80% graphite.

8.2.5 Blend on a Wig-L-Bug (6.6) using Plexiglas grinding balls (6.14).

8.2.6 If the mix (8.2.4) is of sufficient size, transfer 10 mg of the blended mixture to a Type 4880 electrode (7.2.1). If the mix is less than 10 mg, prepare a single electrode (and adjust the calibration accordingly).

8.2.7 Prepare three electrodes for replicate spectrographic exposures, if the quantity of final mix permits.

8.3 Excitation

8.3.1 Arc each sample at 10 amps D.C. (short circuit) in an argon-oxygen atmosphere (7.11) until the sample is completely consumed.

8.3.2 Record all elements, except alkali metals, on SA-1 plates. (Wavelength coverage from 227 to 477 nm.)

8.3.3 Record alkali metals on 1-N plates. (Wavelength coverage from 565 to 815 nm.)

8.3.4 Place appropriate external standards on the same plate with the sample for a calibration check.

8.3.5 A carrier distillation technique may be used whenever the reporting limits listed in Table 1 need to be lowered for one or more elements. Weigh two 25-mg charges from the blended mix (8.1.6) into two electrodes (7.2.3) and excite the samples at 14 amperes D.C. (short circuit) in an argon-oxygen atmosphere for 40 seconds, followed by a 30-second rackdown. Check the plate rackdown step to determine whether the element distills out satisfactorily during the 40-second period.

NOTE 2

Most of the elements listed in Table 1 can be detected at or below the 0.1 μg level when using silver chloride and the carrier distillation technique.

8.3.6 For the alternate procedure, arc samples at 10-15 amps dc in air until the sample is totally consumed. Follow 8.3.2 to 8.3.4.

8.4 Plate Processing

8.4.1 Develop the plates in D-19 developer. (1-N plates must be processed in total darkness.)

8.4.2 Rinse, fix, wash, and dry plates.

8.5 Plate Reading

8.5.1 Using the plate comparator, visually estimate the concentration of 48 metallic elements by comparing the density of the sample line with the corresponding line on a standard reference plate, prepared previously using the same conditions. The recommended spectral lines are listed in Table 1.

8.5.2 Densitometric measurements are performed for Cu, Fe, and Ni. Transmission units are converted to elemental percent concentrations using the calculating board. Based upon the high and low standard values on the same plate with the samples, compensate, if necessary, for any curve shift according to A.S.T.M. Recommended Practices for Establishing and Controlling Spectrochemical Analytical Curves. (Reference 11.2)

9.0 Calibration and Standards

9.1 Standards are prepared by mixing weighed amounts of spectrochemically pure stable metal compounds (7.1) with weighed amounts of pure graphite (7.3 or 7.4). The metal compounds are mixed in appropriate groups and diluted with graphite and buffer to match the blend used with the samples, resulting in a graded series of standards which cover a wide concentration range.

9.2 Commercial graphite matrix standards (Spex Industries or Applied Research Laboratory) may be used, if available, to prepare additional graphite standards at low concentration levels. These mixtures are directly applicable to the Alternate Sample Preparation Procedure (8.2).

9.3 Standard photographic plates are made using excitation conditions identical to those used for the sample plates. The spectrographic lines for each element vary in intensity depending upon the amount of the element arced in the electrode. The line of the element sought is compared with the nearest matching intensity line on the standard plate to determine the amount of the element in the sample.

10.0 Calculations

10.1 Amount of element, μg = Plate reading (% of element in final mix) x 10 x weight of final mix (mg).

11.0 References

11.1 Sugimae, A.; "Emission Spectrographic Determination of Trace Elements in Airborne Particulate Matter"; *Analytical Chemistry*, 46, 1123 (1974).

11.2 *Methods for Emission Spectrochemical Analysis*, ASTM 6th Edition, ASTM Designation E 305-67 (1971).

11.3 *NIOSH Manual of Sampling Data Sheets*, 1977 Edition, DHEW (NIOSH) Publication No. 77-159.

Table 1

LOWEST CONCENTRATIONS REPORTED† AND SUGGESTED SPECTRAL LINES

Element	LCR† (μg)	Suggested Element Wavelengths (nm)			
Ag††	0.3	241.318	243.779	328.068*	338.289
Al	2	236.705	308.215*	309.271	396.153
As	5	228.812	234.984*	278.022	286.044
Au	0.5	242.95	267.595*	274.826	312.28
B	0.3	249.678	249.773*		
Ba	4	230.424	233.527	455.403*	493.409
Be	0.03	234.861*	313.042	313.107	332.134
Bi	2	289.798*	293.30	298.903	306.772
Ca	1	315.887	393.367*	396.847	422.673
Cd	5	228.802*	326.106	346.620	361.051
Co	2	240.725*	252.136	340.512	345.350
Cr	3	267.716	284.325	357.869	425.435*
Cu	0.3	223.008	249.215	324.754*	327.396
Fe	2	247.978*	248.327	248.815	302.064
Ga	5	271.965	287.424	294.364*	294.418
Ge	3	265.118*	265.158	275.459	303.906
Hf	2	277.336	291.648	339.980*	350.523
In	5	256.023	303.936	325.609*	325.856
Ir	1	254.397*	313.332	322.078	351.364
K	10	404.414*	404.721	766.491	769.896
La	10	324.513	333.749	408.672*	433.740
Li	1	323.261*	610.364	670.784	812.634
Mg	1	277.983*	279.553	280.270	285.213
Mn	0.5	257.610*	260.569	280.106	380.672
Mo	2	313.259*	317.035	319.397	390.296
Na	3	330.237*	588.995	589.592	819.482
Nb	2	292.781	309.418	316.340	405.894*
Ni	2	300.249*	310.155	341.476	345.847
P	10	253.401*	255.328	255.493	404.414
Pb	3	280.199*	283.306	368.348	405.783

†These LCRs apply to usual practice, when the final graphite-residue mix totals 100 mg, and 10-mg burns are used.

††Silver cannot be determined when using the silver chloride buffer.

*Preferred wavelength for best sensitivity.

Table 1 (CONTINUED)

LOWEST CONCENTRATIONS REPORTED† AND SUGGESTED SPECTRAL LINES

Element	LCR† (µg)	Suggested Element Wavelengths (nm)			
Pd	3	244.791	324.270*	340.458	342.124
Pt	3	244.006	265.945*	273.396	299.797
Rh	1	339.685*	343.489	352.802	365.799
Sb	5	252.852	259.806*	287.791	323.252
Sc	1	335.373	361.384	363.074	424.683*
Si	1	243.516*	251.432	251.611	252.411
Sn	5	215.143	283.999*	286.333	317.502
Sr	0.5	338.071	346.457	407.771*	421.552
Ta	20	264.747*	265.327	271.467	331.116
Te	10	214.725	225.902	238.325*	238.576
Th	1	256.560*	256.659	275.217	401.913
Ti	1	307.864*	334.941	336.121	337.280
Tl	10	237.969	276.787*	291.832	377.572
U	50	385.958	389.036*	393.203	424.167
V	1	292.402	318.341	318.398*	318.540
W	10	283.138	294.440	294.698	400.875*
Zn	5	213.856	328.233	330.259*	334.502
Zr	2	257.139*	343.823	354.770	360.119

†These LCRs apply to usual practice, when the final graphite-residue mix totals 100 mg, and 10-mg burns are used.

*Preferred wavelength for best sensitivity.

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-165
DATE	August 27, 1980
SUPERSEDES	
PAGE	1 OF 17

METALS (TRACE) IN AIR, ATOMIC ABSORPTION SPECTROPHOTOMETRY

Analyte:	Trace Metals (Tables 1 & 2)	Method No.:	IHA-165 (NIOSH 173)
Matrix:	Air	Range:	Varies with analyte (Table 2)
Procedure:	Filter collection of particulates; atomic absorption spectrophotometry	Precision:	3% RSD (Analytical)

For this analysis, the undersigned committee has approved for inclusion in this manual an existing procedure, exactly as published. Accordingly, the General Procedure for Metals was taken verbatim from the NIOSH Manual of Analytical Methods, Second Edition, Vol. 5, U. S. Department of Health, Education, and Welfare, Method 173, 1979.

* exceptions to NIOSH 173

The following exceptions to NIOSH 173 should be understood:

A. This procedure employs flame atomization of the analyte metals. However, electrothermal (graphite furnace) atomic absorption spectrophotometry may be substituted for the flame technique. The graphite furnace technique applied in accord with manufacturer's instructions will enhance the sensitivity for most of the metals listed in Table 2 by a factor of 10; some sensitivities will be increased 100-fold or more.

B. Under Section 1.3, line 2:

"...Lead-S314..." should be "...Lead-S341..."

C. Under Section 6.6.4:

A sentence should be added: "A commercially available heated nitrous oxide regulator may be used."

APPROVED BY Y-12	LAB A J McElhaney	APPROVED BY ORGDP	LAB T Kwapowski	APPROVED BY UCCND-COORD'R C W Weber
	IH W. S. Everett Jr.		IH D. J. Duncan	
APPROVED BY PGDP	LAB R. E. Simmons	APPROVED BY ORNL	LAB W R Laing	NUMBER IHA-165
	IH C. A. Turak		IH James A. Cole	

Exceptions to NIOSH 173 (continued):

D. Under Section 6.7.1:

The 100-psi cylinder replacement seems unnecessary. Some manufacturers recommend 75 psi.

E. Under 8.1 Cleaning of Equipment:

The use of chromic acid and nitric acid for cleaning glassware to be used for metals procedures requires thorough rinsing. Some laboratories are using commercial detergent-type cleaners in conjunction with, or without, the use of strong acid cleaners.

F. Under Section 8.3.2, line 10:

" . . . footnote 3 . . . " should be " . . . footnote e . . . "

G. Under Section 9.2.1, line 2, and under Section 9.2.2, line 3:

"7.3" should be "7.4."

H. Under Section 9.2.5, lines 11 and 12:

"L" should be "µL."

I. The air sample volume should be calculated in Section 10.1 from sample flow rates corrected to 25°C and 760 mm Hg pressure, using ambient conditions recorded as in Section 8.2.1.

J. Under Table 1, Footnotes d, e, and h:

"g/mL" should be "µg/mL."

K. Under Table 1, Footnote i:

Should be deleted.

L. When using Table 2, the analyst should be reminded of the distinction between "sensitivity" and "detection limit." The definitions for these units and for "working range" are presented in Section 2. Range and Sensitivity.

The following procedure is a photocopied excerpt from: NIOSH Manual of Analytical Methods, Second Edition, Vol. 5, U. S. Department of Health, Education, and Welfare, 1979.

GENERAL PROCEDURE FOR METALS

Measurements Research Branch

Analytical Method

Analyte:	Trace Metals (Tables 1 and 2)	Method No.:	P&CAM 173
Matrix:	Air	Range:	Varies with analyte (Table 2)
Procedure:	Filter collection, acid digestion, AAS	Precision:	3% RSD (Analytical)
Date Issued:	9/17/73		
Date Revised:	5/14/79	Classification:	B (Accepted)

1. Synopsis

1.1 This procedure describes a general method for the collection, dissolution and determination of trace metals in industrial and ambient airborne material. The samples are collected on membrane filters and treated with nitric acid to ash the organic matrix and to dissolve the metals present in the sample. The analysis is subsequently made by atomic absorption spectrophotometry (AAS).

1.2 Samples and standards are aspirated into the appropriate AAS flame. A source of characteristic radiation energy is necessary for each metal. The absorption of this characteristic energy by the atoms of interest in the flame is related to the concentration of the metal in the aspirated sample. The flames and operating conditions for each element are listed in Table 1.

*1.3 Metals for which other AAS procedures exist (e.g., Antimony-P&CAM 261 and Lead-~~S314~~ S341) should be analyzed using that method.

2. Working Range, Sensitivity, and Detection Limit

The sensitivity, detection limit, and optimum working range for each metal are given in Table 2. The sensitivity is defined as that concentration of a given element which will absorb 1% of the incident radiation (0.0044 absorbance units) when aspirated into the flame. The detection limit is defined as that concentration of a given element which produces a signal equivalent to two times the standard deviation of the blank signal for aqueous solutions. Detection limits and blank values for real samples may be greater than those given in Table 2 since the

* [illegible] to NIOSH-173

blanks resulting from the reagents and the filter material have not been taken into account. The working range for an analytical precision better than 3% is generally defined as those sample concentrations which will absorb greater than 10% of the incident radiation and are in the linear region of the calibration curve. The values for the sensitivity and detection limits are instrument dependent and many vary from instrument to instrument.

3. Interferences

3.1 In atomic absorption spectrophotometry, the occurrence of interferences is less common than in many other analytical determination methods. Interferences can occur, however, and when encountered are corrected for as indicated in the following sections. The known interferences and correction methods for each metal are indicated in Table 1. The methods of standard additions and background monitoring and correction (11.1-11.4) are used to identify the presence of an interference problem. Insofar as possible, the matrix of the samples and standards are matched to minimize the possible interference problems.

3.1.1 Background or non-specific absorption can occur from particles produced in the flame which can scatter the incident radiation causing an apparent absorption signal. Light scattering problems may be encountered when solutions of high salt content are being analyzed. Light scattering problems are most severe when measurements are made at the lower wavelengths (i.e., below about 250 nm). Background absorption may also occur as the result of the formation of various molecular species which can absorb light. The background absorption should be accounted for by the use of background correction techniques (use of D_2 or H_2 continuum or a nearby non-absorbing wavelength)(11.1, 11.6).

3.1.2 Spectral interferences are those interferences which occur as the result of an atom different from that being measured absorbing a portion of the incident radiation. Such interferences are extremely rare in atomic absorption. In some cases, multi-element hollow cathode lamps may cause a spectral interference by having closely adjacent radiation lines from two different elements. In such instances, multi-element hollow cathode lamps should not be used, or the use of more narrow spectral slits or alternate wavelengths may be used to alleviate the problem.

3.1.3 Ionization interferences can occur when easily ionized atoms are being measured. The degree to which such atoms are ionized is dependent upon the atomic concentration and presence of other easily ionized atoms in the sample.

Ionization interferences can be controlled by the addition to the sample of a high concentration of another easily ionized element which will buffer the electron concentration in the flame. Typically, 1000-2000 µg/mL of an alkali metal (K, Na, Cs) salt is added to sample and standard solutions.

3.1.4 Chemical interferences occur in atomic absorption spectrophotometry when species present in the sample cause variations in the degree to which atoms are formed in the flame. Such interferences may be corrected for by controlling the sample and standard matrix, by using the method of standard additions, or by use of a higher temperature flame (11.2, 11.6).

3.1.5 Physical interferences may result if the physical properties of the samples vary significantly. Changes in viscosity and surface tension can affect the sample aspiration rate and thus cause erroneous results. Sample dilution and/or the method of standard additions are used to correct such interferences. High concentrations of silicates in the sample can cause an interference for many of the elements and may cause aspiration problems. No matter what elements are being measured, if large amounts of silicates are extracted from the samples, the samples should be allowed to stand for several hours and centrifuged to remove the silicates.

3.2 This procedure describes a generalized method for sample preparation which is applicable to the majority of samples of interest. There are, however, some relatively rare chemical forms of a few of the elements listed in Table 1 which will not be dissolved by this procedure. If such chemical forms are suspected, results obtained using this procedure should be compared with those obtained using an appropriately altered dissolution procedure. Alternatively, the results may be compared with values obtained utilizing a non-destructive technique which does not require sample dissolution (e.g., x-ray fluorescence, activation analysis).

4. Precision and Accuracy

4.1 The relative standard deviation of the analytical measurement is approximately 3% when measurements are made in the ranges listed in Table 2. The overall relative standard deviation will be somewhat larger than this value due to errors associated with the sample collection and preparation steps.

4.2 Collaborative testing of this method by 16 laboratories, using filters loaded at three concentration levels in a dynamic aerosol generation and sampling system, indicated that the average per-

cent recoveries and standard deviations for representative metals are: Cd, 100.8 ± 9.9; Co, 97.6 ± 13.9; Cr, 96.6 ± 10.8; Ni, 98.6 ± 10.3; and Pb, 98.7 ± 12.2.

5. Advantages and Disadvantages

5.1 The sensitivity is adequate for all metals in air samples provided an adequate volume of air is sampled.

5.2 This method has been ruggedized for Be, Cd, Co, Cr, Cu, Mn, Mo, Ni and Pb and collaboratively tested for Cd, Co, Cr, Ni and Pb.

5.3 A disadvantage of the method is that approximately 2 mL of solution is necessary for each metal determination. Also, the necessary dilution limits the detection of small quantities of analyte or replicate analysis of several elements per sample.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the collection of personal air samples has the following components:

6.1.1 The filter unit, consisting of the filter media (6.2) and appropriate cassette filter holder, either a two- or three-piece filter cassette (Millipore Filter Corporation, Bedford, Massachusetts or equivalent).

6.1.2 A personal sampling pump of sufficient capacity to maintain a face velocity of 2.6 cm/sec (1-2 Lpm using a 37-mm filter). This pump must be calibrated so the volume of air sampled can be measured to an accuracy of ± 5%. The pump must be calibrated with a representative filter unit in the line.

6.1.3 Thermometer.

6.1.4 Manometer.

6.1.5 Stopwatch.

6.1.6 Various clips, tubing, spring connectors and belt for connecting sampling apparatus to worker being sampled.

6.2 Cellulose ester membrane filter, 0.8 μm pore size, 37-mm (Millipore Type AA or equivalent).

6.3 Glassware (borosilicate). Before use, all glassware must be cleaned in 1:1 nitric acid and rinsed several times with distilled water.

6.3.1 125-mL Phillips or Griffin beakers with watchglass covers.

6.3.2 15-mL graduated centrifuge tubes.

6.3.3 10-mL volumetric flasks.

6.3.4 100-mL volumetric flasks.

6.3.5 1-L volumetric flasks.

6.3.6 125-mL polyethylene bottles.

6.3.7 Additional auxiliary glassware such as pipettes and different size volumetric glassware will be required depending on the elements being determined and the dilutions required to have sample concentrations above the detection limit and in the linear response range (i.e., see Table 2). All pipettes and volumetric flasks required in this procedure should be calibrated class A volumetric glassware.

6.4 Hotplate (suitable for operation at 165°C).

6.5 Steambath or 100°C hotplate.

6.6 Equipment for Analysis

6.6.1 Atomic absorption spectrophotometer with burner heads for air-acetylene and nitrous oxide-acetylene flames.

6.6.2 Hollow cathode or electrodeless discharge lamps for each metal and a continuum lamp (D_2 or H_2).

6.6.3 Two-stage regulators for air, acetylene and nitrous oxide.

* 6.6.4 Heating tape and rheostat for nitrous oxide regulator (second regulator stage and connecting hose to the instrument should be heated to approximately 60°C to prevent freeze up), a commercially available [illegible] nitrous oxide regulator may [illegible]

6.7 Supplies

* 6.7.1 Acetylene gas (cylinder) of a grade specified by the manufacturer of the instrument employed. (Replace cylinder when pressure decreases below 100 psi.) [illegible] recommend 75 psi

6.7.2 Nitrous oxide gas (cylinder).

6.7.3 Air supply with a minimum pressure of 40 psi filtered to remove oil and water.

7. Reagents

7.1 Purity. ACS analytical reagent grade chemicals or equivalent shall be used in all tests. References to water shall be understood to mean double distilled water or equivalent. Care in selection of reagents and in following the listed precautions is essential if low blank values are to be obtained.

7.2 Concentrated nitric acid (68-71%), redistilled, specific gravity 1.42.

7.3 10% nitric acid.

7.4 Standard stock solutions (1000 µg/mL) for each metal in Table 1, commercially prepared or prepared per instrument manufacturer's recommendations.

7.5 Lanthanum nitrate ($La(NO_3)3 \cdot 6H_2O$).

7.6 Cesium nitrate ($CsNO_3$).

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Before initial use, glassware is cleaned with a saturated solution of sodium dichromate in concentrated sulfuric acid (NOTE: Do not use for chromium analysis) and then rinsed thoroughly with warm tap water, concentrated nitric acid, tap water and deionized water, in that order, and then dried. [illegible] detergent-type [illegible] w/ [illegible] use of strong acid cleaner.

8.1.2 All glassware is soaked in a mild detergent solution immediately after use to remove any residual grease or chemicals.

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, it is not necessary to use the chromic acid cleaning solution.

8.2 Collection and Shipping of Samples

8.2.1 Ambient atmospheric particulate matter and industrial dusts and fumes are sampled with cellulose membrane filters. Sample flow rate is monitored with a calibrated rotameter (11.5) or the equivalent. The flow rate, ambient temperature and barometric pressure are recorded at the beginning and the end of the sample collection period.

8.2.2 For personal sampling, 37-mm diameter filters in holders are used. The personal sampling pumps for this application are operated at 1.5 Lpm. In general, a two-hour sample at 1.5 Lpm will provide enough sample to detect the elements sought at air concentrations of 0.2 x TLV.

8.2.3 After sample collection is complete, plug the openings of the cassette and submit the sampling unit to the laboratory. Losses of sample due to overloading (> 2 mg) of the filter must be avoided.

8.2.4 Filter samples should be sealed in individual plastic filter holders for storage and shipment.

8.3 Preparation of Samples

8.3.1 The samples and blanks (minimum of one filter blank for every 10 filter samples) are transferred to clean 125-mL Phillips or Griffin beakers and 6.0 mL HNO_3 is added. Each beaker is covered with a watchglass and heated on a hotplate (165°C) in a fume hood until the sample dissolves and a slightly yellow solution is produced. Approximately four hours of heating will be sufficient for most air samples. However, subsequent additions of HNO_3 may be needed to completely ash and destroy high concentrations of organic material and, under these conditions, longer ashing times will be needed. Once the ashing is complete, as indicated by a clear solution in the beaker, the watchglass is removed and rinsed into the sample beaker with 10% HNO_3. The beakers are then placed on a 100°C steambath and allowed to go to dryness.

* 8.3.2 Once a sample is dry, rinse the walls of the beaker with 3-5 mL of 10% HNO_3 and reheat for five minutes at 100°C to solubilize the residue. The solution is quantitatively transferred with 10% HNO_3 to a 10-mL volumetric flask. If any elements are being determined which require the ionization buffer, 0.2 mL of 50 mg/mL Cs is added to the volumetric flask (see Table 1, footnote d). If any elements requiring the releasing agent are being determined, 0.2 mL of 50 mg/mL La is added to each volumetric flask (see Table 1, footnote e). The samples are then diluted to volume with 10% HNO_3.

8.3.3 The 10-mL solution may be analyzed directly for any element of very low concentration in the sample. Aliquots of this solution may then be diluted to an appropriate volume for the other elements of interest present at higher concentrations. (NOTE: Approximately 2 mL of

solution are required for each element being analyzed.) The dilution factor will depend upon the concentration of elements in the sample and the number of elements being determined by this procedure.

8.4 Analysis of Samples

8.4.1 Set the instrument operating conditions as recommended by the manufacturer. The instrument should be set at the radiation intensity maximum for the wavelength listed in Table 1 for the element being determined.

8.4.2 Standard solutions should match the sample matrix as closely as possible and should be run in duplicate. Working standard solutions, prepared fresh daily, are aspirated into the flame and the absorbance recorded. Prepare a calibration graph as described in Section 9.2.3 (NOTE: All combustion products from the AA flame must be removed by direct exhaustion through the use of a good separate flame ventilation system).

8.4.3 Blank filters must be carried through the entire procedure each time samples are analyzed.

8.4.4 Aspirate the appropriately diluted samples directly into the instrument and record the absorbance for comparison with standards. Should the absorbance be above the calibration range, dilute an appropriate aliquot to 10 mL. Aspirate water between each sample. A mid-range standard must be aspirated with sufficient frequency (i.e., once every five samples) to assure the accuracy of the sample determinations. To the extent possible, all determinations are to be based on replicate analysis.

9. Calibration and Standardization

9.1 Ionization and chemical interference suppressants

9.1.1 Lanthanum solution (50 mg/mL). Dissolve 156.32 g of lanthanum nitrate ($La(NO_3)3 \cdot 6H_2O$) in 2% (v/v) HNO_3. Dilute to volume in a 1-L volumetric flask with 2% (v/v) HNO_3. When stored in a polyethylene bottle, this solution is stable for at least one year.

9.1.2 Cesium solution (50 mg/mL). Dissolve 73.40 g of cesium nitrate ($CsNO_3$) in distilled water. Dilute to volume in a 1-L volumetric flask with distilled water. When stored in a polyethylene bottle, this solution is stable for at least one year.

9.2 Standard metal solutions

* 9.2.1 Dilute standards (100 µg metal/mL). Pipet 10 mL of the stock (1000 µg metal/mL; Section 7.3) into a 100-mL volumetric flask, add 10 mL HNO_3 and dilute to volume with distilled water. Prepare these standards fresh weekly. (NOTE: Silver standards must be stored in amber bottles away from direct light.)

* 9.2.2 Working standards. Working standards for each metal of interest are prepared by dilution of the dilute standards (9.2.1) or the stock standards (7.3) such that the final acid concentration is the same for the samples and standards (i.e., 10% v/v HNO_3 in most cases). Lanthanum or cesium is added to samples and standards as indicated in Table 1 such that the final concentraton is 1000 µg La or Cs/mL. Concentrations of the working standards should cover the range for the metal of interest (Table 2). Prepare these solutions fresh daily.

9.2.3 The standard solutions are aspirated into the flame and the absorbance (or concentration) recorded. If the instrument used displays transmittance, these values must be converted to absorbance. A calibration curve is prepared by plotting absorbance (units) versus metal concentration. The best fit curve (calculated by linear least square regression analysis) is fitted to the data points. This line or the equation describing the line is used to obtain the metal concentration in the samples being analyzed.

9.2.4 To insure that the preparation procedure is being properly followed, clean membrane filters are spiked with known amounts of the elements being determined by adding appropriate amounts of the previously described standards and carried though the entire procedure. The amount of metal is determined and the percent recovery calculated. These tests will provide recovery and precision data for the procedure as it is carried out in the laboratory for the soluble compounds of the elements being determined.

* 9.2.5 Analysis by the method of standard additions. In order to check for interferences, samples are initially and periodically analyzed by the method of standard additions and the results compared to those obtained by the conventional analytical determination. For this method, the sample is divided into three 2-mL aliquots. To one of the aliquots an amount of metal approximately equal to that in the sample is added. To another aliquot twice this amount is added. (NOTE: Additions should be made

by micropipetting techniques such that the volume does not exceed 1% of the original aliquot volume, i.e., 10 μL and 20 μL additions to a 2-mL aliquot.) The solutions are then analyzed and the absorbance readings are plotted against metal added to the original sample. The line obtained from such a plot is extrapolated to 0 absorbance and the intercept on the concentration axis is taken as the amount of metal in the original sample (11.2). If the result of this determination does not agree to within 10% of the values obtained with the procedure described in Section 9.2.3, an interference is indicated and standard addition techniques should be utilized for sample analysis.

10. Calculations

*10.1 The corrected volume collected by the filter is calculated by averaging the beginning and ending sample flow rates, converting to cubic meters and multiplying by the sample collection time. The formula for this calculation is:

[illegible] air sample volume [illegible] could be calculated [illegible] sample flow rates [illegible] 25°C - 760mm [illegible] ambient [illegible] recorded as [illegible] 9.2.1

$$V = \frac{(F_B + F_E)t}{2000}$$

where: V = sample volume (m^3)
F_B = sample flow rate at beginning of sample collection (Lpm)
F_E = sample flow rate at end of sample collection (Lpm)
t = sample collection time (minutes)

10.2 After any necessary correction for the blank has been made, metal concentrations are calculated by multiplying the micrograms of metal per mL in the sample aliquot by the aliquot volume and dividing by the fraction which the aliquot represents of the total sample and the volume of air collected by the filter:

$$\mu g \text{ metal}/m^3 = \frac{(C \times V_A) - B}{v \times F}$$

where: C = concentration (μg metal/mL) in the aliquot
V_A = volume of aliquot (mL)
B = total μg of metal in the blank
F = fraction of total sample in the aliquot used for measurement (dimensionless)
v = volume of air sampled (m^3)

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R. Delon Hull
Inorganic Methods Development Section

Table 1. Instrument Parameters

Element	Type of Flame o = oxiziding r = reducing	Analytical Wavelength (nm)	Interferences[b]	Remedy[b]	References
Ag	Air-C_2H_2(o)	328.1	IO_3^-,WO_4^{-2},Mn_4^{-3}	c	(5)
Al[a]	N_2O-C_2H_2(r)	309.3	Ionization,SO_4^{-2}, V,Fe,HCl,H SO	c,d,e	(4,6)
As	Air-C_2H_2(o)	193.7	Background absorption	g	(6)
Ba	N_2O-C_2H_2(r)	553.6	Ionization,large conc. of Ca	d,f	(1,4)
Be[a]	N_2O-C_2H_2(r)	234.9	Al,Si,Mn	e,c,g	(4)
Bi	Air-C_2H_2(o)	223.1		g	
Ca	Air-C_2H_2(r) N_2O-C_2H_2(r)	422.7	Ionization and chemical	d,e	(1,4)
Cd	Air-C_2H_2(o)	228.8		e,g	
Co[a]	Air-C_2H_2(o)	240.7		e,g	
Cr[a]	Air-C_2H_2(r)	357.9	Fe,Ni	e,c	(4)
Cu	Air-C_2H_2(o)	324.8			
Fe	Air-C_2H_2(o)	248.3	High Ni conc.,Si	c,g	(1,4)
In	Air-C_2H_2(o)	303.9	Al,Mg,Cu,Zn,$H_xPO_4^{x-3}$	c	(10)
K	Air-C_2H_2(o)	766.5	Ionization	d	(1,4)
Li	Air-C_2H_2(o)	670.8	Ionization	d	(11)
Mg	Air-C_2H_2(o) N_2O-C_2H_2(o)	285.2	Chemical ionization	e d	(1,4)
Mn	Air-C_2H_2(o)	279.5			
Mo	N_2O-C_2H_2(r)	313.5	Ca and other ions	e,h	(6)
Na	Air-C_2H_2(o)	589.6	Ionization	e	(1,4)
Ni	Air-C_2H_2(o)	232.0		e,g	
Pb	Air-C_2H_2(o)	217.0 283.3	Ca,High conc. $SO_4^{=}$	e,c,g	(7)
Pd	Air-C_2H_2(o)	247.6	Al,Co,Ni,Pt,Rh, Ru	e	(6)
Rb	Air-C_2H_2(o)	780.0	Ionization	d	(1,8)
Si	N_2O-C_2H_2(r)	251.6	Avoided by not using multi-element lamp containing Fe		
Sr	Air-C_2H_2(r) N_2O-C_2H_2(r)	460.7	Ionization and chemical	d,e	(1,8)
Te	Air-C_2H_2(o)	241.3		g	(6)
Tl	Air-C_2H_2(o)	276.8			
V[a]	N_2O-C_2H_2(r)	318.4			
Zn	Air-C_2H_2(o)	213.9		g	

a. Some compounds of these elements will not be dissolved by the procedure described here. When determining these elements one should verify that the types of compounds suspected in the sample will dissolve using this procedure (see Section 3.2).

b. High concentrations of silicates in the sample can cause an interference for many of the elements in this table and may cause aspiration problems. No matter what elements are being measured, if large amounts of silicates are extracted from the samples, the samples should be allowed to stand for several hours and centrifuged or filtered to remove the silicates.

c. Samples are periodically analyzed by the method of additions to check for chemical interferences. If interferences are encountered, determinations must be made by the standard additions method or, if the interferent is identified, it may be added to the standards.

d. Ionization interferences are controlled by bringing all solutions to 1000 μg/mL Cs (samples and standards).

e. 1000 μg/mL solution of La as a releasing agent is added to all samples and standards.

f. In the presence of very large Ca concentrations (greater than 0.1%) a molecular absorption from $Ca(OH_2)$ may be observed. This interference may be overcome by using background correction when analyzing for Ba.

g. Use D_2 or H_2 continuum for background correction.

h. Add 1000 μg/mL Al to both standards and samples.

~~i. Use alternate Sb line (231.2 nm).~~

Table 2. Sensitivity Data

Element	Sensitivity[a] µg/mL	Solution Detection Limits[a] µg/mL	Range[a,b] µg/mL	Range[a,b] µg/m^3 [c,d]	Minimum[e,f] TLV µg/m^3
Ag	0.06	0.002	0.5-4.0	21-170	10 (metal and soluble compounds)
Al	1.0	0.02	5-50	210-2100	NL
As	0.8	0.2	10-50	420-2100	50 (arsenic trioxide production)
					500 (arsenic and compounds as As)
Ba	0.4	0.008	1-25	42-1050	500 (soluble compounds)
Be	0.025	0.001	0.1-2.0	4.2-84	2
Bi	0.5	0.025	1-30	42-1250	NL
Ca	0.08	0.005	0.1-5.0	4.2-210	2,000 (CaO)
Cd	0.025	0.001	0.1-2.0	4.2-84	50 (metal dust, soluble salts, cadmium oxide fume)
Co	0.15	0.01	0.5-5.0	21-210	50 (metal fume and dusts)
Cr	0.1	0.003	0.5-5.0	21-210	500 (soluble chromic,chromous salts)
					100 (chromic acid and chromate, as CrO_3)
					100 (chromite ore processing, as CrO_3)
Cu	0.09	0.002	0.5-5.0	21-210	1,000 (dusts and mists)
					200 (fume)
Fe	0.12	0.005	0.5-5.0	21-210	5,000 (iron oxide fume,as iron oxide)
					1,000 (soluble compounds)
In	0.7	0.02	5-50	210-2100	100 (metal and compounds)
K	0.04	0.002	0.1-2.0	4.2-84	2,000 (as KOH)
Li	0.035	0.0003	0.1-2.0	4.2-84	25 (as lithium hydride)

*When using Table 2, the analyst should be reminded [illegible] between [illegible] detection [illegible] The [illegible] are presented in Section 2. Range and Sensitivity.

Element	Sensitivity[a] µg/mL	Solution Detection Limits[a] µg/mL	Range[a,b] µg/mL	Range[a,b] µg/m3 c,d	Minimum[e,f] TLV µg/m3
Mg	0.007	0.0001	0.05-0.50	2.1-21	10,000 (as magnesium oxide fume)
Mn	0.055	0.002	0.5-3.0	21-125	5,000 (metal and compounds)
Mo	0.5	0.02	15-40	625-1650	5,000 (soluble,as Mo) 10,000 (insoluble,as Mo)
Na	0.015	0.0002	0.05-1.0	2.1-42	2,000 (as NaOH)
Ni	0.15	0.005	0.5-5.0	21-210	100 (metal and soluble compounds)
Pb	0.5	0.01	1-20	42-840	150 (inorganic compounds, fumes and dusts)
Pd	0.25	0.02	4-15	170-625	NL
Rb	0.1	0.002	0.5-5.0	21-210	NL
Si	1.8	0.02	50-150	2100-6300	10,000
Sr	0.12	0.002	0.5-5.0	21-210	NL
Te	0.5	0.03	5-25	210-1050	100
Tl	0.5	0.01	5-20	210-840	100 (soluble compounds
V	1.7	0.04	10-150	420-6300	500 (V_2O_5 dust) 50 (V_2O_5 fume)
Zn	0.018	0.001	0.1-1.0	4.2-42	5,000 (ZnO fume)

a. Data from "Analytical Methods for Atomic Absorption Spectrophotometry," Perkin-Elmer Corp., Norwalk, Connecticut, 1976.

b. Data from "Analytical Methods for Flame Spectroscopy," Varian Techtron, Australia, 1972.

c. The atmospheric concentrations were calculated assuming a collection volume of 0.24 m^3 (2 Lpm for two hours) and an analyte volume of 10 mL for the entire sample.

d. For elements whose TLV is less than the lower limits of the range, a larger sampling volume will be required.

e. Threshold limit values of airborne contaminants and physical agents with intended changes adopted by ACGIH for 1976. All values listed are expressed as elemental concentrations except as noted.

f. NL signifies No Limit expressed for this element or its compounds.

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-170
DATE	June 15, 1983
SUPERSEDES	
PAGE	1 OF 8

NITRIC ACID MIST IN AIR, SELECTIVE ION ELECTRODE METHOD

Analyte:	Nitrate Ion	Method:	IHA-170 (NIOSH S319)
Matrix:	Air	Range:	2.60 - 10.8 mg/m^3
Procedure:	Impinger collection; nitrate specific electrode measurement	Precision:	± 8.2% RSD

For this analysis, the undersigned committee has approved for inclusion in this manual an existing procedure, exactly as published. Accordingly, the following pages are taken verbatim from the NIOSH Manual of Analytical Methods, Second Edition, Vol. 4, U.S. Department of Health, Education, and Welfare, Method S319, 1978.

The following exceptions to NIOSH S319 should be understood:

A. Based on the lower limit of detection for the electrode and the sample size used in the procedure, the method is applicable down to the region of about 0.1 mg/m^3; however, the precision and accuracy have not been evaluated at that level.

B. Using the sample collection method described in this procedure, the final measurement of nitrate could also be conducted by the ion chromatography or the brucine method. These techniques are presented in procedures EC-113 and EC-154, respectively, which are included in the UCC-ND Environmental and Effluent Analysis Manual.

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UCN-13234
(1235 1-79)

The following procedure is a photocopied excerpt from: NIOSH Manual of Analytical Methods, Second Edition, Vol. 4, U.S. Department of Health, Education, and Welfare, 1978.

Nitric Acid

Analyte:	Nitrate Ion	Method No:	S319
Matrix:	Air	Range:	2.60 - 10.8 mg/cu m
OSHA Standard:	5 mg/cu m	Precision ($\overline{CV}_T$):	0.082
Procedure:	Impinger collection, ion specific electrode	Validation Date:	8/5/77

1. Principle of the Method

1.1 Samples are collected by drawing a known volume of air through a midget impinger containing distilled water.

1.2 The contents of the impinger are analyzed by direct potentiometry using an ion specific electrode.

1.3 The concentration of nitric acid in the sample is determined by comparison of the potential obtained for the sample solution to a calibration curve obtained by measurement of standard solutions.

1.4 A calibration standard is run before and after each sample to assure that reliable results are obtained.

2. Range and Sensitivity

2.1 This method was validated over the range 2.60 - 10.8 mg/cu m using a 180-liter air sample.

2.2 The lower limit of detection for nitrate using the nitrate ion specific electrode is 6×10^{-6} M or 0.4 ug/ml according to the electrode manufacturer.

3. Interference

Constituents of the buffer solution complex, precipitate, decompose or otherwise remove the common interfering anions including Br^-, Cl^-, F^-, I^-, PO_4^{-3}, and NO_2^- (Reference 11.1). However, high concentrations of any of these species should be avoided.

4. Precision and Accuracy

4.1 The coefficient of Variation ($\overline{CV}_T$) for the total sampling and analytical method in the range of 2.60 - 10.8 mg/cu m was 0.0824. This value corresponds to a 0.4 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of

the validation and experimental test procedures can be found in References 11.2 and 11.3.

4.2 A collection efficiency of 97% was determined for HNO_3 in water; thus, no bias was introduced in the sample collection step from this source.

4.3 The average concentrations "found" at the OSHA standard levels using the overall sampling and analytical method were 4.3% lower than the "true" concentrations found for a limited number of samples analyzed by an alternate method (Reference 11.3). In addition, samples were found to be stable when stored for seven days. Thus, $\overline{CV}_T$ is a satisfactory measure of the precision of the sampling method.

5. Advantages and Disadvantages

5.1 Advantages of the method include simplicity, specificity, and speed.

5.2 Disadvantages of the method are associated with the collection device, the midget impinger. Not only is it inconvenient, but there is the possible loss of sample if the impinger is not maintained in an upright position during sampling.

6. Apparatus

6.1 Sampling Apparatus

6.1.1 Personal Sampling Pump. A calibrated personal sampling pump, the flow of which can be determined within ±5% at the recommended flow rate (Reference 11.3). The pump is protected from splashover or water condensation by a piece of glass wool loosely packed within the tubing used to connect the pump and midget impinger.

6.1.2 Midget impinger.

6.1.3 Distilled water.

6.1.4 Pipet, 20-ml or other suitable device for filling the impinger.

6.1.5 Barometer.

6.1.6 Thermometer.

6.1.7 Stopwatch.

6.2 Orion 92-07 Nitrate Liquid Ion Exchange Membrane Electrode or equivalent.

6.3 Orion 90-02 Double Junction Reference Electrode or equivalent.

6.4 Orion Model 801 Digital pH/mV Meter or equivalent.

6.5 Volumetric flasks, 25-ml.

6.6 Pipets, 20-ml, 5-ml.

6.7 Beakers, 50-ml.

6.8 Magnetic stirrer and Teflon-coated stirring bars.

7. Reagents

All reagents must be ACS reagent grade or better.

7.1 Buffer Solution. Dissolve 4.3g aluminum sulfate, 1.6g boric acid, 3.9g silver sulfate, and 2.4g sulfamic acid in distilled water and dilute to 500 ml. The purpose of this buffer is explained in Reference 11.1.

7.2 Nitric Acid Standards

7.2.1 Nitric Acid Stock Solution. Pipet 5 ml of concentrated nitric acid into a 500-ml volumetric flask and dilute to the mark with distilled water. The concentration of the stock solution should be determined accurately by titration of 15-ml aliquots with 0.1N Sodium hydroxide using phenolphthalein as an indicator. Duplicate titrations should agree within 0.1 ml. Calculate the molarity of the stock solution using the equation

$$\text{Molarity} = \frac{(\text{Molarity of NaOH}) \times (\text{ml of NaOH})}{15 \text{ ml}}$$

7.2.2 Nitric Acid Working Solution. Pipet 5 ml of the nitric acid stock solution into a 500-ml volumetric flask and dilute to the mark with distilled water.

7.2.3 Working Standards. Working standards corresponding to the amounts of nitric acid collected at the 0.5, 1, and 2X the OSHA standard can be prepared by pipeting 5, 10, and 20 ml respectively of the nitric acid working solution into three 25-ml volumetric flasks, each of which contains 5 ml of the buffer solution, and diluting to the mark with distilled water. The concentrations of the working standards are calculated by multiplying the concentration of the nitric acid stock solution by the appropriate dilution factors.

7.3 Saturated Sodium Sulfate Solution. Add sufficient sodium sulfate to distilled water to form a saturated solution. The supernatant is used for the outer chamber filling solution in the double junction reference electrode.

8. Procedure

8.1 Cleaning of Equipment. All glassware should be washed with detergent and rinsed thoroughly with distilled water.

8.2 Calibration of Personal Pump. Each personal pump must be calibrated with a representative midget impinger in the line.

8.3 Collection and Shipping of Samples

8.3.1 Connect a midget impinger containing 20 ml of distilled water to a sampling pump using a piece of flexible tubing. The tubing should be loosely plugged with a piece of glass wool to protect the sampling pump from splashover and condensation.

8.3.2 The impinger must be maintained in a vertical position during sampling.

8.3.3 Air being sampled should not be passed through any hose or tubing before entering the impinger.

8.3.4 A sample size of 180 liters is recommended. Sample at a flow rate of 1.0 liter per minute for 180 minutes. The flow rate should be known with an accuracy of at least ±5%.

8.3.5 Record the ambient temperature and barometric pressure.

8.3.6 Remove the impinger stem and tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Rinse the impinger stem with 1 ml of distilled water and add the wash to the impinger bottle. Seal the impinger with a hard, non-reactive stopper (preferably Teflon). Do not seal with rubber. The stoppers on the impingers should be tightly sealed to prevent leakage during shipping.

8.3.7 With each batch of 10 samples submit one impinger containing 20 ml of distilled water. This impinger should be handled in the same manner as the samples except that no air is drawn through it. Label this impinger as the blank.

8.4 Analysis of Samples

8.4.1 Pipet 5 ml of the buffer solution into a 25-ml volumetric flask.

8.4.2 Transfer the contents of the impinger to the volumetric flask and dilute to the mark with distilled water.

8.4.3 Empty the contents of the volumetric flask into a 50-ml beaker. Add a magnetic stirring bar.

8.4.4 Potentiometric Measurements

8.4.4.1 Immerse the nitrate ion electrode and reference electrode in the sample solution and record the millivolt reading. Both samples and standards should be stirred while readings are taken. The reading should be taken after the meter has stabilized to ± 0.1 mV/10 sec. Follow the instrument manufacturer's instruction manual for proper operation and measurement procedures.

8.4.4.2 Samples should be interspersed between standards as described in Section 9.2.

8.4.5 Appropriate blanks must be analyzed by the same procedure used for the samples.

9. Calibration and Standards

9.1 Nitric acid standards should be prepared as described in Section 7.2. A series of at least three standards should be analyzed prior to the measurement of samples. Plot the potentials in millivolts developed in the standards (on the linear axis) against the molarity of the standards (on the log axis) on semilogarithmic graph paper. The slope of the best straight line fitted to the standards measurements should be equal to 59.2 mV ±1 mV/10-fold change in concentration. If the slope of the line does not fall within these limits, consult the troubleshooting section of the electrode manufacturer's instruction manual.

9.2 Samples should be interspersed between standards having concentrations which bracket the concentrations of the samples. At the conclusion of the analysis of a series of samples, calculate the average response in millivolts for each standard. Plot the data as described in Section 9.1. The resulting calibration line is used to calculate the concentrations of the samples.

10. Calculations

10.1 Determine the molarity of nitric acid in the sample from the calibration line. Calculate the weight of nitric acid in micrograms corresponding to the molarity of the sample using the equation

$$\text{Molarity} \times (1.575 \times 10^6) = \mu g$$

10.2 Corrections for the blank must be made for each sample impinger.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

μg sample = μg found in sample impinger

μg blank = μg found in blank impinger

10.3 Determine the volume of air sampled at ambient conditions in liters based on the appropriate information, such as flow rate in liters per minute multiplied by sampling time. If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is:

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = sample flow rate

t = sampling time

P_1 = atmospheric pressure during calibration of sampling pump (mm Hg)

P_2 = atmospheric pressure of air during sampling (mm Hg)

T_1 = ambient temperature during calibration of sampling pump (°K)

T_2 = ambient temperature of air sampled (°K)

10.4 The concentration of nitric acid in the sampled air can be expressed in mg/cu m (= μg/liter) as follows:

$$\text{mg/cu m} = \frac{\text{ug (Section 10.2)}}{\text{Air volume sampled (Section 10.3)}}$$

Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg):

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = barometric pressure (mm Hg) of air sampled

T = temperature (°C) of air sampled

24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg

MW = molecular weight

760 = standard pressure (mm Hg)

298 = standard temperature (°K)

11. References

11.1 P.J. Milham, A.S. Awad, R.E. Paull, and J.H. Bull, Analyst, 95, 751 (1970).

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11.3 Backup Data Report for Nitric Acid, No. S319, prepared under NIOSH Contract No. 210-76-0123.

11.4 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-172
DATE	October 27, 1982
SUPERSEDES	
PAGE	1 OF 10

NITROGEN OXIDES IN AIR, SPECTROPHOTOMETRIC METHOD

Analyte:	Nitrogen Dioxide, or Total Nitrogen Dioxide plus Nitric Oxide	Method No:	IHA-172
		Range:	0.01 to 10 μg/liter
Matrix:	Air	Precision:	~ 5% RSD
Procedure:	Bubbler sampling; spectrophotometry	Accuracy:	~ 5% negative bias (bubbler inefficiency)

1.0 Principle of the Method

1.1 The nitrogen dioxide (NO_2) is absorbed in an azo-dye forming reagent (Reference 1) in a bubbler sampler.

1.2 A stable pink color is produced within 15 minutes, which may be read visually or in an appropriate instrument at 550 nm wavelength.

1.3 Total NO_2 and NO (nitric oxide) may be determined by oxidizing any NO to NO_2 in the sampling operation.

2.0 Range and Sensitivity

2.1 This method is intended for the manual determination of nitrogen dioxide in the atmosphere in the range of 0.01 to 10 μg/liter, when sampling is conducted in fritted bubblers.

3.0 Interferences

3.1 A sulfur dioxide/nitrogen dioxide ratio of 10 produces no effect. A 30-fold ratio slowly bleaches the color to a slight extent. The addition of 1 percent acetone to the reagent before use retards the fading by forming an intermediate product with sulfur dioxide. This permits reading without appreciable interference within 4 to 5 hours (instead of the 45 minutes maximum when acetone is not added).

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3.2 A fivefold ratio of ozone to nitrogen dioxide will cause a small interference, the maximum effect occurring in 3 hours. The developed color has a slightly orange tint.

3.3 Peroxyacylnitrate (PAN) can give a response of approximately 15 to 35 percent of an equivalent molar concentration of nitrogen dioxide (Reference 2). In ordinary ambient air the concentrations of PAN are too low to cause any significant error.

3.4 The interferences from other gases which might be found in polluted air are negligible.

3.5 If strong oxidizing or reducing agents are present, the color should be measured within 1 hour, to minimize any loss.

4.0 Precision and Accuracy

4.1 A relative standard deviation of 3% can be achieved; one percent RSD has been reported (Reference 3).

4.2 Data on analytical measurement accuracy are not available. A negative bias up to 5% may be expected from bubbler inefficiency.

5.0 Advantages and Disadvantages of the Method

This is a simple method, using direct reaction with the absorbing reagent. The solution can be put directly into cuvettes to measure the optical absorbance, or diluted with additional absorbing reagent and read.

6.0 Apparatus

6.1 Bubbler absorber, all-glass, 40-60 μm pore diameter frit, with 30 mL capacity.

6.1.1 The porosity of the fritted bubbler, as well as the sampling flow rate, affect absorption efficiency. An efficiency of over 95 percent may be expected with a flow rate of 0.4 liter/minute or less and a maximum pore diameter of 60 μm. Frits having a maximum pore diameter less than 60 μm will have a higher efficiency but will

require an inconvenient pressure drop for sampling (see formula in Section 6.1.2). Considerably lower efficiencies are obtained with coarser frits, but these may be utilized if the flow rate is reduced.

6.1.2 Since the quality control by some manufacturers is rather poor, it is desirable to periodically measure the porosity of a fritted bubbler as follows: Carefully clean the apparatus with dichromate-concentrated sulfuric acid solution and then rinse it thoroughly with distilled water. Assemble the bubbler, add sufficient distilled water to just cover the fritted portion, and measure the vacuum required to draw the first perceptible stream of air bubbles through the frit. Calculate the maximum pore diameter as follows:

$$\text{Maximum pore diameter } (\mu m) = \frac{30s}{P}$$

where:

s = surface tension of water at the test temperature in dynes/cm (73 at 18°C, 72 at 25°C, and 71 at 31°C),

P = measured vacuum, mm Hg.

6.1.3 Rinse the bubbler thoroughly with water and allow to dry before using. A rinsed and reproducibly drained bubbler may be used if the volume (r) of retained water is added to that of the absorbing reagent for the calculation of results. This correction may be determined as follows: Pipet into a drained bubbler exactly 10 mL of a colored solution (such as previously exposed absorbing reagent) of absorbance A_1. Assemble the bubbler and rotate to rinse the inside with the solution. Rinse the fritted portion by pumping gently with a rubber bulb. Read the new absorbance, A_2, of the solution. Then:

$$10\ A_1 = (10 + r)A_2$$

or: $$r = 10\left(\frac{A_1}{A_2} - 1\right).$$

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6.2 Bubbler, all-glass, 170-220 μm pore diameter frit, with 30 mL capacity. This bubbler will contain potassium permanganate solution (7.6) to oxidize NO to NO_2 if NO is to be determined.

6.3 Air Metering Device. A glass rotameter capable of accurately measuring a flow of 0.4 liter/minute is suitable. A wet test meter is convenient to check the calibration.

6.4 Sampling Probe. A glass or stainless steel tube, 6 to 10 mm in diameter, provided with a downward-facing intake (funnel or tip) is suitable. A small loosely fitting plug of glass wool may be inserted, when desirable, in the probe to exclude water droplets and particulate matter. The dead volume of the system should be kept to a minimum to permit rapid flushing during sampling to avoid losses of nitrogen dioxide on the surfaces.

6.5 Air Pump. A vacuum pump capable of drawing the required sample flow for intervals of up to 30 minutes is suitable. A tee connection at the intake is desirable. The pump inlet connected to the sampling train should have an appropriate trap and needle valve, preferably of stainless steel. The second inlet should have a valve for bleeding in a large excess flow of clean air to prevent condensation of acetic acid vapors from the absorbing reagent, with consequent corrosion of the pump. Alternatively, soda lime may be used in the trap. A filter and critical orifice may be substituted for the needle valve (Reference 4).

6.6 Spectrophotometer or Colorimeter. A laboratory instrument suitable for measuring the pink color at 550 nm, with stoppered tubes or cuvettes. The wavelength band width is not critical for this determination.

6.7 Assorted laboratory glassware.

7.0 Reagents

All chemicals used should be analytical reagent grade (Reference 5).

7.1 Nitrite-Free Water. All solutions are made in nitrite-free water. If available distilled or deionized water contains nitrite impurities (produces a pink color when added to absorbing reagent), redistill it in an all-glass still after adding a crystal each of potassium permanganate and of barium hydroxide.

7.2 N-(1-Naphthyl) -Ethylenediamine Dihydrochloride, Stock Solution (0.1%). Dissolve 0.1 g of the reagent in 100 mL of water. Solution is stable for several months if kept well stoppered in a brown bottle in the refrigerator. (Alternatively, weighed small amounts of the solid reagent may be stored).

7.3 Absorbing Reagent. Dissolve 5 g of anhydrous sulfanilic acid (or 5.5 g of $NH_2C_6H_4SO_3H \cdot H_2O$) in almost a liter of water containing 140 mL of glacial acetic acid. Gentle heating is permissible to speed up the process. To the cooled mixture, add 20 mL of the 0.1% stock solution of N-(1-naphthyl) -ethylenediamine dihydrochloride, and dilute to 1 liter. Avoid lengthy contact with air during both preparation and use, since discoloration of reagent will result because of absorption of nitrogen dioxide. The solution is stable for several months if kept well-stoppered in a brown bottle in the refrigerator. The absorbing reagent should be allowed to warm to room temperature before use.

7.4 Standard Sodium Nitrite Solution (0.0203 g/liter). One mL of this working solution of sodium nitrite ($NaNO_2$) produces a color equivalent to that of 10 µL of nitrogen dioxide (10 ppm of 1 liter of air at 760 mm of mercury and 25°C: see Section 10.2.1). Prepare fresh just before use by aqueous dilution (see 7.1) from a stronger stock solution containing 2.03 g of the reagent grade granular solid (calculated as 100 percent) per liter. It is desirable to assay (Reference 5) the solid reagent, especially if it is old. The stock solution is stable for 90 days at room temperature, and for a year in a brown bottle under refrigeration.

7.5 Sulfuric Acid Solution (2.5 percent). Dilute 25 mL of conc. H_2SO_4 to 1 liter with distilled water.

7.6 Potassium Permanganate ($KMnO_4$) solution. Dissolve 25 g of $KMnO_4$ in 1 liter of 2.5% sulfuric acid solution.

8.0 Procedure

8.1 Cleaning of Glassware. All washed glassware should be allowed to stand a while in chromic acid solution, and then thoroughly rinsed with single and then double-distilled water.

8.2 Collection and Storage of Samples.

8.2.1 Assemble, in order, a sampling probe (optional), a glass rotameter, fritted absorber (6.1) and pump. Use ground-glass connections upstream from the absorber. Butt-to-butt

glass connections with slightly greased vinyl or pure gum rubber tubing also may be used for connections without losses if lengths are kept minimal. The sampling rotameter may be used upstream from the bubbler provided occasional checks are made to show that no nitrogen dioxide is lost. The rotameter must be kept free from spray or dust.

8.2.2 If the total of NO and NO_2 is to be determined, install the bubbler (6.2) containing 10 mL of $KMnO_4$ solution (7.6), directly upstream of the absorber.

8.2.3 Pipet 10.0 mL of absorbing reagent into the dry fritted bubbler absorber. (See Section 6.1.3.)

8.2.4 Draw an air sample through it at the rate of 0.4 liter/minute (or less) long enough to develop sufficient final color (about 10 to 30 minutes). Note the total volume of air sampled.

8.2.5 Measure and record the sample air temperature and pressure.

8.2.6 Colors may be preserved, if well stoppered, with only 3 to 4% loss in absorbance per day; however, if strong oxidizing or reducing gases are present in the sample in concentrations considerably exceeding that of the nitrogen dioxide, the absorbance should be measured as soon as possible to minimize any loss. (See Section 3 for effects of interfering gases.)

8.3 Analysis of Samples

8.3.1 After collection or absorption of the sample, a red-violet color indicates the presence of NO_2. Color development is completed within 15 minutes at room temperature.

8.3.2 Compare visually with standards or transfer to stoppered cuvettes and read in a spectrophotometer at 550 nm, using unexposed reagent as a reference. Alternatively, distilled water may be used as a reference and the absorbance of the reagent blank deducted from that of the sample.

8.3.3 Colors too dark to read may be quantitatively diluted with unexposed absorbing reagent. The measured absorbance is then multiplied by the dilution factor.

9.0 Calibration

9.1 Add graduated amounts of the $NaNO_2$ solution up to 1 mL (measured accurately in a graduated pipet or small buret) to a series of 25-mL volumetric flasks, and dilute to the mark with absorbing reagent.

9.2 Mix, allow 15 minutes for complete color development and read the absorbance (Section 8.3).

9.3 Plot the absorbances of the standard solutions against the µL of nitrogen dioxide per mL of absorbing reagent. The latter values are equal to the corresponding mL of standard nitrite solution times 0.4 (Section 10.2.2). If preferred, transmittance may be plotted instead of absorbance, using semilogarithmic graph paper. The plot follows Beer's law. Draw the straight line through the origin giving the best fit, and determine the slope, K, which is µL of NO_2 intercepted at absorbance of exactly 1.0 or at 10 percent transmittance. For 1-cm cells, the value of K is about 0.73.

10.0 Calculations

10.1 For convenience, standard conditions are taken as 760 mm Hg and 25°C, at which the molar gas volume is 24.47 liters. [This is identical with standard conditions for Threshold Limit Values of the American Conference of Governmental Industrial Hygienists; it is very close to the standard conditions used (Reference 9) for air-handling equipment, of 29.92 in. Hg, 70°F, and 50 percent relative humidity, at which the molar gas volume is 24.76 liters, or 1.2 percent greater.]

Ordinarily the correction of the sample volume to these standard conditions is slight and may be omitted; however, for greater accuracy, it may be made by means of the perfect gas equation.

10.2 Standardization by nitrite solution is based upon the empirical observation (References 1,6) that 0.72 mole of sodium nitrite produces the same color as 1 mole of nitrogen dioxide.

10.2.1 This factor is applied to calculate the equivalence of the nitrite solution to the volume of NO_2 absorbed as follows: One mL of the working standard solution contains 2.03×10^{-5} g $NaNO_2$. Since the molecular weight

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of $NaNO_2$ is 69.00, this is equivalent to:

$$\frac{2.03 \times 10^{-5}}{69.00} \times \frac{24.47}{0.72} = 1 \times 10^{-5} \text{ L of } NO_2\text{, or}$$

$$= 10\ \mu L \text{ of } NO_2$$

$$= 18.8\ \mu g\ NO_2\ (25°C,\ 760\ mm\ Hg)$$

10.2.2 In Section 9.0, the calibration standard containing 1 mL of nitrite solution (10 μL NO_2) per 25 mL total volume is equivalent to 10/25 or 0.4 μL (0.75 μg) of NO_2 per mL.

10.3 Compute the concentration of nitrogen dioxide in the sample as follows:

Nitrogen dioxide, ppm(μL/L) = AK/V

or Nitrogen dioxide, μg/L = 1.88 X AK/V

where:

A = measured absorbance
K = standardization factor from Section 9.3
V = volume of air sample, at 25°C and 760 mm Hg, in liters/mL of absorbing reagent.
1.88 = μg NO_2/μL(25°C, 760 mm Hg)

10.4 If preferred, the graph from Section 9.3 may be used instead as follows:

Nitrogen dioxide, ppm(μL/L) = μL NO_2 per mL/V

10.4.1 If V is a simple multiple of K, calculations are simplified. Thus, for the K value of 0.73 previously cited, if exactly 7.3 liters of air are sampled through a bubbler containing 10 mL of absorbing reagent, K/V = 1, and the absorbance is also ppm(μL/L) directly. (See Section 10.3.)

10.4.2 For exact work, an allowance may be made in the calculations for sampling efficiency and for fading of the color, using the following equation:

Nitrogen dioxide, ppm(μL/L) = A_cK/VE

where:

A_c = corrected absorbance; the absorbance is corrected for fading of the color (see Section 8.2.6) when there is a prolonged interval between sampling and measurement of the absorbance.

E = sampling efficiency; for a bubbler, E is estimated from prior tests using two absorbers in series (Reference 7 and Section 6.1.1).

11.0 References

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INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-174
DATE	October 27, 1982
SUPERSEDES	
PAGE	1 OF 6

OZONE IN AIR, SPECTROPHOTOMETRIC METHOD

Analyte:	Ozone	Method No.:	IHA-174 (NIOSH 154)
Matrix:	Air	Range:	0.1 to 0.4 mg/m^3 in a 45-liter sample
Procedure:	Impinger collection in alkaline KI; liberation of I_2; spectrophotometric measurement	Precision:	CV_T = 0.08 RSD = 8%
		Accuracy:	2% negative bias

For this analysis, the undersigned committee has approved for inclusion in this manual an existing procedure, exactly as published. Accordingly, the following pages are taken verbatim from the NIOSH Manual of Analytical Methods, Second Edition, Vol. 1, U. S. Department of Health, Education, and Welfare, Method 154, 1977.

The following exceptions to NIOSH 154 should be understood:

A. Under 7.3 Potassium Iodate, Standard Solution.

One milliter of this stock solution is equivalent to 259 µL of ozone (at 25°C and 760 mm Hg).

B. Under 9.4, second sentence:

One milliter of the diluted standard iodate solution....is equivalent to 51 µg of ozone (25.9 µL at 25°C and 760 mm Hg).

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APPROVED BY PGDP	LAB R. E. Simpson IH C. W. Turak	APPROVED BY ORNL	LAB W R Laing IH James A. Eaton	NUMBER IHA-174

UCN-13234
(1235 1-79)

The following procedure is a photocopied excerpt from: NIOSH Manual of Analytical Methods, Second Edition, Vol. 1, U. S. Department of Health, Education and Welfare, 1977.

OZONE IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte: Ozone	Method No.: P&CAM 154
Matrix: Air	Range: 0.1 to 0.4 mg/m³ in a 45 - liter sample
Procedure: Collection *via* impinger, colorimetric alkaline KI method	Precision (CV_T): 0.08 in the range 0.1 to 0.4 mg/m³ in 45 - liter samples
Date Issued: 9/1/72	Classification: C (Tentative)
Date Revised: 1/29/76	

1. **Principle of the Method**

Air containing ozone is drawn through an alkaline solution of potassium iodide. Ozone reacts to form a stable product that can be stored in solution with little loss for several days. Addition of acid to the solution liberates iodine in proportion to the collected ozone. The absorption of iodine at 352 nm is then measured spectrophotometrically.

2. **Range and Sensitivity**

2.1 This method has been validated over the range 0.1 to 0.4 mg/m³. This is the limit of the useful range for the 45-liter sample size. The method is capable of measuring smaller or larger concentrations if the sampling size is adjusted, but it has not been validated for other sample sizes.

2.2 The detection limit for a 45-liter sample size is estimated to be 0.04 mg/m³.

3. **Interferences**

3.1 Chlorine, hydrogen peroxide, organic peroxides, and various other oxidants will liberate iodine by this method. The presence of strong oxidants such as chlorine causes serious positive interferences.

3.2 The positive response in proportion to the nitrogen dioxide present is limited to about 10% by the use of sulfamic acid in the procedure to destroy nitrite, thus minimizing error due to the collection of nitrogen dioxide.

3.3 The negative interferences from reducing gases such as sulfur dioxide and hydrogen sulfide are serious (probably on a mole-to-mole equivalency). It has been shown that the interference due to sulfur dioxide can be eliminated by incorporating into the sampling train upstream from the impinger a glass-fiber paper impregnated with chromium trioxide and sulfuric acid. All of the sulfur dioxide can be removed from a mixture of 15 ppm of sulfur dioxide and 0.15 ppm of ozone when the sample is passed through such an absorber. However, since the absorber is also capable of oxidizing nitric oxide to nitrogen dioxide, it may increase the interference cited in Section 3.2. (See Reference 11.2.)

3.4 The procedure is very sensitive to reducing dusts that may be present in the air or on the glassware. Losses of iodine also occur even on clean glass surfaces and thus the manipulations should minimize this exposure.

4. Precision and Accuracy

4.1 The coefficient of variation (CV_T) for the total analytical and sampling method in the range of 0.1 to 0.4 mg/m³ is 0.08. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.3.

4.2 The average recovery of ozone from vapor samples in the range 0.1 to 0.4 mg/m³ was 98% for the total analytical and sampling method.

5. Advantages and Disadvantages

5.1 The method is simple, accurate, and precise in the absence of interferences.

5.2 Those compounds listed in 3.1 will liberate iodine by this method causing positive interferences. Reducing gases or dusts cause negative interferences.

5.3 A delay of several days is believed to be permissible between sampling and completion of analysis. However, the exact relationship between delay and analytical results has not been established.

6. Apparatus

6.1 Midget impinger with a 1-mm i.d. nozzle, graduation marks, and a Teflon-coated stopper to replace the impinger top during shipment and storage.

6.2 A properly calibrated personal sampling pump capable of sampling at a flow rate of 1 ℓ/min for time intervals of up to 45 min. The pump should be calibrated with the midget impinger containing 10 mℓ of the absorbing reagent in the sampling train. A dry or wet test meter or a glass rotameter that will measure the appropriate flow rate within ±5% may be used for the calibration. The meter should include a prefilter to prevent liquid droplets from reaching it.

6.3 Spectrophotometer capable of measuring the absorbance at 352 nm with stoppered tubes or cuvettes, preferably of quartz or fused silica.

6.4 Associated laboratory glassware.

7. Reagents

The reagents described must be analytical reagent grade. Doubly distilled water should be used in the preparation of solutions and in the analytical procedure.

7.1 **Absorbing Reagent.** Dissolve 40.0 g of sodium hydroxide in almost a liter of water, then dissolve 10.0 g of potassium iodide and dilute the mixture to 1 liter with water. Store in a clean glass bottle with a screw cap (with inert liner) or rubber stopper (previously boiled for 30 min in alkali and washed). Age for at least 1 day before using.

7.2 Acidifying Reagent. Dissolve 5.0 g of sulfamic acid in 100 mℓ of water, then add 84 mℓ of 85% phosphoric acid and dilute to 200 mℓ with water.

7.3 **Potassium Iodate, Standard Solution.** Dissolve 0.758 g of potassium iodate in water and dilute to 1 liter in a volumetric flask. One milliliter of this stock solution is eqivalent to 400 μℓ of ozone. Prepare a dilute standard solution just before it is required by pipetting exactly 5 mℓ of stock solution into a 50-mℓ volumetric flask and diluting to the mark with water.

8. Procedure

8.1 **Cleaning of Equipment.** All glassware should be cleaned with a chromic acid – sulfuric acid cleaning solution followed by three rinses with tap water and three with distilled water.

8.2 **Collection and Shipping of Samples**

8.2.1 Assemble a train composed of a midget impinger, a flow meter, and a pump. Use ground-glass connections upstream from the impinger. Insure that all fittings are vacuum tight.

8.2.2 Pipette exactly 10 mℓ of the absorbing solution into the midget impinger and sample at a flow rate of 1 liter per minute. Note the volume of air sampled. Record atmospheric temperature and pressure.

8.2.3 Cap the impinger with the Teflon-coated stopper supplied for shipment to the laboratory.

8.3 **Analysis of Samples**

8.3.1 If the liquid level is below the 10-mℓ mark in the impinger, add distilled water to bring the level up to the mark.

8.3.2 Add 2 mℓ of the acidifying reagent with a volumetric pipette. Swirl gently to expel the carbon dioxide released immediately. Then cap and shake vigorously until bubbling ceases. It is imperative that *all* of the carbon dioxide is expelled; otherwise more may be released while the absorbance measurement is being made.

8.3.3 Place the stoppered impinger in a water bath at room temperature for 5 to 10 min to dissipate the heat of neutralization.

8.3.4 Transfer a portion of the sample to a cuvette and measure the absorbance at 352 nm. A cuvette containing distilled water is used as the reference. Do not delay the reading since reducing impurities sometimes cause rapid fading of the color.

8.3.5 Prepare a reagent blank by adding 2 mℓ of the acidifying reagent to 10 mℓ of unexposed absorbing reagent. Cool and determine the blank absorbance. The blank absorbance should be determined each day and should be subtracted from the absorbance of the samples.

8.3.6 Aliquots of samples may be taken before or after acidification if very large concentrations of oxidant are expected. When taking aliquots before acidification, dilute the aliquot to 10 mℓ with unexposed absorbing reagent and proceed in the usual manner. When taking aliquots after acidification, dilute the aliquot to 10 mℓ with reagent blank mixture. Dilution after acidification is not as reliable as before acidification and should be used only to save a sample when unexpectedly large concentrations of oxidant are encountered. The calculations should include the dilution factor.

9. **Calibration and Standards**

9.1 Add the freshly prepared, dilute standard iodate solution in graduated amounts of 0.1 to 0.5 mℓ (measured accurately in a graduated pipette or small burette) to a series of 25-mℓ glass-stoppered volumetric flasks. Make at least four standards.

9.2 Add alkaline potassium iodide solution (measured accurately in a graduated pipette) to make the total volume of each exactly 10 mℓ.

9.3 Acidify and determine the absorbances of each standard as was done for the samples.

9.4 Plot the absorbance of each standard (after correction for the blank) against its equivalent ozone concentration in 10 mℓ of absorbing solution. One millliter of the diluted standard iodate solution in a total of 10 mℓ of the absorbing solution (see Section 9.2) is equivalent to 78 μg (40 μℓ) of ozone.

10. Calculations

10.1 After measuring the absorbances of the sample solutions, use the standard absorbance curve to find the micrograms of ozone in each sample.

10.2 The concentration of ozone in air may be expressed in mg/m^3:

$$mg/m^3 = \frac{\text{corrected weight (in } \mu g)}{\text{volume of air sampled (in } \ell)}$$

10.3 The reaction of ozone with alkaline KI is not quantitative and the yield of iodine is concentration dependent. The following correction equation has been developed (see Reference 11.3):

$$O_3 \ (mg/m^3) = 0.038 + 1.038A - 0.010505A^2$$

where A is the concentration of ozone (also in mg/m^3) as determined above.

10.4 The concentration may also be expressed in terms of parts per million (ppm) by volume:

$$ppm = mg/m^3 \times \frac{24.45}{M.W.} \times \frac{760}{P} \times \frac{T+273}{298}$$

where: 24.45 = molar volume (ℓ/mole) at 25°C and 760 mmHg.

M.W. = molecular weight

P = pressure (mmHg) of air sampled.

T = temperature (°C) of air sampled.

11. References

11.1 *"Selected Methods for the Measurement of Air Pollutants."* Public Health Service Publication No. 999-AP-11, U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, 1965.

11.2 Saltzman, B.E., and A.F. Wartburg, "Absorption Tube for Removal of Interfering Sulfur Dioxide in Analysis of Atmospheric Oxidant," Anal Chem., 37, 779 (1965).

11.3 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-180
DATE	June 15, 1983
SUPERSEDES	
PAGE	1 OF 9

SELENIUM IN AIR, GRAPHITE FURNACE ATOMIC ABSORPTION METHOD

Analyte: Selenium

Matrix: Air

Procedure: Filter collection of dust; acid digestion; atomic absorption measurement

Method No.: IHA-180

Range: 1.4 $\mu g/m^3$ to 14 $\mu g/m^3$

Precision: ± 9% RSD

1.0 Principle of Method

1.1 A known volume of air is drawn through a cellulose membrane filter to collect the dust containing the analyte.

1.2 The sample-containing filters are wet ashed with concentrated nitric acid to destroy the filter matrix, followed by dissolution in hydrochloric acid to dissolve the selenium-containing residue. For selenium in steel dust, bulk samples should be tested to verify solubility and final solutions adjusted to contain at least 1% iron.

1.3 The solutions of samples and standards are pipeted into the graphite furnace of an atomic absorption spectrometer (AAS). An electrodeless discharge lamp is used to provide a characteristic selenium line at 196.0 nm. The absorbance is proportional to the selenium concentration.

2.0 Range, Sensitivity and Detection Limit

2.1 The working range for standard selenium solutions, using atomic absorption spectrometry (graphite furnace) as described, is 0.02 µg/mL to 0.2 µg/mL.

2.2 The detection limit of this method, using a 25-mL final volume, is 0.5 µg/sample, which corresponds to 1.4 $\mu g/m^3$ assuming a 360-liter air sample. This detection sensitivity is well below the OSHA allowable limit of 0.2 mg/m^3.

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2.3 The sensitivity is 0.01 µg/mL for 1% absorption based on a 20-µL injection volume. The method may be extended to higher values by dilution of the sample. Measurement of lower atmospheric concentrations can be made by using smaller final solution volumes, by longer sampling times, or by scale expansion to increase instrumental response.

3.0 Interferences

3.1 There are no known spectral line interferences due to other elements. Selenium assay by atomic absorption (graphite furnace) requires an instrument with a background corrector, in order to compensate for potential interferences such as those caused by the presence of salts.

4.0 Precision and Accuracy

4.1 The precision for the total analytical sampling method is 0.018 mg/m^3 standard deviation at the OSHA standard level, which corresponds to ± 9% RSD.

4.2 Analytical recoveries less than 95% are corrected by using appropriate factors (Sections 9.0 and 11.4) to cover the sampling as well as the analytical methods.

5.0 Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Samples collected on filters are readily treated for analysis by an instrumental method.

5.2 Standards must be treated in the same manner as test samples.

6.0 Apparatus

6.1 Filter Unit

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and a 37-mm, three-piece cassette filter holder.

6.1.2 Personal sampling pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of ± 5% at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

6.1.3 Thermometer.

6.1.4 Manometer.

6.1.5 Stopwatch.

6.2 Mixed cellulose ester membrane filter, 37-mm in diameter having 0.8 µm pore size.

6.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 6.5 Å/mm in the ultraviolet region. The instrument must have a graphite furnace attachment and a background corrector.

6.4 Selenium electrodeless discharge lamp.

6.5 Beakers, 25-mL.

6.6 Phillips beakers, 125-mL, with watchglass covers.

6.7 Pipets, delivery or graduated, 1, 5, 10-mL, and other convenient sizes for making standards.

6.8 Volumetric flasks, 25, 50, 100, 250, and 500-mL.

6.9 Hot plates, thermostatically-controlled, capable of reaching 140°C.

6.10 Centrifuge cones, 15-mL, disposable.

7.0 Reagents

All reagents must be ACS Reagent Grade or better.

7.1 Distilled or deionized water.

7.2 Nitric acid, conc.

7.3 Hydrochloric acid, conc.

7.4 Aqua regia, 1 volume conc. nitric acid, 3 volumes conc. hydrochloric acid.

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7.5 Standard selenium stock solution, 1000 µg/mL, aqueous, commercially available.

7.6 Selenium working standard solution, 100 µg/mL. Prepare fresh daily by appropriate dilution of the stock standard solution with 0.1 N nitric acid.

7.7 Iron solution, 1% w/v. Dissolve 48.3 g of ferric chloride, $FeCl_3 \cdot 6H_2O$ in sufficient distilled or deionized water to make 1 L of solution.

7.8 Hydrogen peroxide, 30%, H_2O_2, commercially available.

7.9 Nickel nitrate solution, 5.0% w/v. Dissolve 24.78 g of nickel nitrate, $Ni(NO_3)_2 \cdot 6H_2O$ in sufficent distilled or deionized water to make 100 mL of solution.

8.0 Procedure

8.1 Cleaning of Equipment

8.1.1 Before use, all glassware should initially be soaked in a mild detergent solution to remove any residual grease or chemicals.

8.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, followed by aqua regia, and then rinsed with tap water and distilled water, in that order, and then dried.

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, aqua regia and water rinses are adequate.

8.2 Collection and Shipping of Samples

8.2.1 Each personal sampling pump must be calibrated with a representative filter cassette in the line. This will minimize errors associated with the air sample volume passed through the filter.

8.2.2 Assemble the filter in the three-piece filter cassette holder, and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

8.2.3 Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel. The cassette plugs are replaced after sampling.

8.2.4 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.2.5 A sample size of 360-600 L is recommended. Sample at a flow rate of 1.5-2.0 Lpm. The flow rate should be known with an accuracy of ± 5%.

8.2.6 Turn the pump on and begin sample collection. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.2.7 Terminate the sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.2.8 Carefully record the sample identity and all relevant sampling data.

8.2.9 With each batch of ten samples, submit one filter from the same lot of filters which was used for sample collection and which is subjected to exactly the same handling as the samples except that no air is drawn through it. Label this as a blank.

8.2.10 The cassettes in which the samples are collected should be shipped in a suitable container designed to prevent damage in transit.

8.3 Analysis of Samples

8.3.1 Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of tweezers, and transfer the filter to a 125-mL Phillips beaker.

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8.3.2 Digestion of samples. Treat the filter in the beaker with 1 mL of concentrated nitric acid. Heat at 140°C until the filter is just dissolved. Add 1 mL of concentrated hydrochloric acid and continue heating for one minute. Allow to cool.

8.3.3 Quantitatively transfer the flask contents into a 25-mL volumetric flask. Rinse the digestion flask at least twice with distilled water and make to volume with distilled water.

NOTE: For steel dust samples, use 1% iron solution instead of distilled water in this step.

8.3.4 Pipette 10 mL of the sample into a 15-mL disposable centrifuge cone. Add 0.2 mL of the 5% nickel nitrate solution and 0.1 mL of 30% H_2O_2 to the sample. Swirl to mix.

8.3.5 Preset the AA graphite furnace controls as follows:

	Temp °C	Time (sec.)
Dry	125	30
Ash	1200	30
Vaporize	2700	10

8.3.6 Pipette a measured aliquot of the solution into the graphite furnace and record the absorbance at 196.0 nm. The absorbance is proportional to the sample concentration which can be determined from the appropriate calibration curve. When very low selenium concentrations are found in the sample, scale expansion can be used to increase instrument response.

NOTE: Follow instrument manufacturer's recommendations for specific operating parameters.

8.3.7 Appropriate filter blanks must be analyzed by the same procedure used for the samples.

9.0 Determination of Sample Recovery

9.1 Need for determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the analyte. The sample recovery should be determined in duplicate and should cover the concentration ranges of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the true value.

9.2 Procedure for determining recovery. Use known amounts of the bulk sample dust for this determination. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added in the form of the bulk sample to a representative cellulose membrane filter and air-dried. The analyte is then recovered and analyzed as described in Section 8.3. Determinations should agree with ± 5%.

9.3 In a typical examination of recovery, amounts of analytes not exceeding 300 µg were deposited on six filters. A parallel blank filter was also treated in the same manner except no sample was added to it. All filters were then digested and analyzed as described in Section 8.3. The average recovery value was found to be 93%.

$$\text{Recovery} = \frac{\text{Average weight (µg) recovered}}{\text{Weight (µg) added}}$$

10.0 Calibration and Standardization

10.1 From the selenium working standard solution, prepare at least six standards by adding 10-200 µg of Se to separate 125-mL Phillips beakers containing blank filters. Digest these standards by the same procedure used for samples beginning at Section 8.3.2.

10.1.1 Alternatively, a standard addition calibration procedure may be employed.

10.2 Proceed as in Section 8.3.3.

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10.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in µg/25 mL. It is advisable to run a set of standards both before and after the analysis of a series of samples, to ensure that conditions have not changed.

11.0 Calculations

11.1 Read the weight in µg corresponding to the total absorbance, from the standard curve. No volume corrections are needed because the standard curve is based on µg/25 mL.

11.2 Corrections for the blank must be made for each sample.

$$\text{Se, } \mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where: µg sample = µg found in sample filter.
µg blank = µg found in blank filter.

11.3 Divide the total weight by the recovery to obtain the corrected µg/sample.

$$\text{Corrected } \mu g/\text{sample} = \frac{\text{Total weight}}{\text{Recovery}}$$

11.4 Determine the volume of air sampled at ambient conditions in liters based on the appropriate information such as flow rate in Lpm multiplied by sampling time. If a pump using a rotameter for flow rate control was used for sample collections, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is as follows:

$$\text{Corrected Volume} = f \times t \left(\frac{P_1}{P_2} \times \frac{T_2}{T_1} \right)^{1/2}$$

where: f = flow rate sampled.
t = sampling time.
P_1 = pressure during calibration of sampling pump (mm Hg).
P_2 = pressure of air sampled (mm Hg).
T_1 = temperature during calibration of sampling pump (°K).
T_2 = temperature of air sampled (°K).

11.5 The concentration of the analyte in the air sampled can be expressed in mg/m^3 ($\mu g/L = mg/m^3$).

$$mg/m^3 = \frac{\text{Corrected } \mu g \text{ (Section 11.3)}}{\text{Air volume sampled (L)}}$$

12.0 Reference

12.1 NIOSH Manual of Analytical Methods, Vol. 7, S-190 "Selenium Compounds (as Se)", U.S. Department of Health and Human Services, August 1981.

UCN-10766B (12 8-78)

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-184
DATE	August 26, 1981
SUPERSEDES	
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SODIUM HYDROXIDE (ALKALINITY) IN AIR, TITRIMETRIC METHOD

Analyte:	Sodium Hydroxide	Method No.:	IHA-184 (NIOSH S381)
Matrix:	Air	Range:	0.76 - 3.9 mg/m^3 in a 360-L air sample
Procedure:	Filter Collection, extraction with aqueous acid, back titration with sodium hydroxide	Precision:	0.062 ($\overline{CV}_T$) 6.2% (RSD)
		Accuracy:	No significant bias

For this analysis, the undersigned committee has approved for inclusion in this manual an existing procedure, exactly as published. Accordingly, the following procedure for sodium hydroxide was taken verbatim from the NIOSH Manual of Analytical Methods, Second Edition, Vol. 4, U. S. Department of Health, Education, and Welfare, Method S381, 1978.

The following exceptions to NIOSH S381 should be understood:

A. Because the procedure is not specific for sodium hydroxide, the title should include the term "alkalinity," as shown above.

B. This procedure employs automatic titration of the sample by means of a syringe with constant feed drive to deliver the titrant, and a recorder to plot the titration curve. However, the titration may be done manually with a buret, without the recorder and syringe setup. If the sample is titrated manually, the following changes in the procedure should be made.

1. Section 6.3.1 should read: "A pH meter with expanded scale equipped with pH electrodes."

2. Section 6.3.3 should read: "A 5-ml buret with 0.01 or 0.02-ml graduations."

3. Omit Section 6.3.6, line 1.

4. In the paragraph following Section 6.3.6, line 3: ". . . automatic syringe drive inlet . . ." should be ". . . buret tip . . ."

5. Omit Section 6.5.

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	IH C. N. Turske		IH James A. Early		

B. (cont.)

6. Omit Section 6.6.

7. Section 8.4.1 should read: "Calibrate the pH meter with pH 7 and pH 10 buffers."

8. Section 8.4.5 should read: "After 15 minutes have passed, titrate the solution with 0.01 N sodium hydroxide while maintaining a nitrogen purge in the system. Add the sodium hydroxide incrementally past the pH 7 endpoint, to a pH of about 10. Record the pH reading (expanded scale) for each incremental addition of titrant, and plot the titration curve (pH versus ml of titrant)."

9. Omit all of Section 8.5 (8.5.1 through 8.5.4).

10. Section 8.7.2: In the equation for calculating the sodium hydroxide normality ". . . (mm on chart) x (ml/mm for chart) . . ." in the denominator should be ". . . volume of sodium hydroxide (ml) from titration curve . . ."

11. Section 9.1 should read: "Determine the volume of sodium hydroxide needed to neutralize the excess hydrochloric acid present by reading the volume to the inflection point on the titration curve."

C. Under Section 8.7.2, the volume of hydrochloric acid added is understood to be in ml.

D. Under Section 9.5, the pressures P_1 and P_2 are understood to be absolute.

The following procedure is a photocopied excerpt from: NIOSH Manual of Analytical Methods, Second Edition, Vol. 4, U. S. Department of Health, Education, and Welfare, 1978.

Sodium Hydroxide

Analyte:	Sodium Hydroxide	Method No.:	S381
Matrix:	Air	Range:	0.75 - 3.9 mg/cu m
OSHA Standard:	2 mg/cu m	Precision:	$(\overline{CV}_T)$: 0.062
Procedure:	Filter Collection, extraction with aqueous acid, back titration with sodium hydroxide	Validation Date:	7/8/77

1. Principle of the Method

1.1 A known volume of air is drawn through a polytetrafluorethylene filter to trap the sodium hydroxide aerosol present.

1.2 The sodium hydroxide collected is extracted from the filter by addition of a known amount of excess hydrochloric acid and the resultant solution purged with a stream of nitrogen gas.

1.3 The excess hydrochloric acid is titrated with a standard solution of sodium hydroxide under a nitrogen atmosphere.

1.4 The amount of sodium hydroxide collected is calculated from the difference between the known amount of acid added and the amount of acid remaining after extraction of the filter.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.758-3.88 mg/cu m at an atmospheric temperature and pressure of 23°C and 758 mm Hg, using a 360-liter sample. For a sample size of 360 liters, the working range of the method is estimated to be 0.4-5.4 mg/cu m.

2.2 The method may be extended to higher concentrations by addition of larger aliquots of standard hydrochloric acid. The detection limit of the analytical method is estimated to be 28 µg of sodium hydroxide or 7×10^{-4} mmoles of alkalinity.

3. Interferences

3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities should be transmitted with the sample.

3.2 It must be emphasized that the method determines total alkalinity present in particulate form and thus is not specific to sodium hydroxide.

3.3 If the titration curve obtained in the analysis is not one of a titration of a strong acid with a strong base then the presence of an interfering species is indicated and the results should be confirmed by an alternate method of analysis.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.758 - 3.88 mg/cu m was 0.0622. This value corresponds to a 0.124 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 10.1. Details of the test procedures are found in Reference 10.2.

4.2 A collection efficiency of at least 99.0% was determined for the collection medium; thus, no significant bias was introduced in the sample collection step. There was also no bias in the analytical method — the average recovery from the filters was 99.7%. In addition, the samples were found to be stable when stored on the filters for seven days. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable and involves no liquids. The filters are analyzed by means of a quick, instrumental method.

5.2 The method measures the toxic species, alkalinity, and is free from interference of other non-alkaline sodium compounds.

5.3 The method is not specific for sodium hydroxide but measures total alkalinity and the presence of any other alkaline species will present an interference.

5.4 Interference by carbon dioxide during collection has been minimized by virtue of the back titration used in the analytical procedure.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of aerosols has the following components:

6.1.1 Filter. The filter unit consists of the filter medium (Section 6.2) and 37-mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at the recommended flow rate is needed. The pump must be calibrated with a representative filter holder and filter in the line.

6.1.3 Thermometer.

6.1.4 Barometer.

6.1.5 Stopwatch.

6.2 A polytetrafluoroethylene (PTFE-Fluoropore) membrane filter, 1.0 micrometer pore size and 37-mm diameter. The filter is supported in the three-piece cassette by a cellulose backup pad.

6.3 Titration Assembly

6.3.1 A pH meter equipped with pH electrodes and a recorder (recommended chart drive of 1.5 inches per minute).

6.3.2 A titration vessel made from a 175-ml ointment jar (2.5 inches diameter) with two 5/8-inch holes drilled in the cap for the pH electrodes and two 3/8-inch holes for other inlets.

6.3.3 A constant feed syringe drive and syringe (recommended delivery rate of 1 ml per minute).

6.3.4 Magnetic stirrer and bar.

6.3.5 Glass rod, 5-mm diameter and 15-cm long.

6.3.6 Blunt-end Stainless Steel Needle, 10-cm long.

In the assembled apparatus the titration vessel contains the stirrer bar, solution to be titrated, the pH electrodes, nitrogen purge inlet and automatic syringe drive inlet all inserted through the cap and immersed in the solution. The vessel is positioned on top of the magnetic stirrer.

6.4 Pipets, 5 and 10 ml.

6.5 Balance, capacity of 1.000-100.000 g.

6.6 Ruler, graduated in millimeters.

6.7 Volumetric flasks, 100 and 1000 ml.

6.8 Glass bottle, 1 liter equipped with a stopper containing a trap filled with a suitable CO_2 absorbing material (recommended for storage of dilute sodium hydroxide solution).

6.9 Graduated Cylinder, 100 ml.

7. <u>Reagents</u>

All reagents used must be ACS Reagent Grade or better.

7.1 Distilled water.

7.2 Standard stock hydrochloric acid solution, 0.1N.

7.3 Standard dilute hydrochloric acid, 0.01N. Prepare by diluting 10 ml of the stock solution into 100 ml.

7.4 Stock sodium hydroxide solution, 0.1N.

7.5 Working sodium hydroxide solution, 0.01N. Prepare by dilution of stock with distilled water through which nitrogen has been passed for 30 minutes.

7.6 Nitrogen gas.

7.7 Standard Buffer Solutions, pH 4 and pH 7.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative filter cassette in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The PTFE membrane filter is supported by a cellulose backup pad and the filter holder is held together by plastic tape or a shrinkable cellulose band. If the filter does not lay flat on the backup pad and the middle piece of the filter holder does not fit snugly into the bottom piece of the filter holder, sample leakage will occur around the filter. A piece of flexible tubing is used to connect the filter holder to the pump.

8.3.2 Clip the cassette to the worker's lapel. Air being sampled should not be passed through any hose or tubing before entering the filter cassette.

8.3.3 A sample size of 360 liters is recommended. Sample at a flow rate of 1.5 liters per minute for 4 hours. The flow rate should be known with an accuracy of at least ±5%.

8.3.4 Turn the pump on and begin sample collection. Since it is possible for filters to become plugged by heavy partic-

ulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.3.5 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is unavailable, record the elevation. Replace filter plugs.

8.3.6 Blank. With each batch of ten samples submit one filter from the same lot of filters which was used for sample collection and which is subjected to the same handling as for the samples except that no air is drawn through it. Label this as a blank.

8.3.7 Shipping. The filter cassettes should be plugged and shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Set the pH recorder with the pH 4 and 7 buffers so that the range between pH 3 and 10 is recorded.

8.4.2 Add 75 ml of distilled water to the titration vessel.

8.4.3 Open the cassette filter holder and carefully remove the PTFE membrane filter from the holder and cellulose backup pad with the aid of appropriate tweezers. Transfer the filter to the titration vessel with the collection side face down. Place the end of a glass rod in the center of the filter to maintain it completely below the liquid surface during the complete analytical procedure. Replace the titration vessel cover and place the pH electrode in place.

8.4.4 Pipet 5 ml of 0.01N hydrochloric acid into the vessel, start the magnet stirrer and a nitrogen purge of the solution.

8.4.5 After 15 minutes have passed, titrate the solution with 0.01N sodium hydroxide while maintaining a nitrogen purge in the system. Initiate the syringe drive at a known position on the chart recorder paper so that the amount of NaOH added may be determined from the distance elapsed to the inflection point of the titration curve.

8.4.6 Appropriate filter blanks should be analyzed by the same procedure used for the samples.

8.5 Calibration of Syringe Drive and Chart Recorder

8.5.1 The syringe drive must be calibrated so that the volume

of sodium hydroxide added can be known accurately. Fill the syringe with the titrating solution and connect the delivery tube to a weighing bottle which has been pretared. Activate the syringe drive for a period of time sufficient to allow the delivery rate in grams/min to be determined by weighing the amount of liquid collected.

8.5.2 Determine the syringe delivery rate in ml/min by converting the grams/min to volume/min using the density of the solution at the appropriate temperature.

8.5.3 Calibrate the chart speed on the recorder and accurately determine the speed (in mm/minute).

8.5.4 Using the calibrated syringe delivery rate and the recorder chart speed calculate the volume per mm on the chart paper.

ml per mm = ml per minute/mm per minute

8.6 Determination of Sample Recovery

8.6.1 Need for Determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the compound from the collection device. The sample recovery should be determined in duplicate and should cover the concentration ranges of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the true value.

8.6.2 Procedure for Determining Recovery. An aliquot of a standard solution containing a known amount of the analyte, preferably equivalent to the sample concentration expected is added to a representative PTFE membrane filter and air dried. The analyte is then recovered from the filter and analyzed as described in Section 8.4. Duplicate determinations should agree within ±5%.

For the validation study conducted to determine the precision and accuracy of this method, an amount of the analyte equivalent to that present in a 360-liter sample at the selected level has been used for the recovery studies. Six filters at each of the three levels (0.5, 1.0 and 2.0X the OSHA standard) were spiked accordingly by adding an aliquot of a solution of sodium hydroxide in methanol containing known amounts of alkalinity. A parallel blank filter was also treated in the same manner except that no sample was added to it. All the filters were then extracted and analyzed as described in Section 8.4. The average recovery value obtained was 0.997.

The sample recovery equals the average weight in µg recovered from the filter divided by the weight in µg added to the filter, or

$$\text{Recovery} = \frac{\text{Average Weight (µg) recovered}}{\text{Weight (µg) added}}$$

8.7 Standardization of the Titrating Solution

8.7.1 The sodium hydroxide titrating solution is standardized against the standard 0.0100N hydrochloric acid prepared by dilution of standard 0.1N hydrochloric acid.

8.7.2 The standarization is carried out according to the procedure described in Section 8.4 except for addition of a sample or a blank filter. The standardization is carried out in triplicate. The normality of sodium hydroxide is calculated as follows:

$$\text{Normality of sodium hydroxide} = \frac{\text{(Normality of hydrochloric acid) x (Volume of hydrochloric acid added)}}{\text{(mm on chart) x (ml/mm for chart)}}$$

9. Calculations

9.1 Determine the volume of sodium hydroxide needed to neutralize the excess hydrochloric acid present by multiplying the distance (in mm) elapsed from the initiation of the syringe drive to the endpoint in the titration by the conversion of ml per mm or:

Volume of sodium hydroxide needed (ml) = mm to endpoint x ml/mm

9.2 The amount of sodium hydroxide (alkalinity) present on the filter is determined from the difference between the amount of hydrochloric acid added and the amount of sodium hydroxide needed in the back titration, or:

mmoles of sodium hydroxide present = (Volume of hydrochloric acid added (ml) x Normality of hydrochloric acid) - (Volume of sodium hydroxide added (ml) x Normality of sodium hydroxide)

The amount of sodium hydroxide present is calculated using the molecular weight:

µg sodium hydroxide sample = mmoles of sodium hydroxide present x 40,000.

9.3 Correction for the blank must be made for each sample.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

μg sample = μg found in sample filter

μg blank = μg found in blank filter

9.4 Divide the total weight by the recovery to obtain the corrected μg sample.

$$\text{Corrected } \mu g/\text{sample} = \frac{\text{Total Weight } (\mu g)}{\text{Recovery (Section 8.6)}}$$

9.5 For personal sampling pumps with rotameters only the following correction should be made.

$$\text{Corrected Volume} = f \times t \sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}}$$

where:

f = sampling flow rate

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

9.6 The concentration of the analyte in the air sampled can be expressed in mg/cu m. (μg/liter = mg/cu m)

$$\text{mg/cu m} = \frac{\text{Corrected } \mu g \text{ (Section 9.4)}}{\text{Volume of Air Sampled in Liters (Section 9.5)}}$$

10. References

10.1 Memoranda, Kenneth A. Busch (Chief, Statistical Service, DLCD), to Deputy Director, DLCD, dated 1/6/77, 11/8/77, subject: Statistical Protocol for Analysis of Data from Contract CDC-99-74-45.

10.2 S381 Backup Data Report for Sodium Hydroxide, prepared under NIOSH Contract No. 210-76-0123, 7/8/77.

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-186
DATE	August 26, 1981
SUPERSEDES	
PAGE	1 OF 6

SULFURIC ACID MIST IN AIR, TURBIDIMETRIC METHOD

Analyte: Sulfuric Acid

Matrix: Air

Procedure: Barium sulfate precipitation; turbidimetry

Method No.: IHA-186 (NIOSH 187)

Range: 0.1 to 4.0 mg/m^3 in a 100-L air sample

Precision: 0.09 (CV) 9% (RSD)

For this analysis, the undersigned committee has approved for inclusion in this manual an existing procedure, exactly as published. Accordingly, the following pages are taken verbatim from the NIOSH Manual of Analytical Methods, Second Edition, Vol. 1, U. S. Department of Health, Education, and Welfare, Method 187, 1977.

The following exceptions to NIOSH 187 should be understood:

A. It is recommended that the absorbance measurements in Sections 8.3.4 and 8.3.5 be made against distilled water as the reference.

B. Section 9.3 assumes that a calibration curve has been prepared by plotting absorbance versus sulfate concentration.

C. The calculation in Section 10 would be more accurate if revised to read:

"The concentration of sulfuric acid mist in air is calculated by the following equation:

$$mg/m^3 = \frac{\text{mg } SO_4 \text{ in sample} \times 1.021 \times 1000\ l/m^3}{\text{volume of sample in liters}}$$

where 1.021 = factor for converting SO_4 to H_2SO_4."

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APPROVED BY PGDP	LAB R. E. Simpson IH C. H. Turok	APPROVED BY ORNL	LAB W R Laring IH James A. Ealy	NUMBER IHA-186

The following procedure is a photocopied excerpt from: NIOSH Manual of Analytical Methods, Second Edition, Vol. 1, U. S. Department of Health, Education, and Welfare, 1977.

SULFURIC ACID MIST IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte: Sulfuric acid	Method No.: P&CAM 187
Matrix: Air	Range: 0.1 to 4.0 mg/m^3 in a 100-liter sample of air
Procedure: Turbidimetry	Precision: (CV): 0.09 (analytical) at 2.6 mg/m^3
Date Issued: 3/1/74	
Date Revised:	Classification: E (Proposed)

1. Principle of the Method

Sulfuric acid mist in air is absorbed in 10 to 15 mℓ of water in a midget impinger. The sulfate in the sample solution is precipitated as barium sulfate and the turbidity of the suspension is measured at 420 nm with a spectrophotometer.

2. Range and Sensitivity

2.1 As little as 10 μg of sulfuric acid in 10 mℓ of impinger-bubbler sample solution can be determined. This lower limit of the range corresponds to a concentration of 0.1 mg/m^3 of sulfuric acid in a 100-liter sample of air.

2.2 When the amount of sulfuric acid in 10 mℓ of impinger-bubbler sample solution exceeds 0.4 mg, the suspension of barium sulfate may lose stability and the accuracy of the method may decrease. This upper limit of the range corresponds to a concentration of 4.0 mg/m^3 of sulfuric acid in a 100-liter sample of air. Larger concentrations of sulfuric acid may be determined by appropriate dilution of the impinger-bubbler sample solution.

3. Interferences

3.1 Colored or suspended matter in large concentrations will interfere. Filtration of the sample solution may remove some suspended matter. If the concentration of colored or suspended matter is small in comparison with that of sulfate, a correction may be made by subtracting the turbidity of the sample solution without added barium chloride from that of the barium sulfate suspension.

3.2 Silica in concentrations above 500 mg/ℓ in the sample solution will interfere.

3.3 Large concentrations of organic materials in the sample solution may prevent the satisfactory precipitation of barium sulfate.

3.4 Sulfate salts, if present as particulate material in the sample air, will be reported as sulfuric acid.

4. Precision and Accuracy

In the application of the turbidimetric method to water analysis, a coefficient of variation of 0.09 was found for a synthetic water sample containing a sulfate concentration of 0.26 mg/mℓ; when this synthetic water sample was appropriately diluted for analysis, the concentration of sulfate obtained corresponded approximately to that which would have been obtained from a 100-liter sample of air containing 2.6 mg/m^3 of H_2SO_4. The relative error was approximately 2%. (See Reference 11.2.) For the determination of sulfuric acid mist in air, where sampling errors may be significant, the accuracy and precision probably are poorer than for water analysis.

5. Advantages and Disadvantages

5.1 The method is simple to perform and relatively fast. It requires no elaborate preparation of reagents and no complex equipment other than a spectrophotometer.

5.2 The method is reasonably specific since no common anions other than sulfate form an insoluble barium salt in acid solution. The interferences discussed in Section 3 are not likely to be encountered in air in concentrations that would cause serious difficulty in the determination of sulfuric acid mist.

5.3 Conditions for the precipitation of barium sulfate must be carefully controlled to obtain good reproducibility.

6. Apparatus

6.1 Air Sampling Equipment

6.1.1 **Personal Sampling Pump.** A personal sampling pump capable of sampling accurately at 1.5 ℓ/min is required. The pump should be calibrated with a midget impinger containing 10 mℓ of water in the intake line. A wet or dry test meter or a glass rotameter capable of measuring the required flow rate to within ± 5% may be used in the calibration.

6.1.2 **Midget Impinger.** Glass midget impingers of a size to contain 25 mℓ of solution are required. Provision should be made for connection to the pump and for appropriate mounting during sampling.

6.2 **Sample Containers.** Bottles (25 mℓ) are needed for shipping samples to the laboratory. Alternatively, the samples may be shipped in the midget impingers, if suitable closures are available.

6.3 Magnetic Stirrer. The stirrer should preferably be equipped with a timing device. If it is not, a stopwatch may be used instead. The stirring speed should not vary appreciably.

6.4 Spectrophotometer with absorption cells, for use at 420 nm.

6.5 Volumetric flasks and pipettes.

7. Reagents

7.1 Distilled water for collection of samples.

7.2 SulfaVer IV powder, commercially available from Hach Chemical Company, or the equivalent. This reagent is supplied in a prepackaged "Powder Pillow" in an amount suitable for a single determination. (See Reference 11.1.)

7.3 **Standard Solution of Sulfate (0.1 mg/mℓ).** Dissolve 0.1479 g of ACS reagent grade anhydrous sodium sulfate in distilled water and dilute to 1 liter.

8. Procedure

8.1 **Cleaning of Equipment.** Wash all glassware with detergent solution and then rinse thoroughly with tap water and distilled water. After each use the absorption cells should be cleaned with detergent and a brush to prevent the accumulation of a deposit on the inside walls of the cell.

8.2 Collection and Shipping of Samples

8.2.1 Place approximately 10 mℓ of distilled water in a midget impinger and connect the impinger to the pump.

8.2.2 Pump air sample through the impinger at the rate of 1.5 ℓ/min for at least 60 min. Measure the flow rate and time as accurately as possible. If sulfuric acid concentrations greater that 4 mg/m^3 are expected, sample for a shorter length of time. Alternatively, the sample solution may be diluted in the laboratory.

8.2.3. One of every ten samples collected as directed above should be labeled as a blank. The absorbance of this sample will be measured without the addition of SulfaVer IV reagent to allow a correction to be made for color and suspended matter.

8.2.4 The samples should be packed for shipment to the laboratory in a manner that will prevent loss or damage in transit.

8.3 Analysis of Samples

8.3.1 Adjust the volume of the sample solution to 25 mℓ in a volumetric flask. Transfer the solution to a 100-mℓ Erlenmeyer flask and place the flask on the magnetic stirrer.

8.3.2 Add one package ("Powder Pillow") of SulfaVer IV reagent to the sample solution. The exact amount of SulfaVer IV powder added is not critical. However, the *same* amount must be added to all samples. The amount added must be in excess of the amount required to precipitate all of the sulfate as barium sulfate.

8.3.3 Start the magnetic stirrer immediately upon addition of the SulfaVer IV powder. Stir for exactly 1 min. The speed of stirring is not critical, but it should be constant for each set of samples and standards and should be adjusted to about the maximum rate at which no splashing occurs.

8.3.4 Immediately after the stirring has been stopped, fill an absorption cell and measure the turbidity at 420 nm at 30-sec intervals for 4 min. Record the maximum turbidity (or absorbance reading) observed during the 4-min period. The maximum turbidity usually occurs within 2 min and the readings remain constant thereafter for 3 to 10 min.

8.3.5 Dilute the "blank" sample to 25 mℓ and measure its turbidity (absorbance). Subtract this turbidity value from the sample values to correct for color and suspended matter.

9. Calibration and Standards

9.1 Pipette 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, and 4.0 mℓ of the standard sulfate solution into 25-mℓ volumetric flasks and dilute to the mark.

9.2 Transfer the standards to 100-mℓ Erlenmeyer flasks and follow the procedure outlined in Section 8.3.

9.3 Check the calibration curve periodically by running a standard with every three or four samples.

10. Calculations

The concentration of sulfuric acid mist in air is calculated by the following equation:

$$mg/m^3 = \frac{mg\ H_2SO_4 \text{ in sample} \times 1000\ \ell/m^3}{\text{volume of sample in liters}}$$

11. References

11.1 *"Hach Water Analysis Handbook"*, Hach Chemical Company, Ames, Iowa, 1974.

11.2 *"Standard Methods for the Examination of Water and Wastewater"*, 13th Edition, American Public Health Association, Washington, D.C., 1971, pp. 334-335.

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-190
DATE	August 27, 1980
SUPERSEDES	
PAGE	1 OF 6

URANIUM IN AIR FILTERS, FLUOROMETRIC METHOD

Analyte:	Uranium	Method No.:	IHA-190
Matrix:	Air	Range:	0.05 to 1.0 μg U
Procedure:	Filter digestion in acid; TOPO extraction; fluorescence analysis	Precision:	RSD 5% (fluorometry)

1.0 Principle of the Method

1.1 Air filters (cellulose type) are dissolved with nitric and perchloric acids.

1.2 The uranium is extracted into tri-n-octyl phosphine oxide (TOPO) dissolved in Varsol or hexane.

1.3 An aliquot of the organic phase is fused in a flux of anhydrous sodium fluoride containing 2% lithium fluoride.

1.4 The fluorescence of the pellet is measured using a fluorophotometer and compared to the fluorescence of a uranium standard.

2.0 Range and Sensitivity

2.1 This method, as presented, is used for total uranium levels up to 1.0 μg, with a lower reporting limit of 0.05 μg. The range may be extended upward by sample dilution.

3.0 Interferences

3.1 Essentially all interferences from heavy metals are eliminated by the TOPO extraction.

4.0 Precision and Accuracy

4.1 The fluorometric measurement used in this procedure yields an RSD of ±5% at the 0.05 μg U/ml level. The overall precision and accuracy of the procedure have not been evaluated.

APPROVED BY Y-12	LAB R J McElhaney	APPROVED BY ORGDP	LAB T. Kwasnoski	APPROVED BY UCCND-COORD'R C W Weber
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	IH C. H. Gurak		IH James A. Early	

5.0 Advantages and Disadvantages of the Method

5.1 The procedure is essentially interference-free.

5.2 The sample preparation is rather lengthy and care must be taken to avoid contamination.

6.0 Apparatus

6.1 Fluorophotometer, modified ORNL Model Q-1165, or equivalent.

6.2 Fusion burners, modified Fletcher; or induction furnace.

6.3 Platinum fusion dishes, 11/16-in. dia, 1/16-in. lip width, and 1/8-in. deep.

6.4 Pelletizer, delivering a 0.3-gram or 0.6-gram pellet.

6.5 Infrared lamp, 375-w, and stand.

6.6 Laboratory shaker.

6.7 Mechanical roller.

6.8 Hot plate.

6.9 Pipets, appropriate sizes, Eppendorf semiautomatic, or equivalent.

6.10 Dish holder, aluminum, designed to hold platinum fusion dishes.

6.11 Vial, screw cap with plastic liner, 2 oz (∿50 ml).

7.0 Reagents

7.1 Nitric acid, conc, reagent grade.

7.2 Nitric acid, 2 M: Add 62.5 ml of conc nitric acid to approximately 300 ml of distilled water and dilute to 500 ml.

7.3 Sodium fluoride-2% lithium fluoride flux: Put 1350 grams (3 pounds) of fluorometric grade sodium fluoride and 27 grams of lithium fluoride into a clean 5-pound glass reagent jar. Place the jar on the mechanical roller and roll for 48 hours.

7.3.1 Alternate flux, sodium fluoride: the lithium fluoride additive is unnecessary when fusion is completed by induction heat.

7.4 Tri-n-octyl phosphine oxide (TOPO) dissolved in Varsol, 0.05 M: (Hexane may be substituted for Varsol.) Dissolve 100 grams of tri-n-octyl phosphine oxide in 1500 ml of Varsol in a 2000-ml beaker. Filter the solution through fluted filter paper into a 2-gallon polyethylene bottle. Add sufficient Varsol to make a total volume of 5 liters, and mix thoroughly.

7.5 Stock uranium solution: Dissolve 117.9 mg of natural U_3O_8 in 8 M HNO_3 in a 100-ml beaker. Transfer the solution to a 100-ml flask using 2 M HNO_3. Mix thoroughly. 1 ml = 1 mg U or 1 g/liter.

7.6 Control Standard No. 1: Transfer 10 ml of the stock solution to a 1-liter flask and dilute to volume with 2 M HNO_3. Mix thoroughly. 1 ml = 10 μg U or 10 mg/liter.

7.7 Control Standard No. 2: Transfer 20 ml of control solution No. 1 to a 1-liter flask and dilute to volume with 2 M HNO_3. Mix thoroughly. 1 ml = 0.2 μg U or 0.2 mg/liter.

7.8 Control standard No. 3: Transfer 50 ml of control solution No. 2 to a 1-liter flask and dilute to volume with 2 M HNO_3. Mix thoroughly. 1 ml = 0.01 μg U or 0.01 mg/liter.

7.9 Perchloric acid, 70%, reagent grade.

8.0 Procedure

8.1 Sample Preparation

8.1.1 Place the filter in a 150-ml beaker and add 20 ml of conc nitric acid. Evaporate to dryness on a hot plate.

8.1.2 Dissolve the residue in 20 ml of conc nitric acid and carefully add 2 ml of 70% perchloric acid. Cover with a watchglass and evaporate to dryness in a perchloric hood. (This step is not necessary when using Millipore filters.)

8.1.3 Dissolve the residue in 20 ml of conc nitric acid, cover, and heat to dryness.

8.1.4 Dissolve the residue in 10 ml of 2 M nitric acid, cover, and evaporate to a volume of approximately 2 ml.

8.1.5 Transfer the solution to a 50-ml vial containing 5 ml of TOPO solution. Rinse the beaker several times with small volumes of 2 M nitric acid and add the rinse solution to the vial.

8.1.6 Seal the vial and shake for 2-10 minutes on the laboratory shaker.

8.1.7 Remove the vial from the shaker and let the mixture stand 1 minute, allowing the organic and aqueous layers to separate.

8.1.8 Process a blank and 5 ml of the 0.2- and 0.01-μg U/ml standards along with the samples, starting at Section 8.1.5.

8.2 Fusion using a Modified Fletcher Burner

8.2.1 With a pelletizer, place a 0.3- or 0.6-gram pellet of the fluoride flux into each platinum fusion dish to be used.

8.2.2 Place the platinum dishes on a nichrome screen.

8.2.3 Pipet 100 or 200 microliters of the organic phase from Section 8.1.7 onto each pellet using an Eppendorf pipet. (Use 100 μl for a 0.3-g pellet, and 200 μl for a 0.6-g pellet.)

8.2.4 Place the screen under an infrared heat lamp and allow the samples to dry for 30 minutes. The lamp should be approximately 6 inches above the pellets.

8.2.5 Place the screen over the fusion burner. Fuse for 2 minutes at approximately 1100°C, then reduce the temperature to 950°C and fuse for 1 minute. (An optical pyrometer will provide temperature estimates.)

8.2.6 Remove the screen from the burner and allow the melts to cool.

8.3 Alternate Fusion, using an Induction Furnace

8.3.1 With the pelletizer, place a 0.3-gram pellet of fluoride flux onto each platinum fusion dish to be used.

8.3.2 Place the platinum dishes with the pellets on the aluminum dish holder.

8.3.3 Pipet 200 microliters of the organic phase from Section 8.1.7 onto each pellet using an Eppendorf pipet.

8.3.4 Place the holder under an infrared heat lamp and allow the samples to dry for 30 minutes. The lamp should be approximately 6 inches above the pellets.

8.3.5 Remove the holder from under the lamp and place four dishes at a time in the induction furnace coil.

8.3.6 Apply 600 mA current for 60 seconds.

8.3.7 Transfer the dishes back to the holder to cool. (CAUTION: Use forceps.)

8.4 Sample Analysis and Calibration

8.4.1 Place the platinum dishes containing the blank, uranium standards, and fused samples on the turntable of the fluorophotometer.

8.4.2 Move the blank under the ultraviolet light and adjust the zero control to make the instrument read zero.

8.4.3 Move the 0.2-μg/ml standard under the ultraviolet light and adjust the calibration control until the instrument reads the known value of the standard.

8.4.4 Move the 0.01-μg/ml standard under the ultraviolet light. It should read the correct value of the standard if the instrument is properly calibrated. The fluorophotometer is now calibrated for direct readout of uranium concentration of the TOPO from 0.01 through 0.2 μg/ml.

8.4.5 Move the sample pellet under the ultraviolet light of the fluorophotometer and read the uranium concentration in μg/ml.

9.0 Calculation

9.1 Uranium in Air Filter:

$$\text{Total U in filter, } \mu g = \frac{A}{B} \cdot C \quad ,$$

where:

A = U on pellet, μg,

B = TOPO extract added to pellet, ml, and

C = TOPO volume used in extraction, ml.

$\frac{A}{B}$ may be read directly on a fluorophotometer equipped with direct concentration readout.

9.2 If the fluorophotometer used does not have a direct concentration readout capability, meter readings of fluorescence intensity of standards can be used to plot a calibration curve. Intensity readings from samples are then compared to the calibration curve to obtain amounts of uranium in the solution in μg U/ml.

10.0 References

10.1 White, J. C.; *The Use of Trialkyl Phosphine Oxides as Extractants in the Fluorometric Determination of Uranium*; ORNL-2161, November 1, 1956.

10.2 Centanni, F. A., Moss, A. M., and DeSesse, M. A.; "Fluorometric Determination of Uranium"; Anal. Chem., 28, 1651 (1956).

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-225
DATE	October 27, 1982
SUPERSEDES	
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COAL TAR PITCH VOLATILES (BENZENE-SOLUBLES) IN AIR, GRAVIMETRIC METHOD

Analyte:	Coal Tar Pitch Volatiles; Particulate Polycyclic Aromatic Hydrocarbons; Benzene Solubles	Method No.:	IHA-225 (NIOSH 217)
Matrix:	Air particulates, trapped	Range:	20 μg to 1 mg, per sample
Procedure:	Ultrasonic extraction with benzene; aliquot evaporated to dryness and weighed	Precision (Analytical):	2% RSD for 1 mg; 23% RSD for 20 μg

For this analysis, the undersigned committee has approved for inclusion in this manual an existing procedure, exactly as published. Accordingly, the following pages are taken verbatim from the NIOSH Manual of Analytical Methods, Second Edition, Vol. 1, U. S. Department of Health, Education, and Welfare, Method 217, 1977.

This procedure is successfully applied in UCC-ND, with several minor modifications, as follows:

A. Under 6 Apparatus, is added:

Millipore syringe filter adapter, with filter and 2-mL syringe.

B. Under 8.3:

Six sets of blank filters from the same lots are extracted...

C. Under 8.3.1 Extraction:

Step 2. Pipette 4.0 mL of benzene...
Step 3. ....sonicate the sample for 20 min.
Step 5 (New). As an alternative to Step 4, the particulates can be filtered and removed by using a Millipore filter assembly and syringe. The extracted solvent is pulled through an in-line fine porosity filter into a barrel of a 2-mL syringe. The filter assembly is removed and the filtrate is available for direct transfer to the tared Teflon cup.

D. Under 8.3.2

Step 1. Transfer 2.0 mL of the benzene solution...

E. Under Calculations:

Line 2: ....residue from a 2.0-mL aliquot...
Line 4: ....corrected weight is multiplied by 2...

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UCN-13234
(1235 1-79)

The following procedure is a photocopied excerpt from: NIOSH Manual of Analytical Methods, Second Edition, Vol. 1, U. S. Department of Health, Education, and Welfare, 1977.

BENZENE-SOLUBLE COMPOUNDS IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte: Benzene Solubles	Method No.: P&CAM 217
Matrix: Air particulates trapped on silver membrane and glass fiber filters	Range: 20 μg/sample
	Precision (CV): 0.02 (analytical) for 1 mg; 0.23 (analytical)for 20 μg
Procedure: Ultrasonic extraction with benzene, aliquot evaporated to dryness and weighed	Classification: D (Operational)
Date Issued: 1/29/76	
Date Revised:	

1. **Principle of the Method**

Particulate matter suspended in air is collected on a filter. The filter is extracted with benzene with ultrasonic agitation. An aliquot of the extract is evaporated to dryness and the residue is weighed.

2. **Range and Sensitivity**

The limit of detection is estimated to be 20 μg of benzene-soluble material in a filter sample; this value is two times the standard deviation of values determined for six blank filters. For a 300-liter air sample the limit of detection is, therefore, 0.067 mg/m^3. The range of the method extends upward to any weighable amount greater than 20 μg per sample.

3. **Interferences**

By definition, the method is inherently free of interferences that could occur in the particulate material collected on a filter. Errors may be caused by extraneous dust picked up in handling the filter or by changes in humidity or temperature during weighing. These errors may be avoided if the sample is properly protected and if temperature and humidity are controlled.

4. Precision and Accuracy

4.1 The analytical precision is dependent upon the amount of residue remaining to be weighed after evaporation of the solvent, as illustrated by the following example. Several benzene extracts of samples of aluminum reduction plant emissions were combined to give a solution containing the equivalent of 1.350 mg of benzene-soluble material per sample; nine aliquots of this solution gave residue weights with a coefficient of variation of 0.02. Benzene extracts of six blank filters gave residue weights with a coefficient of variation of 0.23.

4.2 The accuracy of this method has not been determined.

5. Advantages and Disadvantages

5.1 Ultrasonic agitation has been reported to be more efficient than Soxhlet extraction for dissolving organic materials is particulate samples. For example, the recovery of polycyclic arenes is higher with ultrasonic extraction than with Soxhlet extraction (Reference 11.3).

5.2 A major advantage of the method is that it is simple and direct. The analysis can be made by a technician with minimum training. An experienced technician should be able to analyze a set of 12 samples in 4 hr. If the extraction, evaporation, and weighing are staggered, it should be possible to analyze three sets of 12 samples in an 8-hr day.

5.3 The method is free of interference if temperature and humidity are constant during weighing and if the laboratory atmosphere is dust-free.

5.4 The method is empirical and nonspecific, and measures all substances in a sample that are soluble in benzene. It yields no information on the composition of the benzene-soluble material.

6. Apparatus

6.1 Air Sampling Equipment

6.1.1 Glass fiber filters, 37 mm, free of organic binder, with an efficiency of at least 99% as determined by the DOP penetration test.

6.1.2 Silver membrane filters, 37 mm, 0.8 μm pore size, Selas Corporation of America, No. FM-37-(0.8), or equivalent.

6.1.3 Disposable plastic filter holder (cassette) for 37-mm filters, Millipore MOOO 037 PO, or equivalent. In order to accommodate the two filters, the cassette must be held together with tape or a shrinkable band.

6.1.4 Personal sampling pump capable of operating for 4 hr at 1.5 ℓ/min. The pump should be calibrated with a representative filter assembly in the line. A wet or dry test meter or a glass rotameter capable of measuring the flow rate of 1.5 ℓ/min to within ± 5% may be used for the calibration.

6.2 **Electrobalance.** Cahn Instruments, Model G-2, or equivalent.

6.3 **Vacuum oven.** Thelco Model 19, GCA Precision Scientific, or equivalent.

6.4 **Ultrasonic bath.** Dynasonics Corporation Model NT-201, 90 kHz, 60 W, or equivalent. An ultrasonic bath operating at a lower frequency and having a higher power output may improve extraction efficiency. (See Reference 11.4.). A test tube support is needed for use in the ultrasonic bath.

6.5 Test tubes, 100 mm by 16 mm, with Teflon-lined screw caps.

6.6 Teflon weighing cups, Cahn Instruments No. 2034, or equivalent, approximate tare weight, 60 mg.

6.7 Allihn tubes, fine-porosity fritted glass, 30 mℓ.

6.8 Small glass vials with Teflon-lined screw caps.

6.9 Volumetric pipettes, 1 and 5 mℓ.

6.10 Wood applicator sticks, 6 in. long and 1/16 in. diameter.

6.11 Weighing paper, 3.5 by 4.5 in.

6.12 Tweezers.

7. **Reagents**

7.1 Benzene, ACS reagent grade.

7.2 Nitrogen, prepurified.

8. **Procedure**

8.1 **Cleaning of Equipment.** Wash the glassware with detergent solution and rinse with tap water and distilled water. Wash the Teflon weighing cups with reagent grade acetone and allow them to dry.

8.2 Collection and Shipping of Samples

8.2.1 Assemble the filters in the filter holder so that the air being sampled passes first through a glass fiber filter and then through a silver membrane filter. Remove the small plugs from the filter holder and connect the filter holder to the sampling pump by means of an adaptor and a length of tubing. Sample at least 300 liters of air at 1.5 ℓ/min. The optimum sample volume will depend on the type of workroom environment being sampled. Since high concentrations of particulate material or certain types of mists may plug the filters, the flow rate should be checked about once every hour. On completion of sampling, reinsert the small plugs in the inlet and outlet of the filter holder.

8.2.2 With each group of samples prepare at least three blanks consisting of a filter holder with representative filters that have been handled in the same manner as the sample filters, except that no air is drawn through them. The samples and the blanks should be shipped promptly in a light-proof container to prevent photooxidation or damage during transit.

8.3 Analysis of Samples The glass fiber and silver membrane filters are extracted together in the same test tube. At least three sets of blank filters are extracted along with each group of samples.

8.3.1 Extraction

1. Remove the top portion of the filter holder. Hold the bottom portion containing the filters over a piece of weighing paper to catch any particulate material that may fall out. Remove the small plug from the bottom portion of the filter holder and insert an applicator stick through the hole. Gently raise the filters and grasp the unexposed edge with tweezers. Fold the filters in half and then lengthwise so that they can be inserted into a test tube. Push the folded filters to the bottom of the test tube with the applicator stick. Add to the test tube any particulate material remaining in the filter holder or collected on the weighing paper.

2. Pipette 5.0 mℓ of benzene into the test tube. This amount of solvent should completely cover the filters. Be careful during the subsequent extraction and filtering procedures to avoid significant loss of benzene by evaporation.

3. Place the test tubes in the test tube support in the ultrasonic bath so that the level of water in the bath is above the level of the solvent. Turn on the ultrasonic bath and sonicate the sample for 5 min.

4. Decant the solvent into an Allihn tube and collect the filtrate in a small vial. Force the solvent through the Allihn filter under positive nitrogen pressure. This may be accomplished by connecting the nitrogen cylinder to a glass "T," leaving one arm of the "T" open and connecting the other arm to a No. 4 one-hole rubber stopper, which is pressed against the top of the Allihn tube; pressure is controlled with a finger placed against the open arm of the "T." When the filtration has been completed, close the vial tightly with a Teflon-lined screw cup.

8.3.2 **Gravimetric Determination**

1. Transfer 1.0 mℓ of the benzene solution to a tared Teflon cup. Evaporate the solvent in a preheated vacuum oven at 40°C and 200 torr and continue drying for a total of 2 hr. The residue should be visibly dry in about 1 hr and in 2 hr all of the benzene will have been removed.

2. Equilibrate the sample for at least 30 min in a weighing room where the temperature and humidity are kept constant. Determine the weight of the residue to the nearest microgram. Because of the small weight difference being measured, it is critical that the temperature and humidity be the same when the residue is weighed as when the empty Teflon cup is weighed.

9. **Calibration and Standards**

No calibration or standards are required for this method.

10. **Calculations**

The result of this analysis is expressed as the weight (in mg) of benzene-soluble material in a filter sample. The weight of the residue from a 1.0-mℓ aliquot of sample extract is corrected by subtracting the average weight of the residue from aliquots of the blank-filter extracts. This corrected weight is multiplied by 5 to obtain the total amount of benzene-soluble material in the sample.

11. References

11.1 Bolden, C., and E. Sawicki, Int. J.Environ. Anal.Chem., 4, 9 (1975).

11.2 Seim, H.J., W.W. Hanneman, L. R Barsotti, and T.J. Walker, "A Combined Gravimetric and Gas Chromatographic Determination of Airborne Particulate Polycyclic Organic Matter (PPOM)," American Industrial Hygiene Conference, Minneapolis, Minn., June 1975.

11.3 Chatot, G., M. Castegnaro, J.L. Roche, and R. Fontanges, Anal. Chim. Acta,53, 259 (1971).

11.4 Alliger, H., Am. Lab., 7 (10), 75 (1975).

11.5 Richards, R.T., D.T. Donovan, and J.R. Hall, Am. Ind. Hyg. Ass. J., 28, 590 (1967).

The following procedure is a photocopied excerpt from: NIOSH Manual of Analytical Methods, Second Edition, Vol. 2, U. S. Department of Health, Education, and Welfare, 1977.

Dichlorotetrafluoroethane*

Analyte:	Dichlorotetrafluoroethane	Method No.:	S108
Matrix:	Air	Range:	3500-14100 mg/cu m
OSHA Standard:	1000 ppm (7000 mg/cu m)	Precision ($\overline{CV}_T$):	0.064
Procedure:	Adsorption on charcoal, desorption with methylene chloride, GC	Validation Date:	10/29/76

1. Principle of the Method (Reference 11.1)

   1.1 A known volume of air is drawn through two tubes in series containing activated coconut charcoal to trap gaseous dichlorotetrafluoroethane.

   1.2 Dichlorotetrafluoroethane is desorbed from the charcoal with methylene chloride, and the sample is analyzed by gas chromatography.

2. Range and Sensitivity

   2.1 This method was validated over the range of 3540-14090 mg/cu m at an atmospheric temperature of 25°C and atmospheric pressure of 759 mm Hg, using a 3-liter sample. This maximum sample size is based on the capacity of the charcoal to collect vapors of dichlorotetrafluoroethane in air with 90% relative humidity. The method may be capable of measuring smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

   2.2 The upper limit of the range of the method depends on the adsorptive capacity of the charcoal. This capacity may vary with the concentrations of dichlorotetrafluoroethane and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube

*Refrigerant 114

(containing 600 mg of charcoal) reaches 5% of the concentration in the test gas mixture. The criterion for acceptance is that the volume of air that has passed through the tube at the time of breakthrough must be greater than 1.5 times the volume of air that would be passed through the tube for a sample at 2X the OSHA standard level. At a temperature of 24°C and relative humidity of 90%, breakthrough occurred in 158 minutes when a test concentration of 14600 mg/cu m was sampled at a flow rate of 0.046 liter/minute.

3. Interferences

3.1 When interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 Any compound that has the same retention time as dichlorotetrafluoroethane at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 3540-14090 mg/cu m was 0.064. This value corresponds to a 450 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.2. Details of the test procedures are found in Reference 11.3.

4.2 No recovery correction should be applied to the final result in Section 10.6. On the average the concentrations obtained in the laboratory validation study at 0.5X, 1X, and 2X the OSHA standard level were 0.2% lower than the "true" concentrations for 18 samples. Therefore, the method has no bias. The Coefficient of Variation is a good measure of the accuracy of the method since the recoveries and storage stability were good. Storage stability studies on samples collected from a test atmosphere at a concentration of 6900 mg/cu m indicate that collected samples are stable for at least 7 days.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those that occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

5.2 One disadvantage of the method is that the amount of sample that can be taken is limited by the number of milligrams that the tube will hold before overloading. When the amount of dichlorotetrafluoroethane found on the backup charcoal tube exceeds 12 mg, the probability of sample loss exists.

5.3 The precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 Personal Sampling Pump: A calibrated personal sampling pump whose flow rate can be determined within 5% at the recommended flow rate.

6.2 Two charcoal tubes are used in this method. One charcoal tube is used to collect the samples, and a smaller charcoal tube is used as a backup. The charcoal tubes are connected in series with Tygon tubing. The larger charcoal tube is a glass tube, 9-cm long with a 8-mm O.D. and a 6-mm I.D. It has two sections of 20/40 mesh activated coconut charcoal separated by a 2-mm portion of urethane foam. The front section contains 400 mg of charcoal, the back section 200 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than 25 mm of mercury at a flow rate of 0.05 liter per minute. The smaller charcoal tube is 7-cm long with a 6-mm O.D. and a 4-mm I.D. The smaller charcoal tube contains 100 mg of charcoal in the front section and 50 mg in the backup section.

6.3 Gas chromatograph equipped with a flame ionization detector using hydrogen and air for the detector.

6.4 Column (4-ft long x 1/4-in O.D. stainless steel) packed with 80/100 mesh Chromosorb 102.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Microliter syringes: 10-microliter for injection of samples into the gas chromatograph.

6.7 Gas tight syringes: 1, 2, 5, and 10-ml sizes for preparing standards.

6.8 Pipets: 20.0-ml delivery pipets.

6.9 Serum bottles: 30-ml glass bottles with 20-mm O.D. mouth.
Septa: 20-mm rubber septa with Teflon lining.
Aluminum tear-away seals to fit serum bottles.

6.10 Hand crimper for sealing septa to serum bottles.

6.11 Stopwatch.

6.12 Manometer.

7. Reagents

7.1 Methylene chloride, chromatographic quality.

7.2 Dichlorotetrafluoroethane, 99% pure.

7.3 Nitrogen, purified.

7.4 Hydrogen, prepurified.

7.5 Air, filtered, compressed.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed, thoroughly rinsed with tap water and distilled water, and dried.

8.2 Calibration of Sampling Pumps. Each personal sampling pump must be calibrated with representative charcoal tubes in the line to minimize errors associated with uncertainties in the volume sampled. (Reference 11.4)

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the two charcoal tubes to provide an opening at least one-half the internal diameter of the tube.

8.3.2 Connect the larger charcoal tube in series with the smaller charcoal tube by connecting the backup section of the large charcoal tube to the front section of the small charcoal tube with Tygon tubing. The shortest length of tubing compatible with maintaining a leak-free connection should be used. The smaller charcoal tube is used as a backup and should be positioned nearer the pump. Air should flow through the large charcoal tube before entering the small charcoal tube.

8.3.3 Both charcoal tubes should be vertical during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tubes.

8.3.5 A maximum sample size of 3 liters is recommended. Sample at a flow rate between 0.01 and 0.05 liter per minute. The collection time and the flow rate with an accuracy of 5% or better should be recorded. Also record the type of pump that is used.

8.3.6 The temperature, pressure, and relative humidity of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be separated and capped individually with plastic caps immediately after sampling. Under no circumstances should rubber caps be used. Each set of tubes should be marked to identify the large charcoal tube with the corresponding backup charcoal tube.

8.3.8 With each batch of ten samples, submit one set of tubes (a larger charcoal tube and a smaller backup tube) from the same lot of tubes used for sample collection. These tubes must be subjected to exactly the same handling as the samples except that no air is drawn through them. These tubes should be labeled as the blanks.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.4 Analysis of Samples

8.4.1 Desorption of Dichlorotetrafluoroethane. Pipet 20 ml of methylene chloride into the 30-ml serum bottle. Remove the plastic caps from both ends of the larger charcoal tube. Remove the plug of urethane foam from the outlet end of the tube. Transfer the 200-mg portion of charcoal to the serum bottle. Next, remove the glass wool plug from the inlet end of the tube and transfer the 400-mg section of charcoal to the same bottle. Place the Teflon-lined septum over the mouth of the bottle and seal the aluminum seal on with the crimper. It is important that the transfer of the charcoal be carried out as quickly as possible once the methylene chloride has been added to the bottle. The backup charcoal tube should be handled in a similar manner, using a separate serum bottle. The two samples are analyzed separately.

8.4.2 Gently shake the sample. The extract is now ready for analysis. Analyses should be completed within one day after the dichlorotetrafluoroethane is desorbed. Prepare standards as in Section 8.5.3. Fresh standards should be prepared daily.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow rate
2. 65 ml/min (24 psig) hydrogen gas flow rate to detector
3. 500 ml/min (50 psig) air flow rate to detector
4. 240°C injector temperature
5. 275°C detector temperature
6. 110°C column temperature

A retention time of approximately 1.7 minutes is to be expected for dichlorotetrafluoroethane under these conditions and using the column recommended in Section 6.4. The methylene chloride will elute from the column after the dichlorotetrafluoroethane.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or evaporation of solvent within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. It is not advisable to use an automatic sample injector for dichlorotetrafluoroethane in methylene chloride.

8.4.5 The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine the fraction of the specific compound that is removed in the desorption process for a particular batch of charcoal.

8.5.2 Known amounts of dichlorotetrafluoroethane are sorbed from the gas phase on the charcoal in the tubes as described below.

The apparatus to be used for spiking charcoal with known amounts of dichlorotetrafluoroethane consists of a union tee connected to a source of purified nitrogen, a charcoal tube, and a septum for introducing dichlorotetrafluoroethane from a gas tight syringe. A known amount of dichlorotetrafluoroethane is injected through the septum where nitrogen at a flow rate of approximately 20 ml/min carries the dichlorotetrafluoroethane into the charcoal tube. The nitrogen is allowed to flow through the tube for an additional 30 seconds after discharge of the contents of the syringe through the septum. The charcoal tube is capped with plastic caps.

The amount sorbed is equivalent to that present in a 3-liter air sample at the selected level. This requires 1.5, 3, and 6 ml of the dichlorotetrafluoroethane for 0.5X, 1X, and 2X the OSHA standard level, respectively. The atmospheric temperature, pressure, and relative humidity at which the tubes are prepared should be recorded.

Six tubes at each of the three levels are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of dichlorotetrafluoroethane onto the charcoal in the tube. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it.

8.5.3 Desorption and analysis experiments are done on the contents of the larger charcoal tube as described in Section 8.4.1.

In preparation of the standards, 20 ml of methylene chloride is added to a 30-ml serum bottle. The bottle is then sealed using a Teflon-lined septum and aluminum seal. An appropriate amount of dichlorotetrafluoroethane is bubbled slowly into the methylene chloride, using a gas tight syringe.

The syringe needle should be immersed in the methylene chloride during discharge of dichlorotetrafluoroethane from the syringe. The bottle should be shaken gently after removal of the syringe needle. Standards should be prepared at the same time that the sample analysis is done, and analyzed with the samples.

The weight (mg) of dichlorotetrafluoroethane in each standard and sample is calculated by the formula in Section 9.

The desorption efficiency (DE) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$DE = \frac{\text{Average weight recovered (mg)}}{\text{Weight added (mg)}}$$

The desorption efficiency is dependent on the amount of dichlorotetrafluoroethane collected on the charcoal. Plot the desorption efficiency versus weight of dichlorotetrafluoroethane found. This curve is used to correct for losses, as described in Section 10.4.

9. Calibration and Standards

A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. The standards are prepared as described in Section 8.5.3. Curves are established by plotting concentration in mg/20 ml versus peak area.

It is convenient to express concentration of standards in terms of mg/20 ml methylene chloride, because samples are desorbed in this amount of methylene chloride. The number of mg in the standard is calculated as follows:

$$mg = V \times \frac{M.W.}{24.45} \times \frac{298}{T + 273} \times \frac{P}{760}$$

where:

V	=	ml of dichlorotetrafluoroethane used to prepare the standard
T	=	temperature (°C) at which the sample was prepared
P	=	pressure (mm Hg) at which the sample was prepared
24.45	=	molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	=	molecular weight of dichlorotetrafluoroethane
298	=	standard temperature (°K)
760	=	standard pressure (mm Hg)

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed because the standard curve is based on mg/20 ml methylene chloride and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in both sections of sample tube

mg blank = mg found in both sections of blank tube

A similar procedure is followed for the backup tubes.

10.3 Add the weights found in the front and backup tubes to get the total weight of the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.3) for the amount found in the first tube. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{DE}$$

10.5 For personal sampling pumps with rotameters only, the following correction should be made.

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = flow rate sampled
t = sampling time
P_1 = pressure during calibration of sampling pump (mm Hg)
P_2 = pressure of air sampled (mm Hg)
T_1 = temperature during calibration of sampling pump (°K)
T_2 = temperature of air sampled (°K)

10.6 The concentration of dichlorotetrafluoroethane in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liters/cu m)}}{\text{Corrected air volume sampled (liters) (Section 10.5)}}$$

10.7 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	=	pressure (mm Hg) of air sampled
T	=	temperature (°C) of air sampled
24.45	=	molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	=	molecular weight (g/mole) of dichlorotetrafluoroethane
760	=	standard pressure (mm Hg)
298	=	standard temperature (°K)

11. References

11.1 White, L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31, 225, (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

11.3 Backup Data Report for Dichlorotetrafluoroethane, prepared under NIOSH Contract No. 210-76-0123.

11.4 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-235
DATE	August 27, 1980
SUPERSEDES	
PAGE	1 OF 10

DIOCTYL PHTHALATE (DOP) IN AIR, GAS CHROMATOGRAPHIC METHOD

Analyte:	Dioctyl phthalate (DOP); more correctly: Di-2-ethylhexyl phthalate	Method No.:	IHA-235 (NIOSH S40)
		Range:	2.03 - 10.9 mg/m^3
Matrix:	Air	Precision:	
		CV_T:	0.057
Procedure:	Filter collection; extraction with carbon disulfide; GC with flame ionization detector	RSD:	5.7%

For this analysis, the undersigned committee has approved for inclusion in this manual an existing procedure, exactly as published. Accordingly, the following pages are taken verbatim from the NIOSH Manual of Analytical Methods, Second Edition, Vol. 2, U. S. Department of Health, Education, and Welfare, Method S40, 1977.

The following exceptions to NIOSH S40 should be understood:

A. The chromatographic column (Section 6.4) could also be packed with 5% SP-2100 on 100/120 mesh Chromosorb W-HP to give comparable results.

B. The GC column temperature (Section 8.4.3) can be set at 260°C, rather than 230°C, to shorten the analysis time.

C. Peak height, rather than peak area, can be used for calibration and analysis; however, the precision has not been evaluated for that alternative.

D. The NIOSH procedure contains a typographical error. Under Section 9.0, paragraph 1, line 7 should be deleted.

E. Acceptable sample extraction can be achieved by cutting the filter into small pieces on a clean dry surface, inserting the pieces into a 2-ml sample bottle (fitted with a septum cap) and shaking in a developing vibrator (e.g., Supelco, Cat. No. 2-2951) for 45 min with 1 ml of carbon disulfide. Analytical precision for this technique has not been evaluated; however, this approach eliminates the need for the modified container in Section 6.6.1, simplifies the involved procedures in Sections 8.4.1 and 8.4.2 for sample preparation and extraction, and yields the final sample extract in a more direct manner. Mechanical shaking can be substituted for ultrasonics. If an automatic sample injector is used on the GC, the corresponding vials may be used in the extraction.

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The following procedure is a photocopied excerpt from: NIOSH Manual of Analytical Methods, Second Edition, Vol. 2, U. S. Department of Health, Education, and Welfare, 1977.

Di-2-Ethylhexyl Phthalate*

Analyte:	Di-2-ethylhexyl phthalate	Method No.:	S40
Matrix:	Air	Range:	2.03 - 10.9 mg/cu m
OSHA Standard:	5 mg/cu m	Precision:	$(\overline{CV}_T)$: 0.057
Procedure:	Filter collection extraction with carbon disulfide, GC	Validation Date:	1/17/75

1. Principle of the Method

1.1 A known volume of air is drawn through a cellulose membrane filter to trap the organic aerosol present.

1.2 The filter in the cassette is transferred into a disposable glass pipet and eluted with carbon disulfide.

1.3 An aliquot of the eluted sample is injected into a gas chromatograph.

1.4 The area of the sample peak is determined and the concentration is determined from the calibration curve.

2. Range and Sensitivity

2.1 This method was validated over the range of 2.03 - 10.9 mg/cu m at an atmospheric temperature and pressure of 23°C and 761 mm Hg, using a 32-liter sample. Under the conditions of sample size (30 liters), the probable useful range of this method is 0.5 - 15 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for the 0.45 mg sample.

2.2 The upper limit of the range of the method is dependent on the filtration efficiency of the cellulose membrane filter. If higher concentrations than those tested are to be sampled, smaller sample volumes should be used. The filtration efficiency for di-2-ethylhexyl phthalate aerosol is greater than 95% when sampled for 30 minutes at 1 liter per minute from a test atmosphere containing 10 mg/cu m.

* Listed incorrectly as di-sec-octyl phthalate in 29 CFR 1910.93.

3. Interference

3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 2.03 - 10.9 mg/cu m is 0.057. This value corresponds to a standard deviation of 0.29 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.1.

4.2 On the average the values obtained using the overall sampling and analytical method were 8% higher than the "true" values at the OSHA standard level.

These data are based on the validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

The sampling device is small, portable and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The filters are analyzed by means of a quick, instrumental method.

6. Apparatus

6.1 Sampling equipment - The sampling unit for the collection of personal air samples for the determination of organic aerosol has the following components:

6.1.1 The filter unit consisting of the filter media (Section 6.2) and appropriate 37 mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of ± 5% (reference 11.2) at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

6.2 Mixed cellulose ester membrane filter, 0.8 micrometer pore size and 37 mm diameter. The filter is held in the three piece cassette supported by a cellulose backup pad.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (6-ft x 1/8-in stainless steel) packed with 5% OV-101 on 100/120 mesh Supelcoport.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Assembly for sample elution.

6.6.1 Extraction tube, Fisher brand disposable Pasteur pipet (Cat. No. 13-678-5A) modified as follows: cut off the upper 1-inch portion, i.e., just below the notch to eliminate the constricted portion, and flame seal the lower tapered end.

6.6.2 Dumont No. 5 precision watchmakers tweezers, rustproof.

6.6.3 Volumetric flask, 1 ml.

6.6.4 Ultrasonic cleaner.

6.6.5 Triangular file.

6.7 Microliter syringes: 10-microliter and other convenient sizes for making standard solutions.

6.8 Volumetric flasks: 10-ml and other convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Di-2-ethylhexyl phthalate, reagent grade.

7.3 Tricosane, or other suitable internal standard.

7.4 Purified helium.

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

8. Procedure

8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative filter cassette in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the three piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

8.3.2 Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel.

8.3.3 Air being sampled should not be passed through any hose or tubing before entering the filter cassette.

8.3.4 A maximum sample size of 30 liters is recommended. Sample at a flow rate of 1.0 liter per minute. The flow rate should be known with an accuracy of at least $\pm$ 5%.

8.3.5 Turn the pump on and begin sample collection. Since it is possible for filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.3.6 Terminate sampling after the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.3.7 Collected sample cassette should be firmly sealed with the plugs in both the inlet and outlet.

8.3.8 Carefully record sample identity and all relevant sample data.

8.3.9 Blank: With each batch of samples submit one filter which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as a blank.

8.3.10 The cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Preparation of Samples

1. Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad.

2. With the aid of the Dumont tweezers, carefully roll the filter into a narrow cylinder. To do so, place the filter (sample side upwards) on a clean surface such as a watch glass and imagine a tangent to any edge of the circular filter. Pinch the filter with the long, sharp prongs of the tweezers along a line parallel to the imaginary tangent and about 1 cm inwards from the tangential point and start rolling the filter by gradually and carefully turning the tweezers' handle.

3. Insert the rolled filter into the modified pipet.

4. Add a known aliquot of the internal standard solution in carbon disulfide (ca. 100 microliters only) to the filter.

   Note: If the external standard method is used, this last step should be eliminated.

8.4.2 Extraction of Samples

1. Position pipets upright and add ca. 1 ml of carbon disulfide to the filter in the disposable pipet. Be sure that the entire filter is submerged in carbon disulfide and that there are no air bubbles trapped.

2. Seal the top of the pipet with a wad of glass wool to avoid sample contamination and loss during the next step.

3. Arrange the sample-containing pipets upright in a beaker and place the beaker in the ultrasonic vibrator for 30 minutes.

4. With a sharp file, very carefully score the tip (about 1 cm above the sealed end) of the pipet and break the tip inside the 1 ml volumetric flask. Allow the carbon disulfide eluent to drain completely into the flask. Apply air pressure, if necessary, to aid draining.

5. Rinse the filter inside the pipet with more carbon disulfide by dropwise addition of solvent until the total volume of eluent collected is 1.0 ml. If the 1.0 ml mark is overshot, concentrate sample to 1.0 ml by using a slow nitrogen flush.

6. If an automatic sample injector is used, transfer the sample extracts into the automatic sample injector vials prior to analysis.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) helium carrier gas flow
2. 35 ml/min (25 psig) hydrogen gas flow to detector
3. 400 ml/min (60 psig) air flow to detector
4. 300°C injector temperature
5. 300°C manifold temperature (detector)
6. 230°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10 microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9 - 5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed in Section 9.

8.5 Determination of Sample Recovery

8.5.1 Need for determination. Since the extraction scheme may be dependent on operator skill, it is necessary to determine the recovery of the compound. The sample recovery should be determined in duplicates and should cover the concentration ranges of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the "true" value.

8.5.2 Procedure for determining extraction efficiency. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then extracted from the filter and analyzed as described in Section 8.4. Duplicate determinations should agree within 5%.

For this validation study, an amount of the analyte equivalent to that present in a 30-liter sample at the selected level has been used for the extraction studies. Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) have been dosed accordingly and a known amount of internal standard was added to each filter prior to extraction. A parallel blank filter was also treated in the same manner except that no sample was added to it. All filters were then extracted and analyzed as described in Section 8.4. The recovery values obtained were at least 95% and as such no correction factor has been used in the determination of the "true" values.

The sample recovery equals the average weight in mg recovered from the filter divided by the weight in mg added to the filter, or

$$\text{Recovery} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same conditions
under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the OSHA standard level. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in sample filter
mg blank = mg found in blank filter

10.3 Divide the total weight by the extraction efficiency to obtain the corrected mg/sample

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{Recovery}}$$

10.4 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg(Section 10.3)} \times 1000 \text{ (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.5 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.2 Final Report, NIOSH Contract HSM-99-71-31. "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-247
DATE	October 27, 1982
SUPERSEDES	
PAGE	1 OF 6

OIL MIST IN AIR, INFRARED SPECTROPHOTOMETRIC METHOD

Analyte:	Oil Mist, Water-insoluble	Method No.:	IHA-247
Matrix:	Air	Range:	0.5 to 15 mg/m^3
Procedure:	Filter collection; solvent extraction; infrared spectrophotometry	Precision (Analytical):	5% RSD

1.0 Principle of the Method

1.1 Air samples are collected using 37-mm membrane filters.

1.2 Oil mist is extracted from the filters with carbon tetrachloride, CCl_4, or refrigerant-113 (1,1,2-trichloro-1,2,2-trifluoroethane).

1.3 The extractant solution is analyzed for oil content using infrared spectrophotometry to measure the C-H absorbance near 2940 cm^{-1}.

2.0 Working Range, Sensitivity, and Detection Limit

2.1 For a 100-liter air sample, the working range is linear up to at least 15 mg/m^3 and can easily be extended by dilution.

2.2 The sensitivity is approximately 35 μg/mL/0.1 absorbance unit. The sensitivity will vary somewhat, depending on the actual oil being analyzed.

2.3 The detection limit varies slightly with oil types, but is about 2 μg oil/mL of solvent, which corresponds to 0.3 mg/m^3 for a 100-liter air sample.

3.0 Interferences

3.1 Filters must be handled with care to avoid any oil contamination since this method is sensitive to any C-H containing compound. Such compounds in the form of aerosols would be a positive interference. Also, in some cases gaseous hydrocarbons could interfere if they were adsorbed or absorbed by the membrane filter.

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UCN-13234
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3.2 Tobacco smoke is an interference and workers should not be allowed to use smoking materials while an oil mist sample is being collected, since the smoke will invalidate the sample.

4.0 Precision and Accuracy

4.1 The accuracy has not been determined at this time.

4.2 The precision of the analytical procedure is estimated to be 5% RSD.

5.0 Advantages and Disadvantages

5.1 The method is simple and fast, but it can be used only for water-insoluble oils (oils soluble in CCl_4 or R-114).

5.2 The instrumentation required is available in most laboratories.

5.3 Since the method is not specific for a particular oil, it will give only an approximation of total oil mist exposure in locations where several oils are in use.

6.0 Apparatus

6.1 Sampling Equipment. The sampling unit for the filter-collection method has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) supported by a backup pad and 37-mm 3-piece cassette filter holder secured with tape or a shrinkable band.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of ± 5% at the recommended flowrate. The pump must be calibrated with a representative filter holder and filter in the line.

6.1.3 Thermometer

6.1.4 Manometer

6.1.5 Stopwatch

6.2 Mixed cellulose ester membrane filter, 0.8-micrometer pore size, 37-mm diameter. Prepackaged aerosol monitors may be used.

6.3 Infrared Spectrophotometer, double-beam dispersive, with scanning capabilities in the 3400--2700 wavenumber region.

6.4 Glassware

6.4.1 Scintillation vials with aluminum foil or Teflon-lined caps for desorption of samples.

6.4.2 Volumetric flasks for preparing standards, 50-mL.

6.4.3 Transfer pipets.

6.4.4 Reagent dispenser or pipet, 15-mL delivery capacity for adding solvent to samples.

6.4.5 Two 1-cm optical cells, infrared quartz with Teflon stoppers; mounted in removable cell holders.

7.0 Reagents

7.1 Carbon tetrachloride, distilled reagent grade, or refrigerant-113, reagent grade.

7.2 Stock Solution, 10 mg/mL - Weigh 0.500 g of oil (see Section 8.2.6.) into a 50-mL volumetric flask and add the solvent (7.1) to volume. Working standards should be prepared in the range of 1 to 100 µg oil/mL. Working standards are stable for at least one week if flasks are tightly closed.

8.0 Procedure

8.1 Cleaning of Equipment

8.1.1 Wash in detergent solution and follow with tap water and distilled or deionized water rinses. Dry.

8.1.2 Rinse with reagent grade solvent (7.1) and allow to dry.

CAUTION: All work with CCl_4 or R-113 should be performed in a ventilated hood. All waste solvent should be collected, labelled and disposed of properly.

8.2 Collection and Shipping of Samples

8.2.1 Assemble the filter unit by mounting the filter disc and backup pad in the filter cassette and securing the cassette with tape or a shrinkable band.

8.2.2 Connect the exit end of the filter unit to the pump with a short piece of flexible tubing.

8.2.3 Turn on the pump to begin sample collection. The flowrate, sample, and/or volume must be measured as accurately as possible. A minimum air sample of 100 liters should be filtered. Larger sample volumes are encouraged, provided the filters do not become loaded to the point that loose material might fall off or the filter become plugged.

8.2.4 The sample cassettes should be protected in a suitable container to minimize contamination and to prevent damage in transit to the laboratory. Care must be taken during storage and transit that no part of the sample is dislodged from the filter, nor that the sample surface be disturbed in any way. Loss of sample from heavy deposits on the filter may be prevented by mounting a clean filter in the cassette on top of the used sample filter.

8.2.5 With each batch of samples, one filter, labeled as a blank, must be submitted. No air should be drawn through this filter.

8.2.6 An unused, undiluted sample (5-10 mL is sufficient) of the oil being used in the area must be obtained and sent to the laboratory for use as a standard material in the analysis. To prevent contamination, the bulk oil should <u>not</u> be shipped in the same container as the filter samples.

8.3 Analysis of Samples

8.3.1 Use tweezers to transfer the sample and blank filters into individual scintillation vials, exercising care to avoid contaminating the filters with oil from hands. Add 15.0 mL of solvent (7.1) and cap the vial. Allow the vials to stand for 30 minutes with occasional agitation. At this point the oil is in solution and the samples are ready for analysis.

8.3.2 Fill both spectrophotometer cells with reagent solvent and scan the region from 3400 - 2700 cm^{-1}. All scans should be done in absorbance mode, if available. Otherwise data must be converted to absorbance units.

8.3.3 Fill one cell with sample or blank filter extracts, one at a time and scan each solution, against the solvent in the reference beam.

8.3.4 The absorbance at the wavenumber of the peak used to plot the calibration curve, generally about 2940 cm^{-1}, is measured and used to determine the oil concentration from the calibration curve prepared from the bulk sample (Section 8.2.6).

9.0 Calibration and Standardization

9.1 Appropriate dilutions of the stock solution are prepared to obtain working standards in the range of 2-100 µg/mL. (See Section 7.2).

9.2 Each working standard is transferred to a 1-cm cell and an infrared spectrum of the region from 3400 - 2700 cm^{-1} is recorded.

9.3 A calibration curve is constructed by measuring the peak height of the largest absorbance peak and plotting this value vs concentration in µg/mL.

10.0 Calculations

10.1 Blank values, if any, should first be subtracted from each sample value.

10.2 The concentration of oil in the air sampled can be calculated as µg oil/L of air, or mg oil/m^3 of air (C) as follows.

$$C = \frac{K}{V_s} \times V$$

where:

K = concentration of oil from calibration curve, µg oil/mL

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V = final volume (mL) of sample solution including any dilution factor

V_s = volume of air in liters sampled, corrected to 25°C and 760 mm Hg

11.0 References

11.1 American Public Health Association, Standard Methods for the Examination of Water and Wastewater, 14th Ed., 516, 1975.

11.2 Gruenfeld, M., "Extraction of Dispersed Oils from Water for Quantitative Analysis of Infrared Spectrophotometry," Environ. Sci. and Technol., 7, 636 (1973).

11.3 NIOSH Manual of Analytical Methods, "Oil Mist", Second Edition, Vol. 4, p. 283, 1978.

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-250
DATE	May 28, 1980
SUPERSEDES	
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ORGANIC SOLVENTS IN AIR, GAS CHROMATOGRAPHIC METHOD

Analyte:	Organic solvents (See Table 1)	Method No.:	IHA-250 (NIOSH 127)
Matrix:	Air	Range:	See Table 1, specific compound
Procedure:	Adsorption on charcoal; desorption with carbon disulfide; GC with flame ionization detection	Precision:	10.5% RSD
		Accuracy:	10%

For this analysis, the undersigned committee has approved for inclusion in this manual an existing procedure, exactly as published. Accordingly, the following pages are taken verbatim from the NIOSH Manual of Analytical Methods, Second Edition, Vol. 1, U. S. Department of Health, Education, and Welfare, Method 127, 1977.

The following exceptions to NIOSH 127 should be understood:

A. Peak heights may be used instead of peak areas for calibration and determination of these organic solvents.

B. The list of organic solvents in Table 1 may be expanded generally to include any which can be sampled by charcoal adsorption, desorbed by carbon disulfide, and detected in a gas chromatograph with a flame ionization detector.

C. Within the practice of UCC-ND, the following organics have also been determined by this method. They are listed with several parameters relevant to analysis:

Organic Solvent	Detection Limit (mg/sample)	Sample Volume (liters)* Minimum	Maximum	GC Column Temp. (°C)	Molecular Weight
Acetonitrile	0.10	5	15	180	41.05
Tetrahydrofuran	0.50	5	27	185	72.10
1,1,2-Trichloro-1,1,2-trifluoroethane (Refrigerant-113)	1.1	1	80	150	187.39

*See Table 1, Footnotes, of NIOSH 127.

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UCN-13234
(1235 1-79)

The following procedure is a photocopied excerpt from: NIOSH Manual of Analytical Methods, Second Edition, Vol. 1, U. S. Department of Health, Education, and Welfare, 1977.

ORGANIC SOLVENTS IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Organic Solvents (See Table 1)	**Method No.:**	P&CAM 127
Matrix:	Air	**Range:**	For the specific compound, refer to Table 1
Procedure:	Adsorption on charcoal desorption with carbon disulfide, GC		
Date Issued:	9/15/72	**Precision:**	10.5% RSD
Date Revised:	2/15/77	**Classification:**	See Table 1

1. **Principle of the Method**

   1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

   1.2 The charcoal in the tube is transferred to a small, graduated test tube and desorbed with carbon disulfide.

   1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

   1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. **Range and Sensitivity**

   The lower limit in mg/sample for the specific compound at 16 × 1 attenuation on a gas chromatograph fitted with a 10:1 splitter is shown in Table 1. This value can be lowered by reducing the attenuation or by eliminating the 10:1 splitter.

3. **Interferences**

   3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.

   3.2 When two or more solvents are known or suspected to be present in the air, such information (including their suspected identities), should be transmitted with the sample, since with differences in polarity, one may displace another from the charcoal.

   3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Hence, retention time data on a single column, or even on a number of columns, cannot be considered as proof of chemical identity. For this reason it is important that a sample of the bulk solvent(s) be submitted at the same time so that identity(ies) can be established by other means.

3.4 If the possibility of interference exists, separation conditions (column packing, temperatures, etc.) must be changed to circumvent the problem.

4. **Precision and Accuracy**

4.1 The mean relative standard deviation of the analytical method is 8% (11.4).

4.2 The mean relative standard deviation of the analytical method plus field sampling using an approved personal sampling pump is 10% (11.4). Part of the error associated with the method is related to uncertainties in the sample volume collected. If a more powerful vacuum pump with associated gas-volume integrating equipment is used, sampling precision can be improved.

4.3 The accuracy of the overall sampling and analytical method is 10% (NIOSH–unpublished data) when the personal sampling pump is calibrated with a charcoal tube in the line.

5. **Advantages and Disadvantages of the Method**

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more solvents suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists. During sample storage, the more volatile compounds will migrate throughout the tube until equilibrium is reached (33% of the sample on the backup section).

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. **Apparatus**

6.1 An approved and calibrated personal sampling pump for personal samples. For an area sample, any vacuum pump whose flow can be determined accurately at 1 liter per minute or less.

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 lpm.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (20 ft × ⅛ in) with 10% FFAP stationary phase on 80/100 mesh, acid-washed DMCS Chromosorb W solid support. Other columns capable of performing the required separations may be used.

6.5 A mechanical or electronic integrator or a recorder and some method for determining peak area.

6.6 Microcentrifuge tubes, 2.5 ml, graduated.

6.7 Hamilton syringes: 10 μl, and convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. **Reagents**

7.1 Spectroquality carbon disulfide (Matheson Coleman and Bell).

7.2 Sample of the specific compound under study, preferably chromatoquality grade.

7.3 Bureau of Mines Grade A helium.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. **Procedure**

8.1 **Cleaning of Equipment:** All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 **Calibration of Personal Pumps.** Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 **Collection and Shipping of Samples**

8.3.1 Immediately before sampling, the ends of the tube should be broken to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The small section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be vertical during sampling to reduce channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 The flow, time, and/or volume must be measured as accurately as possible. The sample should be taken at a flow rate of 1 lpm or less to attain the total sample volume required. The minimum and maximum sample volumes that should be collected for each solvent are shown in Table 1. The minimum volume quoted must be collected if the desired sensitivity is to be achieved.

8.3.6 The temperature and pressure of the atmosphere being sampled should be measured and recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly before they are shipped to minimize tube breakage during shipping.

8.3.10 Samples of the suspected solvent(s) should be submitted to the laboratory for qualitative characterization. These liquid bulk samples should not be transported in the same container as the samples or blank tube. If possible, a bulk air sample (at least 50 l air drawn through tube) should be shipped for qualitative identification purposes.

8.4 **Analysis of Samples**

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a small stoppered test tube. The separating section of foam is removed and discarded; the second section is transferred to another test tube. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, one-half ml of carbon disulfide is pipetted into each test tube. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 85 cc/min. (70 psig) helium carrier gas flow.
2. 65 cc/min. (24 psig) hydrogen gas flow to detector.
3. 500 cc/min. (50 psig) air flow to detector.
4. 200°C injector temperature.
5. 200°C manifold temperature (detector).
6. Isothermal oven or column temperature — refer to Table 1 for specific compounds.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blowback or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10 μl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 μl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-μl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back a short distance to minimize evaporation of the sample from the tip of the needle. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 **Determination of Desorption Efficiency**

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process for a given compound, provided the same batch of charcoal is used. NIOSH has found that the desorption efficiencies for the compounds in Table 1 are between 81% and 100% and vary with each batch of charcoal.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 5-cm, 4-mm I.D. glass tube, flame-sealed at one end (similar to commercially available culture tubes). This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the compound is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. The amount injected is usually equivalent to that present in a 10-liter sample at a concentration equal to the federal standard.

At least five tubes are prepared in this manner and allowed to stand for at least overnight to assure complete absorption of the specific compound onto the charcoal. These five tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of CS_2 with the same syringe used in the preparation of the sample. These are analyzed with the samples.

The desorption efficiency equals the difference between the average peak area of the samples and the peak area of the blank divided by the average peak area of the standards, or

$$\text{desorption efficiency} = \frac{\text{Area sample} - \text{Area blank}}{\text{Area standard}}$$

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml CS_2 because samples are desorbed in this amount of CS_2. To minimize error due to the volatility of carbon disulfide, one can inject 20 times the weight into 10 ml of CS_2. For example, to prepare a 0.3 mg/0.5 ml standard, one would inject 6.0 mg into exactly 10 ml of CS_2 in a glass-stoppered flask. The density of the specific compound is used to convert 6.0 mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area.

NOTE: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 The weight, in mg, corresponding to each peak area is read from the standard curve for the particular compound. No volume corrections are needed, because the standard curve is based on mg/0.5 ml CS_2 and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{Correct mg} = mg_s - mg_b$$

where:

mg_a = mg found in front section of sample tube

mg_b = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 The corrected amounts present in the front and backup sections of the same sample tube are added to determine the total measured amount in the sample.

10.4 This total weight is divided by the determined desorption efficiency to obtain the corrected mg per sample.

10.5 The concentration of the analyte in the air sampled can be expressed in mg per m^3.

$$mg/m^3 = \frac{\text{Corrected mg (Section 10.4)} \times 1000\ (\text{liters}/m^3)}{\text{Air volume sampled (liters)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$ppm = mg/m^3 \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L. D., D. G. Taylor, P. A. Mauer, and R. E. Kupel, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere", Am Ind Hyg Assoc J 31:225, 1970.

11.2 Young, D. M. and A. D. Crowell, Physical Adsorption of Gases, pp. 137-146, Butterworths, London, 1962.

11.3 Federal Register, 37:202:22139-22142, October 18, 1972.

11.4 NIOSH Contract HSM-99-72-98, Scott Research Laboratories, Inc., "Collaborative Testing of Activated Charcoal Sampling Tubes for Seven Organic Solvents", pp. 4-22, 4-27, 1973.

TABLE 1

Parameters Associated With P&CAB Analytical Method No. 127

Organic Solvent	Method Classification	Detection limit (mg/sample)	Sample Volume (liters) Minimum[a]	Sample Volume (liters) Maximum[b]	GC Column Temp.(°C)	Molecular Weight
Acetone	D	—	0.5	7.7	60	58.1
Benzene	A	0.01	0.5	55	90	78.1
Carbon tetrachloride	A	0.20	10	60	60	154.0
Chloroform	A	0.10	0.5	13	80	119
Dichloromethane	D	0.05	0.5	3.8	85	84.9
p-Dioxane	A	0.05	1	18	100	88.1
Ethylene dichloride	D	0.05	1	12	90	99.0
Methyl ethyl ketone	B	0.01	0.5	13	80	72.1
Styrene	D	0.10	1.5	34	150	104
Tetrachloroethylene	B	0.06	1	25	130	166
1,1,2-trichloroethane	B	0.05	10	97	150	133
1,1,1-trichloroethane (methyl chloroform)	B	0.05	0.5	13	150	133
Trichloroethylene	A	0.05	1	17	90	131
Toluene	B	0.01	0.5	22	120	92.1
Xylene	A	0.02	0.5	31	100	106

(a) Minimum volume, in liters, required to measure 0.1 times the OSHA standard

(b) These are breakthrough volumes calculated with data derived from a potential plot (11.2) for activated coconut charcoal. Concentrations of vapor in air at 5 times the OSHA standard (11.3) or 500 ppm, whichever is lower, 25°C, and 760 torr were assumed. These values will be as much as 50% lower for atmospheres of high humidity. The effects of multiple contaminants have not been investigated, but it is suspected that less volatile compounds may displace more volatile compounds (See 3.1 and 3.2)

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-260
DATE	August 26, 1981
SUPERSEDES	
PAGE	1 OF 9

PENTACHLOROPHENOL IN AIR, HPLC METHOD

Analyte: Pentachlorophenol

Matrix: Air

Procedure: Filter & bubbler collection; ethylene glycol extraction; HPLC

Method No.: IHA-260 (NIOSH S297)

Range: 0.265 - 1.130 mg/m in 180-L sample

Precision: 0.072 (CV_T)
7.2% (RSD)

Accuracy: No significant bias

For this analysis, the undersigned committee has approved for inclusion in this manual an existing procedure, exactly as published. Accordingly, the following pages are taken verbatim from the NIOSH Manual of Analytical Methods, Second Edition, Vol. 4, U. S. Department of Health, Education, and Welfare, Method S297, 1978.

The following exceptions to NIOSH S297 should be understood:

A. Under Section 8.4.3 HPLC Conditions:

The water portion of the mobile phase (eluent) should be adjusted to pH 4.0 with acetic acid prior to addition of the methanol. Without this adjustment the pentachlorophenol peak is severely distorted. This non-Gaussian peak shape results in decreased accuracy in measurement of the peak area. This effect becomes greater as the pentachlorophenol concentration decreases. Also, resolution of pentachlorophenol from lower chlorinated phenols is enhanced by the pH adjustment.

B. Under Section 10.4, the pressures P_1 and P_2 are understood to be absolute.

C. Under Section 10.5, the factor 1000 (liters/cu m) should be deleted, since the concentration in μg/liter is equivalent to mg/m^3.

APPROVED BY Y-12	LAB R.J. McElhaney	APPROVED BY ORGDP	LAB D. H. Frazier	APPROVED BY UCCND-COORD'R	C W Weber
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	IH C. H. Turak		IH James A. Ely		

The following procedure is a photocopied excerpt from: NIOSH Manual of Analytical Methods, Second Edition, Vol. 4, U. S. Department of Health, Education, and Welfare, 1978.

Pentachlorophenol

Analyte:	Pentachlorophenol	Method No.:	S297
Matrix:	Air	Range:	0.265-1.130 mg/cu m
OSHA Standard:	0.5 mg/cu m - skin	Precision ($\overline{CV}_T$):	0.072
Procedure:	Filter and bubbler collection, ethylene glycol extraction, HPLC	Validation Date:	12/23/77

1. Principle of the Method

1.1 A known volume of air is drawn through a mixed cellulose ester membrane filter connected in series to a midget bubbler containing 15 ml of ethylene glycol to collect pentachlorophenol.

1.2 The filter and bubbler are disconnected. The filter is removed from the filter holder and added to the bubbler flask.

1.3 Just before analysis, ten milliliters of methanol is added to the bubbler flask. The resulting sample is analyzed by high performance liquid chromatography using a UV detector set at 254 nm.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.2654-1.131 mg/cu m at an atmospheric temperature of 24°C and pressure of 761 mm Hg, using 180-liter samples.

2.2 The upper limit of the range of the method is dependent on the capacity and collection efficiency of the sampling system. The method may be extended to higher values than those tested by dilution of the sample solution.

3. Interferences

3.1 When interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 Any compound that has the same retention time as pentachlorophenol at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total sampling and analytical method in the range of 0.2654-1.131 mg/cu m was 0.0721. This value corresponds to a standard deviation of 0.036 mg/cu m at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedures can be found in Reference 11.2.

4.2 A collection efficiency of at least 99% was determined for the collection media (filter and bubbler in series), thus, no significant bias was introduced in the sample collection step. There was also no bias in the analytical method. The average recovery from the filters was 100.9%. The average recovery from samples that were stored eight days was 95.3%. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

5.1 Collected samples are analyzed by means of a quick, instrumental method.

5.2 A disadvantage of the method is the awkwardness in using midget bubblers for collecting personal samples. If the worker's job performance requires much body movement, loss of the collection solution during sampling may occur.

5.3 The precision of the method is limited by the reproducibility of the pressure drop across the filter and bubbler. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one filter/bubbler combination only.

5.4 The bubblers are more difficult to ship than adsorption tubes or filters due to possible breakage and leakage of the bubblers during shipping.

6. Apparatus

6.1 Filter Units. The filter unit consists of a 37-mm diameter cellulose ester membrane filter (Millipore Type AA or equivalent) with a pore size of 0.80 micrometer, supported by a stainless steel screen on a 37-mm three-piece filter holder. It is important that a stainless steel screen be used since other filter supports may retain part of the vapor.

6.2 Flexible Teflon or polyethylene tubing to connect the holder to the bubbler.

6.3 A glass midget bubbler containing 15 ml of ethylene glycol.

6.4 Personal Sampling Pump. A calibrated personal sampling pump whose flow can be determined within ±5% is used. The sampling pump is protected from splashover or solvent condensation by a second empty bubbler positioned between the exit arm of the first bubbler and the pump.

6.5 Barometer.

6.6 Thermometer.

6.7 High performance liquid chromatograph capable of UV detection at a wavelength of 254 nm and a sample injection valve with a 20-microliter external sample loop.

6.8 Column (30-cm x 3.9-mm I.D. stainless steel) packed with μBondapak C_{18}. The porous packing material consists of silica particles with a bonded coating of C_{18} organo-silane. This packing can be obtained from Waters Associates, Milford, Massachusetts.

6.9 An electronic integrator or some other suitable method for measuring peak areas.

6.10 Tweezers.

6.11 Microliter syringes, 50 and 100-microliter.

6.12 Volumetric flasks, convenient sizes for preparing standard solutions.

6.13 Pipets, convenient sizes for preparing standard solutions and 10 and 15-ml pipets for measuring the extraction medium.

6.14 Teflon tubing (15-cm long x 7-mm I.D.) or Teflon plugs for sealing the inlet and outlet of the bubbler stem before shipping.

7. Reagents

All reagents used must be ACS reagent grade or better.

7.1 Pentachlorophenol.

7.2 Dowicide EC-7 (purified pentachlorophenol).

7.3 Ethylene glycol.

7.4 Methanol, distilled in glass.

7.5 Isopropanol.

7.6 Water, deionized and distilled.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water, and dried.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter holder, bubbler and splashover trap in the line to minimize errors associated with uncertainties in the volume sampled.

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the three-piece filter holder and close firmly. The filter is backed up by a stainless steel screen. Secure the filter holder together with tape or shrinkable band.

8.3.2 Pipet 15 ml of ethylene glycol into each midget bubbler, and mark the liquid level. Be sure that the bubbler frit is completely immersed in the ethylene glycol.

8.3.3 Remove the filter holder plugs and attach the outlet of the filter holder to the inlet arm of the midget bubbler using a short piece of flexible polyethylene or Teflon tubing. Connect the outlet arm of the midget bubbler to a second empty bubbler and then to the personal sampling pump, using short pieces of flexible tubing. The bubblers must be maintained in a vertical position during sampling.

8.3.4 Air being sampled should not pass through any hose or tubing before entering the filter holder.

8.3.5 A sample size of 180 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known to within $\pm 5\%$.

8.3.6 Turn the pump on and begin sample collection. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be checked frequently and readjusted as needed. Sampling should be terminated when the rotameter cannot be readjusted.

8.3.7 Terminate sampling at the predetermined time and record sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation. Also record the type of sampling pump used.

8.3.8 After sampling, disconnect the filter and bubblers. Remove first the bubbler stem, and remove the filter from the filter holder with clean tweezers and add it to the bubbler. It is necessary to place the filter in the bubbler solution at this time, otherwise loss of pentachlorophenol from the filter by vaporization might occur. Replace the bubbler stem. The inlet and outlet of the bubbler stem should be sealed by connecting a piece of Teflon tubing between them or inserting Teflon plugs in the inlet and outlet. Do not seal with rubber. The splashover trap should have the inlet and outlet of the bubbler stem sealed in a similar manner. The standard taper joint of the bubblers should be taped securely to prevent leakage during shipping.

8.3.9 With each batch or partial batch of ten samples submit one bubbler containing ethylene glycol and a blank filter from the same lot of filters used for sample collection. This filter and bubbler must be subjected to exactly the same handling as the samples except that no air is drawn through them. Label this filter and bubbler as the blank.

8.3.10 The bubblers should be shipped in a suitable container, designed to prevent damage in transit. The samples should be shipped to the laboratory as soon as possible.

8.3.11 Bulk Sample. A bulk sample of the suspected material should be submitted to the laboratory in a glass container closed by a Teflon-lined cap. Label of the bulk sample should match air samples for identification purposes.

8.4 Analysis of Samples

8.4.1 If the sample volume is less than 15 ml, add ethylene glycol until the volume reaches the 15-ml mark. If the sample volume is more than 15 ml, determine the volume and make an appropriate volume correction in the calculations indicated in Section 10.1.

8.4.2 Add 10 ml of methanol to each sample just before analysis and mix the solution gently but thoroughly.

8.4.3 HPLC Conditions. The typical operating conditions for the high pressure liquid chromatograph are:

Column Temperature: Ambient
Column Pressure: 2300 psi
Flow Rate: 1.6 ml/min
Mobile Phase: 60% methanol/40% water (V/V)
Detector: UV photometer at 254 nm
Capacity Ratio: 1.8

8.4.4 Injection. The first step in the analysis is to inject the sample into the high pressure liquid chromatograph. The chromatograph is fitted with a sample injection valve and a 20-microliter sample loop. Flush this loop thoroughly with solvent (300 microliters), then fill the loop with sample solution and inject.

8.4.5 The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed below.

8.5 Determination of Analytical Method Recovery

8.5.1 Need for Determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the compound. The sample recovery should be determined in duplicate and should cover the concentration range of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the "true" value.

8.5.2 Procedure for Determining Recovery. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The filter is then immediately placed into 15 ml of ethylene glycol. Prior to analysis, as described in Section 8.4, 10 ml of methanol is added.

For the validation studies conducted to determine the precision and accuracy of this method, an amount of the analyte equivalent to that present in a 180-liter sample at the selected level was used to determine the analytical method recovery. A stock solution containing 10.00 milligrams of pentachlorophenol per milliliter of isopropanol was prepared. Aliquots of 4.5, 9 and 18 microliters were added to the cellulose membrane filters and air-dried to produce samples equivalent to 180-liter collections at 0.5, 1 and 2X the OSHA standard level. The analytical samples were then placed in 15 ml of ethylene glycol and allowed to stand overnight. A parallel blank filter was also prepared except that no sample was added to it. Just prior to analysis, as described in Section 8.4, 10 ml of methanol was added.

The sample recovery equals the average weight in µg recovered from the filter divided by the weight in µg added to the filter, or

$$\text{Recovery} = \frac{\text{Average Weight (µg) recovered} - \text{Blank (µg)}}{\text{Weight (µg) added}}$$

The recovery value is used in Section 10.3 if the recovery is less than 95%.

9. Calibration and Standards

A series of standards, varying in concentration over the range corresponding to approximately 0.25 to 3 times the OSHA standard for the sample under study, is prepared and analyzed under the same LC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in µg/25 ml versus peak area. Note: Since no internal standard is used in this method, standard solutions must be analyzed at the same time as the samples. This will minimize the effect of known day-to-day variations and variations during the same day of the UV detector response.

9.1 Prepare a 10 mg/ml pentachlorophenol stock standard solution by dissolving 100 mg pentachlorophenol in isopropanol and diluting to 10 ml in a volumetric flask.

9.2 From the above stock solution, appropriate aliquots are withdrawn and added to a mixture of 15 ml ethylene glycol and 10 ml methanol. Prepare at least five working standards to cover the range of 22.5-270 µg/25 ml. This range is based on a 180-liter sample. Analyze samples as per Section 8.4.

9.3 Prepare a standard calibration curve by plotting concentration of pentachlorophenol in µg/25 ml versus peak area.

10. Calculations

10.1 Read the weight, in µg/25 ml, corresponding to each peak area from the appropriate standard curve. No volume correction is needed, because the standard curve is based on µg/25 ml of ethylene glycol/methanol and the volume of sample injected is identical to the volume of the standards injected.

10.2 A correction for the blank must be made for each sample.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

µg sample = µg found in sample solution

µg blank = µg found in blank solution

10.3 Divide the total weight by the recovery (Section 8.5.2) to obtain the corrected µg/sample.

$$\text{Corrected } \mu g/\text{sample} = \frac{\text{Total Weight}}{\text{Recovery}}$$

10.4 For personal sampling pumps with rotameters only, the following volume correction should be made:

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = sampling flow rate

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.5 The concentration of pentachlorophenol in the air sample can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected } \mu g \text{ (Section 10.3) x 1000 (liters/cu m)}}{\text{Corr. Air Volume Sampled (liters) (Section 10.4)}}$$

11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

11.2 Backup Data Report for Pentachlorophenol, prepared under NIOSH Contract No. 210-76-0123.

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-270
DATE	May 28, 1980
SUPERSEDES	
PAGE	1 OF 13

POLYCHLORINATED BIPHENYLS (PCBs) IN AIR, GAS CHROMATOGRAPHIC METHOD

Analyte:	Polychlorinated biphenyls (PCBs)	Method No.:	IHA-270 (NIOSH 244)
Matrix:	Air	Range:	0.01 - 10 mg/m^3
Procedure:	Adsorption on Florisil; hexane desorption; gas chromatography with electron capture detection	Precision:	4.4% RSD (Analytical)
		Accuracy:	See Section 4

For this analysis, the undersigned committee has approved for inclusion in this manual an existing procedure, exactly as published. Accordingly, the following pages are taken verbatim from the NIOSH Manual of Analytical Methods, Second Edition, Vol. 1, U. S. Department of Health, Education, and Welfare, Method 244, 1977.

The following exceptions to NIOSH 244 should be understood:

A. Under Section 9. Calibration and Standards, both the Standard and the Webb-McCall Analytical Procedures may be calibrated in terms of peak heights, as well as peak areas. This is consistent with Section 10. Calculations, in which both measurements are applicable to the determination of PCB concentrations.

B. Under 6. Apparatus, the electron capture detector (Section 6.3) does not need to be the ^{63}Ni type. Any commercially available electron capture detector is suitable.

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UCN-13234
(1235 1-79)

The following procedure is a photocopied excerpt from: NIOSH Manual of Analytical Methods, Second Edition, Vol. 1, U. S. Department of Health, Education, and Welfare, 1977.

POLYCHLORINATED BIPHENYLS (PCB) IN AIR

Measurements Research Branch

Analytical Method

Analyte:	Polychlorinated biphenyls (PCB)	**Method No.:**	P&CAM 244
Matrix:	Air	**Range:**	0.01 - 10 mg/m³
Procedure:	Adsorption on Florisil®, hexane desorption, gas chromatography with electron capture detection	**Precision:**	4.4% RSD (Analytical)
Date Issued:	10/1 76	**Classification:**	E (Proposed)
Date Revised:			

1. **Principle of the Method**
   - 1.1 Sampling. A measured volume of air is drawn through a small sorbent tube containing Florisil which adsorbs the PCB present in the air sample.
   - 1.2 Standard Analytical Procedure. The collected PCB are desorbed in hexane and the resulting solutions are analyzed using gas chromatography with electron capture detection. The concentration of PCB relative to a PCB standard (Aroclor) is read from a standard curve.
   - 1.3 The Webb-McCall Analytical Procedure. If the air sample is found to differ significantly in composition from the PCB standard, the method of Webb and McCall is used (11.2 and 11.4). Using gas chromatography with electron capture detection, the concentration of PCB is determined by comparison with a standard supplied by Webb. The weight percent of each peak in this standard is known and thus the weight for each corresponding peak in the sample can be calculated, regardless of overall composition.
2. **Range and Sensitivity**
   - 2.1 Standard Analytical Procedure. The estimated useful range of this method is 0.01 to 10 mg/m³. The minimum detectable quantity of PCB (Aroclor 1016) from a standard curve was found to be 32 picograms per injection. In laboratory experiments, no breakthrough was detected after sampling 48 liters of 10 mg/m³ of Aroclor 1016 at 75% relative humidity at a sampling rate of 200 cc min through a 100-mg bed of Florisil. Field samples analyzed by this method ranged from 0.1 to 1.5 mg/m³.
   - 2.2 The Webb-McCall Analytical Procedure. This procedure has not been evaluated by NIOSH, but probably has the same detection limit and range as the standard analytical procedure.
3. **Interferences**
   - 3.1 Strict measures to avoid contamination are required when using the electron capture detector. Foremost the syringe must be thoroughly cleaned after each injection. Hexane used for desorption and back flush should be injected periodically for a purity check. It should show no peaks having retention times greater than 45 seconds, providing that not more than 5 μl have been injected.
   - 3.2 Any compound which has nearly the same retention time on the GC column as one of the PCB is an interference. This type of interference can often be overcome by changing the GC

operating conditions or by selecting another column. Retention time data on a single column, or even on a number of columns, cannot be considered as conclusive proof of chemical identity. It is important, therefore, that a sample of the bulk mixture of PCB be submitted at the same time as the sample tubes so that chemical identification of possible interferences can be made.

3.3 Chlorinated pesticides, such as DDT, DDE, etc., have been reported as interferences which arise due to coextraction with PCB during workup of environment samples such as water, tissue, soil, or biological fluids. In the case of personal air sampling in an industrial environment, these interferences would not be present unless these were being manufactured in the same area. Thus, unless these chlorinated pesticides are known to specifically be present, there need be no extra cleanup or separation step for these materials.

3.4 Sulfur-containing compounds in petroleum products have been reported as interferences (11.5).

4. **Precision and Accuracy**

4.1 The volume of air sample can be measured to within ± 1% if a pump with a calibrated volume indicator is used. Volumes calculated from initially set flow rates may be less accurate (± 5%) because of changes in flow rates during sampling.

4.2 The front section of the Florisil tube has a 100% collection efficiency for 50-l air samples at airborne concentrations up to 10 mg/m^3.

4.3 No loss of PCB was observed in sealed tubes or desorbed samples stored for two months.

4.4 The precision of the analysis is dependent upon the precision and sensitivity of the technique used to quantitate the gas chromatograph peaks of samples and standards. Known quantities of PCB which were spiked on Florisil and allowed to sit overnight were quantitatively (100%) recovered. The precision of the standard analytical procedure is indicated by a relative standard deviation of 4.4% for 27 spiked samples.

4.5 The accuracy of these procedures is not known. Accuracy depends upon the ability to separate and identify each compound in the PCB mixture and compare each with a known standard. Many of the isomers in the commercial PCB mixtures have not been separated or identified, nor are standards of these compounds available. Therefore, the task of assessing accuracy is very difficult. Despite this drawback, the Webb and McCall procedure has produced good results (11.3).

5. **Advantages and Disadvantages of the Method**

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick instrumental method.

5.2 The capacity of the solid sorbent sampling device for PCB is large and recovery from the sorbent is quantitative.

5.3 A substantial difference in air sample composition and the commercial PCB mixture being used will result in a large error when the standard analytical procedure is used, since the standardization is based on comparison with the PCB mixture being used. The Webb-McCall Analytical Procedure should provide a more accurate quantitation since standardization is based on a factor. Thus, a weight can be assigned to a percent weight/peak specific peak in the chromatogram of the sample.

6. **Apparatus**

6.1 A personal-sampling pump which operates in the range of 50-200 cc/min is used. These pumps should be calibrated with a representative sorbent tube in the sampling line. A wet or dry test meter or a glass rotameter capable of measuring a flow rate of 200 cc/min within ± 5% may be used in the calibration.

6.2 Sorbent Tubes. Each glass tube is at least 7 cm long with 4 mm inside diameter and contains two sections of 30-48 mesh deactivated Florisil. The front section is preceded by glass wool and contains 100 mg and the backup section contains 50 mg. Urethane foam is placed between the sections and after the backup section. The ends of the tube are flame sealed to prevent contamination before use.

6.3 Gas chromatograph equipped with an electron capture detector (^{63}Ni foil).

6.4 Glass column (6 ft × 4 mm I.D.) packed with 3% SE-30 or 3% OV-1 on 80/100 mesh Supelcoport or Gas Chrom Q.

6.5 Vials, 20-ml, with aluminum-lined caps.

6.6 Microliter syringe, 10-μl.

6.7 Volumetric flasks, 10-ml, with glass stoppers.

6.8 A mechanical or electronic integrator or a recorder and some method for determining peak area.

7. **Reagents**

ACS reagent grade or better.

7.1 Hexane, Pesticide Quality.

7.2 Florisil® (Registered Trademark of the Floridin Co.), 30-48 mesh chromatographic adsorbent, deactivated. Florisil 30-60 mesh is sieved to the proper mesh size. Prior to packing tubes, dry a weighed amount of Florisil at 105°C for 45 minutes. After cooling to room temperature, the Florisil is added to a round bottom flask which can be attached to a rotary evaporator. Three milliliters of water per 100 gm of Florisil (i.e., 3% w/w water) are added and the mixture is turned in the rotary evaporator for one hour or until it is free flowing.

7.3 Nitrogen, prepurified.

7.4 Standard PCB mixtures. A sample of the specific PCB mixture under study or being used in the environment which was sampled is used as the standard. Webb-McCall Aroclor PCB standards in isoctane may be obtained from Dr. Ronald G. Webb, Southeast Environmental Research Laboratory, National Environmental Research Center-Corvallis, Environmental Protection Agency, Athens, Georgia 30601.

7.5 p,p′-DDE [1,1-Dichloro-2,2-bis(p-chlorophenyl)ethene].

8. **Procedure**

8.1 **Cleaning of Equipment.** All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water, distilled water, pesticide grade acetone, and finally pesticide grade hexane and dried.

8.2 **Collection and Shipping of Samples**

8.2.1 Immediately before sampling, break each end of the sorbent tube so as to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.2.2 The smaller section of Florisil is used as a backup and is positioned nearest the sampling pump.

8.2.3 The sorbent tube is vertical during sampling.

8.2.4 Air being sampled is not passed through any hose or tubing before entering the sorbent tube.

8.2.5 The air sample is taken at a flow rate of 200 cc/min or less to attain the total sample volume required. The recommended sample volume is 50 liters.

8.2.6 The sorbent tube is capped with the supplied plastic caps immediately after sampling. Under no circumstances are rubber caps to be used.

8.2.7 One tube is handled in the same manner as the sample tubes (break, seal, and ship) except that no air is pumped through it. Label this tube as a blank.

8.2.8 The tubes are packed tightly before shipping to minimize breakage in transit. The tubes are not subjected to extremes of high temperatures or low pressure during shipment.

8.2.9 Samples of the PCB whose presence in the environment is suspected are submitted to the laboratory performing the analyses. These bulk materials are not transported in the same container as the samples or blank tubes. If possible, a bulk air sample is shipped for qualitative identification purposes.

8.3 **Analysis of Samples**

8.3.1 Preparation of Samples. Each tube is scored with a file and the glass wool and front section are placed in a clean, dry vial. The separating urethane foam plug, the back section of the sorbent, and the retaining urethane foam plug are placed in a second clean, dry vial.

8.3.2 Desorption of Samples. Prior to analysis, 5.0 ml of hexane is pipetted into each vial. Florisil particles should not be allowed to cling to the glass above the solvent. A minimum of 10 minutes desorption time is required before analysis.

8.3.3 Preliminary Analysis. An injection of 1 μl hexane backflush and 1 μl of sample is made at the conditions specified under 8.3.4. If the sample is too concentrated, further dilutions will be necessary to bring the concentration of the sample solution into the linear range of the electron capture detector. Once the concentration of the sample is appropriately adjusted, the chromatogram of this sample should be compared to that of a standard to determine if the air sample is qualitatively different in composition from the standard. If there is little difference in the two chromatograms, then proceed via the Standard Analytical Procedure (8.3.5). If there is a significant difference in the two chromatograms, the Webb and McCall Analytical Procedure is followed (8.3.6).

8.3.4 Gas Chromatographic conditions for PCB determination by the Standard Analytical Procedure are:

1. Nitrogen carrier gas flow, 90 ml/min
2. Injector temperature, 300°C
3. Interface and detector temperatures both 325°C
4. Column temperature, 200°C

8.3.5 Standard Analytical Procedure. An aliquot of the sample solution is injected under the gas-chromatographic conditions in 8.3.4. The solvent flush technique is used for injection. The volume of back flush is 1 μl and the volume of standard or sample solution is equal to 4 μl. Larger volumes may give a solvent peak which interferes with sample components. The syringe must be cleaned with hexane after each injection. The peak heights or areas of at least five prominent peaks in the sample chromatogram are selected and compared with those of the standard PCB mixture and the weight of PCB present is calculated.

8.3.6 The Webb-McCall Analytical Procedure. An aliquot of the sample solution is injected under the gas-chromatographic conditions in 8.3.4. The solvent flush technique is used for injection. The volume of backflush is 1 μl and the volume of the standard or sample solution is equal to 4 μl. Larger volumes may give a solvent peak which interferes with sample components. The syringe must be cleaned with hexane after each injection. An aliquot of p,p′-DDE (0.02 ng/μl) is also injected under the same conditions and the relative retention time (RRT) of each peak is determined using p,p′-

DDE as the reference standard equal to 100. Retention time (RT) is the distance between the first appearance of the solvent peak and the maximum of the peak of interest. Thus,

$$RRT = \frac{RT \times 100}{RT\,(DDE)}$$

where RT = retention time of peak of interest

RT (DDE) = retention time of DDE.

The area of each peak in the sample is compared with the appropriate standard curve of the peak having the same RRT and the concentration is read from the curve. If the sample contains more than one Aroclor, use Figure 1 to identify the Aroclor standard to be used.

8.4 **Determination of Desorption Efficiency.** In various experiments, 5.46 μg and 3.42 μg (3 sets) of PCB (Aroclor 1016) in hexane were spiked on 100 mg sections of Florisil and allowed to sit overnight. Desorption with 5 ml of hexane the next day gave recoveries of 95.73%, 100.78%, 98.39%, and 102.12% (overall average, 99.3%). Thus, results of sample analysis need not be corrected by desorption efficiency.

9. **Calibration and Standards**

9.1 **Standard Analytical Procedure.** The particular PCB mixture being used in the work area in which air samples were taken is used as the standard. Standards are prepared in hexane at concentrations ranging from 8 to 500 ng/ml (within the linear range of the electron capture detector — upper limit is approximately 3 ng per injection). Calibration curves should be established daily since the electron capture detector response may vary from day to day. The standard curve is plotted in terms of concentration (ng/ml) versus area. Since the injection volumes of the standard and the sample are identical, the concentration of the sample can be read directly from the standard curve.

9.2 **The Webb-McCall Analytical Procedure.** The standard Aroclor mixtures supplied by Webb (see 7.4) are prepared at concentrations ranging from 0.008 to 0.5 ng/μl. Calibration curves are established daily since the electron capture detector responses may vary from day to day. Standard curves for each peak to be used in the determination are constructed in terms of concentration (ng/ml) versus area. The concentration of each peak may be determined with the use of Tables 1-6 (taken from Ref. 11.2) by multiplying the total concentration of the Aroclor standard by the appropriate mean-weight percent factor and dividing by 100.

10. **Calculations**

10.1 **Standard Analytical Procedure.** The following are the steps in the calculation of air concentrations of PCB determined with PCB mixture as the standard.

10.1.1 The height or area of several selected prominent peaks (at least 5) in the chromatogram are added, compared to the total height or area of those same peaks in the standard, and the concentration of the sample solution is read from the standard curve.

10.1.2 The concentration, in ng/ml, of the sample solution is multiplied by the total volume, in ml, of the sample solution and the weight of the PCB in the sample is calculated. Corrections for the blanks are made if necessary.

10.1.3 The weights found on the front and the back sections of the tube are summed to find the total weight of the PCB in the air sample.

10.1.4 The total weight of the PCB in the air sample is divided by the volume, in liters, of air sampled and the air concentration is reported in ng/l or the equivalent units, $\mu g/m^3$.

10.2 **The Webb-McCall Analytical Procedure.** The following are the steps in the calculation of air concentration of PCB determined using the method of Webb and McCall.

10.2.1 The height or area of each peak in the chromatogram is compared to the corresponding standard curve for that peak from the Webb-McCall standard and the concentration of that particular PCB (represented by that peak) is read from the standard curve.

10.2.2 The concentrations of each PCB are summed. This total concentration of the PCB is then multiplied by the total volume, in ml, of the sample solution and the weight of the PCB in the sample is calculated. Corrections for blanks should be made if necessary.

10.2.3 The weights found on the front and the back section of tube are summed to find the total weight of the PCB in the air sample.

10.2.4 The total weight of the PCB in the air sample is divided by the volume, in liters, of air sampled and the air concentration is reported in ng/l or the equivalent units, $\mu g/m^3$.

11. References

11.1 Gian, C. S., H. S. Chan, and C. S. Neff, Anal Chem 47:2319, 1975.

11.2 Webb, R. G. and A. C. McCall, J Chromatogr Sci 11:366, 1973.

11.3 Chau, A. S. Y. and R. C. J. Sampson, Environ Lett 8:89, 1975.

11.4 U. S. Environmental Protection Agency: Method for Polychlorinated Biphenyls [PCB's] in Industrial Effluents. Environment Monitoring Support Laboratory, EPA, Cincinnati, Ohio, 1973.

11.5 Hofstader, R. A., C. A. Bache, and D. J. Lisk, Bull Environ Contam Toxicol 11:136, 1974.

TABLE 1

Composition of Aroclor 1221*

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	Number of Chlorines[c]	
11	31.8	15.8	1	
14	19.3	9.1	1	
16	10.1	9.7	2	
19	2.8	9.7	2	
21	20.8	9.3	2	
28	5.4	13.9	2 3	85% 15%
32	1.4	30.1	2 3	10% 90%
37 40	1.7	48.8	3 3	
Total	93.3			

[a]Retention time relative to p,p'-DDE = 100. Measured from first appearance of solvent. Overlapping peaks that are quantitated as one peak are bracketed.

[b]Standard deviation of 17 results as a percentage of the mean of the results.

[c]From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

*Taken from Reference 11.2

TABLE 2
Composition of Aroclor 1232*

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	Number of Chlorines[c]	
11	16.2	3.4	1	
14	9.9	2.5	1	
16	7.1	6.8	2	
20	17.8	2.4	2	
21			2	
28	9.6	3.4	2	40%
			3	60%
32	3.9	4.7	3	
37	6.8	2.5	3	
40	6.4	2.7	3	
47	4.2	4.1	4	
54	3.4	3.4	3	33%
			4	67%
58	2.6	3.7	4	
70	4.6	3.1	4	90%
			5	10%
78	1.7	7.5	4	
Total	94.2			

[a]Retention time relative to p,p'-DDE = 100. Measured from first appearance of solvent. Overlapping peaks that are quantitated as one peak are bracketed.

[b]Standard deviation of four results as a mean of the results.

[c]From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

*Taken from Reference 11.2

TABLE 3
Composition of Aroclor 1242*

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	Number of Chlorines[c]
11	1.1	35.7	1
16	2.9	4.2	2
21	11.3	3.0	2
28	11.0	5.0	2 } 25% 3 } 75%
32	6.1	4.7	3
37	11.5	5.7	3
40	11.1	6.2	3
47	8.8	4.3	4
54	6.8	2.9	3 } 33% 4 } 67%
58	5.6	3.3	4
70	10.3	2.8	4 } 90% 5 } 10%
78	3.6	4.2	4
84	2.7	9.7	5
98	1.5	9.4	5
104	2.3	16.4	5
125	1.6	20.4	5 } 85% 6 } 15%
146	1.0	19.9	5 } 75% 6 } 25%
Total	98.5		

[a]Retention time relative to p,p'-DDE = 100. Measured from first appearance of solvent.
[b]Standard deviation of six results as a percentage of the mean of the results.
[c]From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.
*Taken from Reference 11.2

TABLE 4
Composition of Aroclor 1248*

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	Number of Chlorines[c]
21	1.2	23.9	2
28	5.2	3.3	3
32	3.2	3.8	3
47	8.3	3.6	3
40	8.3	3.9	3 } 85% 4 } 15%
47	15.6	1.1	4
54	9.7	6.0	3 } 10% 4 } 90%
58	9.3	5.8	4
70	19.0	1.4	4 } 80% 5 } 20%
78	6.6	2.7	4
84	4.9	2.6	5
98	3.2	3.2	5
104	3.3	3.6	4 } 10% 5 } 90%
112	1.2	6.6	5
125	2.6	5.9	5 } 90% 6 } 10%
146	1.5	10.0	5 } 85% 6 } 15%
Total	103.1		

[a]Retention time relative to p,p'-DDE = 100. Measured from first appearance of solvent.
[b]Standard deviation of six results as a percentage of the mean of the results.
[c]From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.
*Taken from Reference 11.2

TABLE 5
Composition of Aroclor 1254*

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	Number of Chlorines[c]
47	6.2	3.7	4
54	2.9	2.6	4
58	1.4	2.8	4
70	13.2	2.7	4 } 25% 5 } 75%
84	17.3	1.9	5
98	7.5	5.3	5
104	13.6	3.8	5
125	15.0	2.4	5 } 70% 6 } 30%
146	10.4	2.7	5 } 30% 6 } 70%
160	1.3	8.4	6
174	8.4	5.5	6
203	1.8	18.6	6
232	1.0	26.1	7
Total	100.0		

[a]Retention time relative to p,p'-DDE = 100. Measured from first appearance of solvent.
[b]Standard deviation of six results as a percentage of the mean of the results.
[c]From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.
*Taken from Reference 11.2

TABLE 6
Composition of Aroclor 1260*

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	Number of Chlorines[c]
70	2.7	6.3	5
84	4.7	1.6	5
98	3.8	3.5	} d
104			5 } 60% 6 } 40%
117	3.3	6.7	6
125	12.3	3.3	5 } 15% 6 } 85%
146	14.1	3.6	6
160	4.9	2.2	6 } 50% 7 } 50%
174	12.4	2.7	6
203	9.3	4.0	6 } 10% 7 } 90%
232			} e
244	9.8	3.4	6 } 10% 7 } 90%
280	11.0	2.4	7
332	4.2	5.0	7
372	4.0	8.6	8
448	0.6	25.3	8
528	1.5	10.2	8
Total	98.6		

[a]Retention time relative to p,p'-DDE = 100. Measured from first appearance of solvent. Overlapping peaks that are quantitated as one peak are bracketed.

[b]Standard deviation of six results as a percentage of the mean of the results.

[c]From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

[d]Composition determined at the center of peak 104.

[e]Composition determined at the center of peak 232.

*Taken from Reference 11.2

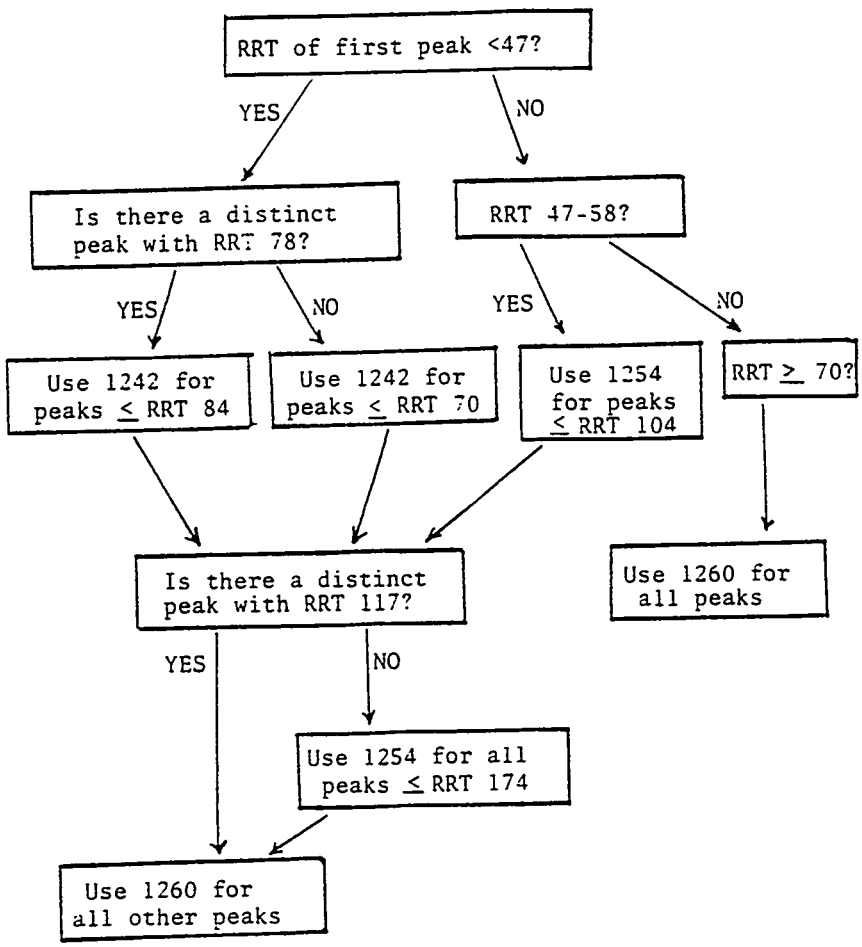

FIGURE 1. Chromatogram Division Flowchart (from Reference 11.2)

UCN-10766E (12 8-78)

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-285
DATE	August 27, 1980
SUPERSEDES	
PAGE	1 OF 9

TRIBUTYL PHOSPHATE (TBP) IN AIR, GAS CHROMATOGRAPHIC METHOD

Analyte:	Tributyl phosphate (TBP)	Method No.:	IHA-285 (NIOSH S208)
Matrix:	Air	Range:	2.7 - 12.6 mg/m^3
Procedure:	Membrane filter collection, extraction with ether, gas chromatography with flame photometric detection	Precision:	0.076 (CV_T) 7.6% (RSD)
		Bias:	None recognized

For this analysis, the undersigned committee has approved for inclusion in this manual an existing procedure, exactly as published. Accordingly, the following pages are taken verbatim from the NIOSH Manual of Analytical Methods, Second Edition, Vol. 3, U. S. Department of Health, Education, and Welfare, Method S208, 1977.

The following exceptions to NIOSH S208 should be understood:

A. Either peak heights or peak areas may be used for calibration and analysis.

B. Under 7. Reagents, the term "ether" is intended to mean "diethyl ether."

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APPROVED BY PGDP	LAB R.E. Simpson	APPROVED BY ORNL	LAB W.R. Laing	NUMBER IHA-285
	IH C.W. Gurak		IH James A. Fahy	

The following procedure is a photocopied excerpt from: NIOSH Manual of Analytical Methods, Second Edition, Vol. 3, U. S. Department of Health, Education, and Welfare, 1977.

Tributyl Phosphate

Analyte:	Tributyl Phosphate	Method No.:	S208
Matrix:	Air	Range:	2.7-12.6 mg/cu m
OSHA Standard:	5.0 mg/cu m	Precision ($\overline{CV}_T$):	0.076
Procedure:	Filter collection, extraction with ether, GC/FPD	Validation Date:	11/21/75

1. Principle of the Method

1.1 A known volume of air is drawn through a cellulose ester membrane filter to trap the organic aerosol present.

1.2 The filter in the cassette is transferred into a jar and extracted with ether.

1.3 An aliquot of the eluted sample is injected into a gas chromatograph with a flame photometric detector (FPD).

1.4 The area of the resulting sample peak is determined and compared with corresponding areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 2.7-12.6 mg/cu m at an atmospheric temperature and pressure of 19°C and 761 mm Hg, using a 100-liter sample. Under the conditions of sample size (100 liters), the probable useful range of this method is 0.5-15 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for the 1.5-mg sample.

2.2 The upper limit of the range of the method is dependent on the filtration capacity of the cellulose membrane filter. If higher concentrations than those tested are to be sampled, smaller sample volumes should be used. The collection efficiency for tributyl phosphate aerosol was found to be 100% when sampled for 66 minutes at 1.5 liters per minute from a test atmosphere containing 12.6 mg/cu m and at an atmospheric temperature and pressure of 19°C and 761 mm Hg.

3. Interferences

3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 Dibutyl phosphate frequently coexists with tributyl phosphate. However dibutyl phosphate is non-volatile and does not interfere with the gas chromatographic analysis of tributyl phosphate.

3.3 It must be emphasized that any phosphorus-containing compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical indentity.

3.4 At higher atmospheric temperatures some distribution between tributyl phosphate particulate and vapor may occur which can yield erroneous values if only the front filter is analyzed. The vapor is absorbed to a limited extent by the cellulose back-up pad. Refer to Section 8 for Sample Collection and Analysis.

Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 2.7-12.6 mg/cu m was 0.076. This value corresponds to a standard deviation of 0.38 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference. 11.1.

4.2 A collection efficiency of 100% was determined for the collecting medium under special consideration of atmospheric temperature and pressure noted. Thus, no bias was introduced in the sample collection step. Likewise, there was no bias in the analytical method - the average recovery from the filters was 100.4%. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

The sampling device is small, portable and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The filters are analyzed by means of a quick, instrumental method.

6. Apparatus

6.1 Sampling equipment - The sampling unit for the collection of personal air samples for the determination of organic aerosol has the following components:

6.1.1 The filter unit consisting of the filter media (Section 6.2) and appropriate 37-mm, 3-piece cassette filter holder. Front and backup filter units are needed when sampling atmospheres at temperatures above 23°C.

6.1.2 Personal Sampling Pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at the recommended flow rate. The pump must be calibrated with the representative filter holders and filters in the line.

6.2 Mixed cellulose ester membrane filter, 0.8 micrometer pore size and 37-mm diameter. The filter is held in the three-piece cassette supported by a cellulose backup pad.

6.3 Gas chromatograph equipped with a flame photometric detector and phosphorus-filter.

6.4 Column (6-ft x 1/8-in stainless steel) packed with 3% OV-101 on 100/120 mesh Supelcoport, or equivalent column capable of achieving the desired resolution.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Jars for sample extraction: 2 oz. ointment jars, squat form with aluminum-lined screw caps.

6.7 Microliter syringes: 10-microliter and other convenient sizes for making standard solutions.

6.8 Volumetric flasks: 10-milliliter and other convenient sizes for making standard solutions.

6.9 Pipets: 10-milliliter and other convenient sizes for making standard solutions.

7. Reagents

7.1 Anhydrous ether, reagent grade

7.2 Tributyl phosphate, reagent grade

7.3 Purified hydrogen

7.4 Prefiltered, compressed air

7.5 Purified nitrogen

8. Procedure

8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent-washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of personal pumps. Each personal pump must be calibrated with the representative filter cassettes in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

8.3.2 Remove the cassette plugs and connect the cassette filter to the personal sampling pump tubing. Clip the cassette to the worker's lapel.

Note: If the ambient temperature to be sampled is above 23°C, use two filter cassettes connected in series with a short piece of flexible tubing for sample collection. This arrangement is necessary because some tributyl phosphate vapor may exist at temperatures above 23°C.

8.3.3 Air being sampled should not be passed through any hose or tubing before entering the filter cassettes.

8.3.4 A sample size of 100 liters is recommended, but a larger sample size can be collected if desired. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of at least ±5%.

8.3.5 Turn the pump on and begin sample collection. Since it is possible for filters to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.3.6 Terminate sampling after the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.3.7 Separate the front and backup filter cassettes (if two cassettes were used) and seal. Collected sample cassettes should be firmly sealed with the plugs in both the inlet and outlet.

8.3.8 Carefully record sample identity including front and backup filter designation, if any, and all relevant sample data.

8.3.9 Blank: With each batch of 10 samples submit one filter which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as a blank.

8.3.10 The cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Preparation and Extraction of Samples

1. Open the cassette filter holder and carefully transfer the cellulose membrane filter and cellulose backup pad with the aid of Millipore filter tweezers to the jar. (Both filter and pad are analyzed.)

2. Pipet into the jar 10.0 ml of ether. Seal the jar immediately to minimize evaporation.

3. Allow the samples to stand for at least 30 minutes with occasional agitation. Tests indicate that this period is adequate for complete extraction.

4. The front filter/pad and backup filter/pad should be analyzed. This applies to sampling at temperatures above 23°C.

8.4.2 GC Conditions. The typical operating condtions for the gas chromatograph are:

1. 50 ml/min (50 psig) Nitrogen carrier gas flow
2. 70 ml/min Hydrogen gas flow to detector
3. 150 ml/min air flow to detector
4. 240°C injector temperature
5. 240°C detector temperature
6. 150°C column temperature

8.4.3 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed

from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

8.4.4 Measurement of area. The total area of the sample peaks is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed in Section 9.

8.5 Determination of Sample Recovery

8.5.1 Need for determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the compound. The sample recovery should be determined in duplicate and should cover the concentration range of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the "true" value.

8.5.2 Procedure for determining recovery. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to to a representative cellulose membrane filter and air-dried. The analyte is then extracted from the filter and analyzed as described in Section 8.4. Duplicate determinations should agree within $\pm 5\%$.

For the validation study conducted to determine the precision and accuracy of this method, an amount of the analyte equivalent to that present in a 100-liter sample at the selected level has been used for the extraction studies. Six filters at each of the three levels (0.5X, 1X and 2X the OSHA standard) have been dosed accordingly using a solution of tributyl phosphate in ether. A parallel blank filter was also treated in the same manner except that no sample was added to it. All filters were then extracted and analyzed as described in Section 8.4.

The average recovery value obtained was 100% and as such no correction factor has been used in the determination of the "true" values.

The sample recovery equals the average weight in µg recovered from the filter divided by the weight in µg added to the filter, or

$$\text{Recovery} = \frac{\text{Average Weight (µg) Recovered}}{\text{Weight (µg) Added}}$$

9. Calibration and Standards

It is convenient to express concentration of standards in terms of micrograms per 10.0 ml ether, because samples are desorbed in this amount of ether. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in micrograms per 10.0 ml versus peak area.

Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FPD response. The FPD response is very sensitive to minor variations in hydrogen flow rate and, therefore, it is recommended that calibration standards must be carefully interspersed with the samples.

10. Calculations

10.1 Read the weight, in µg, corresponding to the total peak area from the standard curve. No volume corrections are needed because the standard curve is based on µg per 10.0 ml ether, and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

µg = µg sample - µg blank

where:

µg sample = µg found in sample filter
µg blank = µg found in blank filter

10.3 Add the amount found in the front filter/pad and backup filter/pad to determine total weight in the sample. This applies to samples collected at temperatures above 23°C.

10.4 Divide the total weight by the recovery to obtain the corrected µg/sample.

$$\text{Corrected µg/sample} = \frac{\text{Total Weight}}{\text{Recovery}}$$

10.5 If air samples were taken under conditions significantly different from standard conditions of 25°C and 760 mm Hg, a volume correction for the air sampled should be made as follows:

$$V_s = V \times \frac{P}{760} \times \frac{298}{T + 273}$$

where:

V_s = volume of air in liters @ 25°C and 760 mm Hg
V = volume of air sampled
p = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

10.6 The concentration of the analyte in the air sampled can be expressed in mg per cu m (µg per liter = mg per cu m).

$$\text{mg/cu m} = \frac{\text{Corrected µg (Section 10.4)}}{\text{Air Volume Sampled (Liter)}}$$

11. Reference

11.1 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-294
DATE	August 26, 1981
SUPERSEDES	
PAGE	1 OF 11

VINYL CHLORIDE IN AIR, GAS CHROMATOGRAPHIC METHOD

Analyte: Vinyl chloride

Matrix: Air

Procedure: Adsorption on activated carbon; desorption with carbon disulfide; gas chromatography with flame-ionization detector

Method No.: IHA-294 (NIOSH 178)

Range: 0.008 to 5.2 mg/m in a 5-L air sample

Precision: 0.08 (CV_T)
8% (RSD)

Accuracy: Within 6% relativ

For this analysis, the undersigned committee has approved for inclusion in this manual an existing procedure, exactly as published. Accordingly, the following pages are taken verbatim from the NIOSH Manual of Analytical Methods, Second Edition, Vol. 1, U. S. Department of Health, Education, and Welfare, Method 178, 1977.

The following exception to NIOSH 178 should be understood:

A. Either peak heights or peak areas may be used for calibration and analysis; however, the precision of peak height measurement has not been evaluated.

APPROVED BY Y-12	LAB R J McElhaney IH G. L. Bean	APPROVED BY ORGDP	LAB D. H. Frazier IH David T. Dunn	APPROVED BY UCCND-COORD R C W Weber
APPROVED BY PGDP	LAB R. E. Simpson IH C. H. Turak	APPROVED BY ORNL	LAB W R Laing IH James A. Craig	NUMBER IHA-294

The following procedure is a photocopied excerpt from: NIOSH Manual of Analytical Methods, Second Edition, Vol. 1, U. S. Department of Health, Education, and Welfare, 1977.

VINYL CHLORIDE IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte: Vinyl Chloride	Method No.: P&CAM 178
Matrix: Air	Range: 0.008 to 5.2 mg/m³ in a 5 - liter air sample
Procedure: Adsorption on activated carbon, desorption with carbon disulfide, gas chromatography	Precision (CV_T): 0.08 at levels of 7 and 71 mg/m³
Date Issued: 9/3/74	Classification: B (accepted)
Date Revised: 1/29/76	

1. Principle of the Method

A known volume of air is drawn through two small sorbent tubes in series containing activated carbon (made from coconut shells), which adsorbs the vinyl chloride present in the air sample. The collected vinyl chloride is then desorbed with carbon disulfide, and the resulting solutions are analyzed by gas chromatography with a flame ionization detector. The areas under the resulting peaks are compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 The minimum detectable amount of vinyl chloride was found to be 0.2 ng per injection at a 1 x 1 attenuation on a gas chromatograph. This corresponds to an estimated concentration of 0.008 mg/m³ in a 5-liter air sample analyzed by this method. However, the desorption efficiency from activated carbon of amounts of vinyl chloride as small as 40 ng (0.008 μg/ℓ x 5 liters) has not been determined. Therefore, the detection limit of the overall method may be somewhat higher than 0.008 mg/m³.

2.2 At the recommended sampling flow rate of 50 mℓ/min, the total volume to be sampled should not exceed 5 liters. This value is based upon data which indicated that more than 10 liters of air containing 2.6 μg/ℓ (1 ppm) of vinyl chloride could be sampled on activated carbon before 5% breakthrough was observed. This indicates that 5 liters of air containing no more than 5.2 mg/m³ may be sampled without significant breakthrough. (The sorbent tube consists of two sections of activated carbon separated by a section of urethane foam. [See Section 6.2.]) If a particular atmosphere is suspected of containing a high concentration of contaminants or a high humidity is suspected, the sampling volume should be reduced by 50%. A safety factor has been included in the recommended 5-liter volume and the capacity of the first tube should be within these limits except under the most extreme conditions.

3. Interferences

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped effectively. Experiments indicate that high humidity severely decreases the capacity of activated carbon for organic vapors.

3.2 When two or more substances are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample since these compounds may interfere with the analysis for vinyl chloride.

3.3 Any compound that has the same retention time as vinyl chloride at the operating conditions described in this method is an interference. Hence, retention time data on a single column, or even on a number of columns, may not provide proof of chemical identity. Often, operating conditions can be modified to eliminate interferences. Samples should be analyzed by an independent method when overlapping gas chromatographic peaks cannot be resolved.

4. Precision and Accuracy

4.1 The coefficients of variation resulting from the analysis of two sets of sorbent tubes, one set of 27 tubes exposed to a vinyl chloride concentration of 7.2 mg/m^3 in air and another set of 29 tubes exposed to a concentration of 71.3 mg/m^3, were 0.076 and 0.075, respectively. These values reflect total sampling and analytical error as well as desorption efficiency correction errors.

4.2 Experiments were performed to obtain some indication of the accuracy, although accuracy was difficult to evaluate in the absence of a primary standard. These experiments generally involved six sorbent tube samples exposed to a synthetic atmosphere. The calculated value was the concentration expected based on the measured amounts of vinyl chloride and air mixed to prepare the synthetic atmosphere. Therefore the calculated value was not the "true" value, since it was subject to experimental error. The value found from analysis of each sorbent tube, after correction for desorption efficiency, was also compared to that found by the direct injection of gas samples from the same synthetic atmosphere used in loading the tubes. The results of these experiments are shown in the table below. It should be noted that average concentrations determined by analysis of sorbent tubes were within 6% of the average concentrations determined by analysis of gas samples.

Experiment No.		Concentration, calculated, mg/m³	Concentration, experimental, mg/m³	Estimated error, %[a]
I	Gas samples	64	71.2 ± 0.7[b]	
	Sorbent tubes	64	69.8 ± 1.5	-2
II	Gas samples	13	14.5 ± 0.5	
	Sorbent tubes	13	13.6 ± 0.4	-6
III	Gas samples	2.6	2.88 ± 0.07	
	Sorbent tubes	2.6	2.91 ± 0.13	+1
IV	Gas samples	1.3	-	
	Sorbent tubes	1.3	1.27 ± 0.09	–

a. The estimated error is the average of concentrations determined from sorbent tubes minus the average of concentrations determined from gas samples, divided by the average of concentrations determined from gas samples, multiplied by 100.

b. The number given is the mean value plus or minus the 95% confidence level. The 95% confidence level is defined as the standard deviation multiplied by Student's t at the 0.05 significance level, divided by the square root of the number of samples.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those that do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a rapid instrumental method. The method can also be used for the simultaneous determination of two or more components suspected to be present in the same sample by changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample that can be taken is limited by the amount of vinyl chloride that the tube will hold before it becomes overloaded. When the sample value obtained for the backup section of the sorbent tube exceeds 20% of that found on the front section, the possibility of sample loss exists. During storage, volatile compounds such as vinyl chloride will migrate throughout the tube until equilibrium is reached. At this time, 33% of these compounds will be found in the backup section. This may lead to some confusion as to whether sample loss has occurred. This migration effect can be considerably decreased by shipping and storing the tubes at -20°C. (See Section 8.2.10.)

5.3 The precision of the method is limited by the reproducibility of the pressure drop and, therefore, the flow rates across the tubes. Because the pump is usually calibrated for one particular tube, differences in flow rates can occur when sampling through other tubes and can cause sample volumes to vary.

6. Apparatus

6.1 Personal Sampling Pump. The pump should be a properly calibrated personal sampling pump for personal and area samples. It should be calibrated with a representative sorbent tube in the sampling line. A dry or wet test meter or a glass rotameter that will determine the flow rate (50 mℓ/min) to within ±5% may be used for the calibration.

6.2 Sorbent Tubes. The glass tubes have both ends flame sealed. Each is 7 cm long, 6-mm o.d., 4-mm i.d., and contains two sections of 20/40-mesh activated carbon separated by a 2-mm portion of urethane foam. The activated carbon is prepared from coconut shells and is fired at 600°C prior to packing to remove adsorbed materials. The primary adsorbing section contains 100 mg of sorbent, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silanized glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than 2 in. of water at a flow rate of 0.2 ℓ/min.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Stainless steel column (20 ft x 0.125 in.) packed with 10% SE-30 on 80/100-mesh Chromosorb W (acid washed, silanized with dimethyldichlorosilane). Other columns capable of performing the required separations may be used.

6.5 A mechanical or electronic integrator or a recorder and some method for determining peak area.

6.6 Vials (2-mℓ) that can be sealed with caps containing Teflon-lined silicone rubber septa.

6.7 Microliter syringes (10-μℓ, and convenient sizes for making standards).

6.8 Gas-tight syringe (1-mℓ, with a gas-tight valve).

6.9 Pipettes (0.5-mℓ delivery pipettes or 1.0-mℓ type graduated in 0.1-mℓ increments).

6.10 Volumetric Flasks (10-mℓ, or convenient sizes for making solutions). It is preferable to have plastic stoppers for the volumetric flasks.

7. Reagents

7.1 Carbon disulfide, spectroquality or better grade.

7.2 Vinyl chloride, lecture bottle, 99.9% minimum purity.

7.3 Toluene, chromatographic quality.

7.4 Purified helium.

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be washed with detergent and thoroughly rinsed with distilled water.

8.2 Collection and Shipping of Samples

8.2.1 Immediately before sampling, the ends of two tubes are broken to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.2.2 The second sorbent tube is used as a backup and is positioned next to the sampling pump in tandem with the first tube.

8.2.3 The sorbent tubes are placed in a vertical position with the larger section of sorbent pointing up during sampling to minimize channelling of the vinyl chloride through the sorbent.

8.2.4 Air being sampled is not to be passed through any hose or tubing before entering the sorbent tubes.

8.2.5 The flow rate and time, or volume, must be measured as accurately as possible. The sample is taken at a flow rate of 50 mℓ/min. The maximum volume to be sampled should not exceed 5 liters. (See Section 2.2.)

8.2.6 Relatively large volumes (10 to 20 liters) of air also should be sampled through other sorbent tubes at the same time personal samples are taken. These bulk air samples will be used by the analyst to identify possible interferences before the personal samples are analyzed.

8.2.7 If the temperature and pressure of the atmosphere being sampled are significantly different from 25°C or 760 mmHg, they should be measured and recorded.

8.2.8 The sorbent tubes are capped with the supplied plastic caps immediately after sampling. Under no circumstances are rubber caps to be used.

8.2.9 One tube is handled in the same manner as a sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube is labeled as a blank.

8.2.10 Capped tubes are packed tightly before they are shipped to minimize tube breakage during transport to the laboratory. The use of two tubes in series has eliminated the need for cooling during shipping. However, if *two* tubes are *not* used, *i.e.*, only one tube is used, and if the samples will spend a day or more in transit, then cooling (*e.g.*, with Dry Ice) is necessary to minimize migration of vinyl chloride to the backup section.

8.2.11 Samples received at the laboratory are logged in and immediately stored in a freezer (around - 20°C) until time for analysis. Samples may be stored in this manner for long periods of time with no appreciable loss of vinyl chloride (2 months). Even around -20°C, vinyl chloride will equilibrate between the two sections of activated carbon, *i.e.*, it will migrate to the backup section. This phenomenon is observable after 2 weeks and may be confused with sample loss after 1 to 2 months.

8.3 Analysis of Samples

8.3.1 **Preparation and Desorption of Samples.** The two tubes used in the collection of a single sample are analyzed separately. Each tube is scored with a file and broken open at each end. The glass wool is discarded. Both sections of each tube are transferred to a small vial containing 1 mℓ of carbon disulfide. It is important to add the sorbent to the carbon disulfide and not the carbon disulfide to the sorbent. The vial is topped with a septum cap. The separating section in each tube is discarded. Tests indicate that desorption is complete in 30 min if the sample is agitated occasionally during this period. The samples should be analyzed within 60 min after addition to carbon disulfide. If only one tube is used for sampling, then each section of activated carbon should be analyzed separately.

8.3.2 **Gas Chromatographic Conditions.** The typical operating conditions for the gas chromatograph are:

1. Helium carrier gas flow, 40 mℓ/min (80 psig).

2. Hydrogen gas flow to detector, 65 mℓ/min (20 psig).

3. Air flow to detector, 500 mℓ/min (50 psig).

4. Injector temperature, 230°C.

5. Detector temperature, 230°C.

6. Column temperature, 60°C.

8.3.3 **Injection.** The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blowback or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-μℓ syringe is first flushed with solvent several times to wet the barrel and plunger. Two microliters of solvent is drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent and the plunger is pulled back about 0.4 μℓ to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-μℓ aliquot is withdrawn to the 7.4 μℓ mark (2 μℓ solvent + 0.4 μℓ air + 5 μℓ sample = 7.4 μℓ). After the needle is removed from the sample and prior to injection the plunger is pulled back a short distance to minimize evaporation of the sample from the tip of the needle. Duplicate injections of each sample and standard are made. No more than a 3% difference in area is to be expected. Automatic sampling devices may also be used.

8.3.4 **Measurement of Area.** The area under the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.4 **Determination of Desorption Efficiency**

8.4.1 **Importance of Determination.** The efficiency of desorption of a particular compound can vary from one laboratory to another and also from one batch of sorbent to another. Thus, it is necessary to determine at least once the percentage of vinyl chloride that is removed in the desorption process. Desorption efficiency should be determined on the same batch of sorbent tubes used in sampling. Results indicate that desorption efficiency varies with loading (total vinyl chloride on the tube), particularly at lower values, *e.g.*, 2.5 μg.

8.4.2 **Procedure for Determining Desorption Efficiency.** Sorbent tubes from the same batch as that used in obtaining samples are used in this determination. A measured volume of vinyl chloride gas is injected into a bag containing a measured volume of air. The bag is made of Tedlar (or a material that will retain the vinyl chloride and not absorb it) and should have a gas sampling valve and a septum injection port. The concentration in the bag may be calculated if room temperature and pressure are known. A measured volume is then sampled through a sorbent tube with a calibrated sampling pump. At least five tubes are prepared in this manner. These tubes are desorbed and analyzed in the same manner as the samples. (See Section 8.3.) Samples taken with a gas-tight syringe from the bag are also injected into the gas chromatograph. The concentration in the bag is compared to the concentration obtained from the tubes.

The desorption efficiency equals the amount of vinyl chloride desorbed from the sorbent divided by the quantity of vinyl chloride contained in the volume of synthetic atmosphere sampled, or

$$\frac{\text{(amount of vinyl chloride from sorbent)}}{\left(\begin{matrix}\text{concn of vinyl chloride}\\ \text{in bag}\end{matrix}\right) \times \left(\begin{matrix}\text{vol of atmosphere}\\ \text{sampled}\end{matrix}\right)}$$

9. Calibration and Standards

CAUTION: Laboratory Operations Involving Carcinogens

Vinyl chloride has been identified as a human carcinogen and appropriate precautions must be taken in handling this gas. The Occupational Safety and Health Administration has promulgated regulations for the use and handling of vinyl chloride. They may be found in 29 CFR 1910.93q (Section 1910.93q in Title 29 of the Code of Federal Regulations available in the Federal Register, Vol. 39, No. 194, Friday, October 4, 1974, pp. 35890-35898).

A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same gas chromatographic conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in μg/mℓ *versus* peak area. There are two methods of preparing standards and, as long as highly purified vinyl chloride is used, both are comparable.

If no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of day-to-day variations of the flame ionization response.

9.1 Standard Preparation

9.1.1 **Gravimetric Method.** Vinyl chloride is slowly bubbled into a weighed 10-mℓ volumetric flask containing approximately 5 mℓ of toluene. After 3 min, the flask is again weighed. A weight change of 100 to 300 mg is usually observed. The solution is diluted to exactly 10 mℓ with carbon disulfide and is used to prepare other standards by removal of aliquots with different sized syringes. Subsequent dilution of these aliquots with carbon disulfide results in a series of values that are linear from the range of 0.2 ng per injection, the minimum detectable amount of vinyl chloride, to 1.5 μg per injection.

9.1.2 Volumetric Method. A 1-mℓ gas sample of pure vinyl chloride is drawn into a gas-tight syringe and the valve is closed. The tip of the needle is inserted into a 10-mℓ volumetric flask containing approximately 5 mℓ of CS_2. The valve is opened and the plunger is withdrawn slightly to allow the CS_2 to enter the syringe. The action of the vinyl chloride dissolving in the CS_2 creates a vacuum and the syringe becomes filled with the solvent. An air bubble (2%) is present and has been found to be due to the void volume in the needle of the syringe. The solution is returned to the flask and the syringe is rinsed with clean CS_2 and the washings added to the volumetric flask. The volumetric flask is then filled to the mark with CS_2. Other standards are then prepared from this stock solution.

Standards are stored in a freezer at -20°C and have been found to be stable at this temperature for 3 days. Tight-fitting plastic tops on the volumetric flasks seem to retain the vinyl chloride better than ground-glass stoppers.

10. Calculations

10.1 The weight, in μg, corresponding to the area under each peak is read from the standard curve for vinyl chloride. No liquid volume corrections are needed because the standard curve is based on the number of micrograms in 1.0 mℓ of CS_2 and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank are made for each sample.

$$\mu g = \mu g_s - \mu g_b$$

where: μg_s = μg found on sample tube.

μg_b = μg found on blank tube.

A similar procedure is followed for the backup sections.

10.3 The amounts present in the front and backup sections of the same sample tube are added to determine the total amount of vinyl chloride in the sample.

10.4 The total amount is corrected for the desorption efficiency at the level of vinyl chloride measured.

$$\text{Corrected amount (in } \mu g) = \frac{\text{amount (in } \mu g)}{\text{desorption efficiency}}$$

10.5 The concentration of vinyl chloride in air may be expressed in mg/m^3 :

$$mg/m^3 = \frac{\text{corrected weight (in } \mu g)}{\text{volume of air sampled (in } \ell)}$$

10.6 The concentration may also be expressed in terms of parts per million (ppm) by volume:

$$ppm = mg/m^3 \times \frac{24.45}{M.W.} \times \frac{760}{P} \times \frac{T+273}{298}$$

where: 24.45 = molar volume (ℓ/mole) at 25°C and 760 mmHg.

M.W. = molecular weight.

P = pressure (mmHg) of air sampled.

T = temperature (°C) of air sampled.

11. References

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INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-310
DATE	August 27, 1980
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ALPHA AND BETA (GROSS ACTIVITIES) IN AIR, RADIOCHEMICAL METHOD

Analyte: Alpha and beta, gross activities

Matrix: Air

Procedure: Particulate collection on air filter; gross activities counted with alpha and beta sensitive detectors

Method No.: IHA-310

Range: See Section 2.0

Precision: See Section 4.0

Accuracy: See Section 4.0

1.0 Principle of the Method

1.1 Air particulates collected on a filter paper possessing a high surface retention are counted with alpha and beta sensitive detectors, to establish the gross concentrations of alpha and beta emitters present in the sampled ambient air.

1.2 Since a given alpha or beta emitter cannot be present at a concentration greater than the gross alpha or beta concentration of a mixture of unidentified radionuclides, a gross analysis (assuming insignificant self-absorption) may eliminate the need for a more time-consuming and expensive analysis for specific radionuclides.

2.0 Range and Sensitivity

2.1 The method is suitable over the entire range of concentrations of airborne alpha and beta emitters expected to be encountered in the environment.

2.2 A sample of 100 m^3 of air with an alpha particulate concentration of 0.005 pCi/m^3 will contain 1.11 dpm, sufficient to produce acceptable precision with a counting time of less than 1 hour in most alpha counters.

2.3 A sample of 100 m^3 of air with a beta particulate concentration of 0.025 pCi/m^3 will contain 5.55 dpm, sufficient to produce acceptable precision with a counting time of 1 hour in most beta counters.

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3.0 Interferences

3.1 The principal interference is from the progeny of naturally occurring radon and thoron usually present in the atmosphere. Since the effective radioactive half-lives of the progeny of these naturally occurring radionuclides are controlled by relatively short half-life radionuclides, namely, 26.8-min ^{214}Pb and 19.7-min ^{214}Bi for radon, and 10.6-hr ^{212}Pb for thoron, their interferences may be nullified by waiting until these daughter activities are negligible before counting. This would require about 3 days for the long-lived thoron progeny. Less accurate, but more rapid, evaluations of long-lived gross alpha and beta concentrations can be made using a dual-counting procedure.

3.2 Inert dust loadings may cause serious interference, particularly for measurement of alpha and low energy beta emitters. Reasonably accurate self-absorption corrections may be made, provided these loadings do not exceed a few mg/cm^2 of filter area. Correction factors are determined by measurements of a series of standards of constant specific activity, but varying thickness. A graph of apparent activity versus thickness yields a range of correction factors, which are applied by the analyst.

4.0 Precision and Accuracy

4.1 A sample of 100 m^3 of air with an alpha particulate concentration of 0.005 pCi/m^3 contains 1.1 dpm. This sample, when counted for 1 hour with 50% counting efficiency in a counter with a background of 0.20 cpm, will measure 1.10 ± 0.48 dpm (at the 95% confidence level), which approximates 22% relative standard deviation (RSD).

4.2 A sample of 100 m^3 of air with a beta particulate concentration of 0.025 pCi/m^3 contains 5.5 dpm. This sample, when counted for 1 hour at 30% counting efficiency in a counter with a background of 1.0 cpm, will measure 5.5 ± 1.6 dpm (at the 95% confidence level), which approximates 15% RSD.

4.3 The above evaluations involved no errors in sample volume measurements and no significant self-absorption. When necessary, self-absorption corrections can be applied empirically; this practice depends upon the condition of the sample and the judgment of the analyst. Thorough discussions of the derivation and use of these factors may be found in References 11.3 and 11.4.

5.0 Advantages and Disadvantages of the Method

5.1 The method is simple, rapid, and inexpensive.

5.2 The method does not yield specific information on the radionuclide composition of a filtered particulate sample.

6.0 Apparatus

6.1 The basic requirements for gross alpha and beta analysis are an air mover, a calibrated and properly situated device for measuring a flow rate or sample volume, a particulate filter, an alpha and a beta detector, and counters designed to accommodate the filter samples.

6.2 A windowless or very-thin-window alpha-sensitive detector should be used to count the sample. Solid-state detectors are attractive because of their stability and low background.

6.3 A beta-sensitive detector such as an end-window Geiger-Muller tube, thin window proportional flow counter, plastic scintillator, or solid-state detector can be used.

7.0 Reagents

7.1 None.

8.0 Procedure

8.1 Operate the sampler in a location representative of the atmosphere for which the gross alpha and beta concentration is to be determined, for a period long enough to collect measurable alpha and beta activity, considering the minimum quantities needed.

8.2 Remove the filter from its holder carefully, and place it in a protective cover or container to minimize the possibility of dislodging the collected particulates.

8.3 Place the filter sample in a planchet or holder for reproducible positioning under the detector.

8.4 Count the sample for an interval (or total count) sufficient for a statistically significant result.

9.0 Calibration and Standards

9.1 The efficiency of an alpha or beta counter should be determined with an alpha or beta standard resembling the sample in size and matrix. If the matrix is unknown, an alpha standard may be prepared from a uranium solution and a beta standard may be prepared from a ^{137}Cs solution.

9.2 Determine the background of the counter over an interval similar to or longer than the sample counting time. Most alpha and beta counters are relatively stable, and it is sufficient to make one daily determination of background to ascertain that major shifts due to malfunction, drift, or contamination have not occurred.

10.0 Calculations

10.1 Calculate the counter efficiency, E:

$$E = \frac{A}{B} ,$$

where:

A = net counting rate of standard, cpm, and

B = disintegration rate of standard, dpm.

10.2 Calculate the net sample (alpha or beta) disintegration rate, C:

$$C, \text{ dpm} = \frac{D-F}{E} ,$$

where:

D = gross sample counts, cpm, and

F = background counts, cpm.

10.3 Calculate the gross activity (alpha or beta) in air:

$$\text{Activity, pCi/m}^3 = \frac{C}{V \cdot G} ,$$

where:

V = air sample volume, m^3, and

G = conversion factor: 2.22 dpm/pCi.

10.4 The standard deviation (σ) of the count is calculated as follows:

$$\sigma, \text{ cpm} = \pm\sqrt{\frac{D}{H} + \frac{F}{I}} ,$$

$$\sigma, \text{dpm} = \pm \frac{\sigma, \text{cpm}}{E} ,$$

where:

D, E, and F are as defined above,

H = sample count time, min, and

I = background count time, min.

10.5 The statistical significance of the count may be expressed as the uncertainty of the count at a specified confidence level, such as 95% (1.96 σ).

11.0 References

11.1 Katz, M., Editor; *Methods of Air Sampling and Analysis*, 2nd Edition; Amer. Public Health Assoc., Methods 601 and 602, pp. 630 and 632 (1977).

11.2 Setter, L. R. and Coats, G. I.; *The Determination of Airborne Radioactivity*; AIHA J, Vol. 22, p. 64 (1961).

11.3 Schulte, H. F.; Chapter on *Monitoring Airborne Radioactivity*; Air Pollution, 2nd Edition, Vol. 11; Academic Press, New York (1968).

11.4 Wang, C. H., Willis, D. L., and Loveland, W. D.; Chapter on *Correction Factors in Radiotracer Assay*; Radiotracer Methodology in the Biological, Environmental, and Physical Sciences; Prentice-Hall, New Jersey (1975).

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-360
DATE	Nov. 27, 1979
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TECHNETIUM-99 IN AIR FILTER SAMPLES AND WIPE SAMPLES, RADIOCHEMICAL METHOD*

Analyte:	Technetium-99	Method No.:	IHA-360
Matrix:	Filters and Wipes	Range:	180 pCi - 1,000 pCi
Procedure:	Leaching, followed by precipitation. Beta counting of supernate.	Precision:	RSD 6% (estimated) at the 500 pCi level.

1.0 Principle of the Method

1.1 Total sample is leached in nitric acid to solubilize Tc.

1.2 Uranium and its daughters are separated by coprecipitation with $Fe(OH)_3$.

1.3 Beta activity of the supernate is determined by comparison to a standard ^{99}Tc solution.

2.0 Range and Sensitivity

2.1 The lower limit of this procedure is approximately 180 pCi of ^{99}Tc per sample.

2.2 Without dilution of the leach solution, the upper limit of this procedure is approximately 1,000 pCi per sample.

3.0 Interferences

3.1 The commonly encountered beta-emitting radionuclides such as Th and Pa, descendants of uranium, are removed by precipitation. Radionuclides such as ^{137}Cs, ^{40}K, or ^{90}Sr will remain in solution and interfere.

3.2 The energy discrimination of the liquid-scintillation counter will reduce interference from higher energy beta (>0.3 MeV) emitters such as ^{137}Cs and ^{40}K.

*Because it is not specific for the analyte, this procedure is not appropriate for samples at ORNL, where many radioactive interferences might be present.

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4.0 Precision and Accuracy

4.1 The relative standard deviation is 6% (estimated) at the 500 pCi level.

4.2 There is no evidence of a bias.

5.0 Advantages and Disadvantages

5.1 The advantages of this technique are its speed and high sensitivity.

5.2 A disadvantage of this technique is the possibility of positive bias if beta emitters are present which are not coprecipitated with $Fe(OH)_3$. This is not a serious drawback for industrial hygiene purposes, however, since the possible bias is positive. If significant beta activity is detected, confirmatory tehniques can be used to positively identify the emitter.

6.0 Apparatus

6.1 Liquid-scintillation beta counter with 3 adjustable energy selection channels.

6.2 Clinical centrifuge, accessories, and 50-ml graduated centrifuge tubes.

6.3 Miscellaneous laboratory glassware.

6.4 Liquid-scintillation counting vials.

7.0 Reagents

7.1 Standard ^{99}Tc solution, 200,000 dpm/ml, prepared by appropriate dilution of standard solution available from Amersham/Searle.

7.2 Ferric nitrate solution, 10% w/v: dissolve 16.7 g of $Fe(NO_3)_3 \cdot 9H_2O$ in distilled water and dilute to 100 ml.

7.3 Nitric acid, 4 M: add 125 ml of conc HNO_3 to 300 ml of water and dilute to 500 ml.

7.4 Potassium persulfate solution, 5% w/v: dissolve 5 g $K_2S_2O_8$ in distilled water and dilute to 100 ml.

7.5 Ammonium hydroxide, conc, reagent grade.

7.6 Liquid-scintillation mix: Insta Gel, Packard Instrument Co.

8.0 Procedure

8.1 Leach the sample (filter or wipe) with 100 ml of 4 M HNO_3 for 20 minutes at 75°C in a water bath, stirring occasionally. NOTE: Do not overheat; technetium might be lost by volatilization. Filter the leach solution into a 250-ml beaker and evaporate to 30-40 ml.

8.2 Transfer the solution to a 50-ml volumetric flask and dilute to volume.

8.3 Transfer 25 ml of the solution to a graduated centrifuge tube. Add 2 ml of potassium persulfate solution, mix, and heat to 75°C for 10 minutes to oxidize Tc to the +7 valence state.

8.4 Cool the sample tube to ambient temperature and add 1 ml of ferric nitrate solution and sufficient conc ammonium hydroxide to make the solution basic. Test with pH paper.

8.5 Dilute the contents of the centrifuge tube to 40 ml with water; mix well; and centrifuge for about 3 minutes.

8.6 Pipet 2.0 ml from the centrifuge tube into a liquid-scintillation counting vial; mix thoroughly with 15 ml of liquid scintillation mix.

8.7 Count the sample for an appropriate interval (10 minutes or longer), directing the count into the channel with upper energy of 0.3 MeV.

8.8 Add a known ^{99}Tc spike and recount the mixture to establish counter efficiency. The spike should be ∿10 times measured sample activity.

8.9 Run a reagent blank for background.

9.0 Calculations

Sample activity is calculated as follows:

$$\text{Tc-99, pCi} = 40\ A/\left(\frac{C-A}{B}\right)$$

where: A = count rate of sample aliquot, corrected for background, cpm,

B = ^{99}Tc added with standard spike, pCi,

C = count rate of sample aliquot plus spike, corrected for background, cpm, and

40 = dilution factor based on above volumes.

NOTE: High activity samples will require dilution to avoid excessive counting rates.

UCN-10766B (12 8-78)

10.0 Reference

10.1 Anders, Edward; The Radiochemistry of Technetium, NAS-NS-3021; National Academy of Sciences, November, 1960.

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-411
DATE	August 26, 1981
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CHROMIUM IN URINE, FURNACE ATOMIC ABSORPTION METHOD

Analyte:	Chromium	Method No.:	IHA-411
Matrix:	Urine	Range:	See Section 2.2
Procedure:	Graphite Furnace Atomic Absorption Spectrophotometry	Precision:	15% RSD
		Accuracy:	No significant bias

1.0 Principle of the Method

1.1 Chromium is determined directly in the urine sample by atomic absorption spectrometry, using graphite furnace atomization.

1.2 A tungsten-halogen background corrector* is necessary for accurate background correction during atomization and the method of standard additions is necessary to correct for matrix interferences.

2.0 Range and Sensitivity

2.1 The lowest concentration reported for chromium is 0.005 μg/ml of urine.

2.2 The upper limit is about 0.1 μg/ml; but this may be extended upward by adjusting the aliquots used for the sample and/or for injecting into the graphite furnace.

3.0 Interferences

3.1 The principal interferences are due to the inability to completely ash the sample in the furnace prior to atomization of the metal. The background correction removes the "smoke" contribution to absorbance during atomization; and calibration by the method of standard additions eliminates interferences due to variable matrices.

*In tests of direct Cr measurement in urine on a Perkin-Elmer 5000 AA at 357.9 nm, using both the deuterium lamp and the tungsten-halogen background correctors, only the latter system was successful.

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INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

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UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-415
DATE	May 28, 1980
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DELTA-AMINOLEVULINIC ACID (ALA) IN URINE, SPECTROPHOTOMETRIC METHOD

Analyte:	ALA	Method No.:	IHA-415
Matrix:	Urine	Range:	0.02-10 mg/100 ml
Procedure:	Ion exchange separation; elution with 1.0 M sodium acetate; add acetylacetone, heat, and add Ehrlich's reagent; spectrophotometric measurement	Precision:	RSD of 2.4% at 0.47 mg/100 ml
		Accuracy:	See Section 3.0.

1.0 Principle of Method

1.1 ALA is separated from porphobilinogen and urea using ion-exchange (anion and cation) resin chromatography.

1.2 The ALA is eluted from the cationic column with 1.0 M sodium acetate.

1.3 The ALA fraction is heated with acetylacetone at 90°C.

1.4 Fresh Ehrlich's reagent is added.

1.5 The solution absorbance is read at 553 nm.

1.6 The ALA determination should be completed on urine samples within a few hours after delivery; if necessary, the samples may be held up to 1 week under refrigeration.

2.0 Range and Sensitivity

2.1 The range is 0.02-10 mg ALA/100 ml urine.

2.2 The limit of sensitivity is 0.15 μg ALA.

3.0 Precision and Accuracy

3.1 Measurement of 5 replicate samples containing 0.47 mg/100 ml gave the average result, 0.466 ± 0.011 (S.D.), representing an RSD of 2.4%.

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3.2 Measurement of 5 replicate samples containing 0.72 mg/100 ml gave the average result, 0.722 ± 0.013, representing an RSD of 1.8%.

4.0 Apparatus

4.1 Spectrophotometer, Beckman Model B, or equivalent, with 1-cm matched cells.

4.2 Urinary ALA kit, Bio-Rad Laboratories, containing:

4.2.1 Ion exchange columns, disposable: anionic (blue column) and cationic (clear column).

4.2.2 Sodium acetate solution, 1.0 M.

4.2.3 Acetylacetone.

4.2.4 p-Dimethylaminobenzaldehyde (DMAB), USP.

4.2.5 Standard solution of delta-aminolevulinic acid (ALA), 100 µg/ml.

4.3 Test tubes, 18 x 150-mm, with a test tube rack.

4.4 Water bath, 90-100°C.

5.0 Reagents

5.1 Perchloric acid, conc.

5.2 Glacial acetic acid.

5.3 Ehrlich's Reagent.

5.3.1 Add 420 ml of glacial acetic acid to an empty amber bottle with stopper.

5.3.2 Add 10 g of p-dimethylaminobenzaldehyde (DMAB) to the bottle and mix.

5.3.3 Transfer 100 ml of the DMAB solution (5.3.2) to another amber bottle with stopper. Add 19 ml of perchloric acid to complete the preparation of Ehrlich's reagent. This is sufficient reagent for a calibration curve and 6 sample aliquots. This freshly prepared solution is stable for up to 6 hours.

5.3.4 The remaining DMAB solution may be stored in a refrigerator where it will solidify. It may be used by subsequent thawing (by running warm water over the amber bottle); addition of perchloric acid as outlined above will provide fresh Ehrlich's reagent.

6.0 Procedure

6.1 Remove from the Urinary ALA Kit one blue-tinted column and one clear column for each sample to be analyzed. Shake each column vigorously until all the resin is suspended. Allow the resin to settle, break the tip from each column, and remove the top cap. Place each blue column into a clear column to make a column unit of two columns, the blue on top emptying into the clear column; allow each unit to drain.

6.2 Add distilled water (~10 ml) to the top of the blue column and allow it to drain through both columns.

6.3 Pipet 0.5 ml of each urine sample into the top of a blue column.

6.4 Add distilled water (~10 ml) to the top of the blue column and allow it to drain through both columns. Repeat two more times for a total of three washes (approx. 30 ml).

6.5 Remove the blue column and discard. (This contains the porphobilinogen extracted from the urine.)

6.6 Place each clear column over a test tube which has been previously numbered. Use a test tube rack for convenience.

6.7 To the rack add test tubes for a blank and duplicate standards of 1, 5, and 10 μg of ALA. Pipet aliquots of the standard ALA (7.1) into the labeled test tubes.

6.8 Add 7.0 ml of 1.0 M sodium acetate to each column and to each of the test tubes containing the blank and standard ALA solutions. (The sodium acetate elutes the ALA from the cationic column, separating the ALA from urea.)

6.9 After the columns have been fully drained, pipet 0.2 ml of acetylacetone to each test tube and mix thoroughly.

6.10 Place the test tubes in the hot water bath (90-100°C) for 10 minutes. Remove and cool to room temperature.

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6.11 Pipet 7.0 ml of fresh Ehrlich's reagent into each tube, mix, and allow to stand for 15 minutes for complete color development.

6.12 Read the absorbance of each sample and standard versus the blank at 553 nm, using 1-cm cells. [The spectrophotometer dark current is adjusted to ∞ at 553 nm; absorbance is set at zero with the blank.]

7.0 Standards and Calibration

7.1 The ALA standards are prepared from the stock solution of ALA (100 μg/ml) in the kit. Aliquots of 0.01, 0.05, and 0.10 ml contain 1, 5, and 10 μg of ALA, respectively.

7.2 Prepare a calibration curve by plotting the amount (μg) of ALA in the standards versus absorbance.

8.0 Calculations

8.1 The amount of ALA in the sample is determined from the calibration curve.

8.2 ALA concentration in urine:

$$\text{ALA, mg/100 ml} = \frac{\mu\text{g ALA (from calibration curve)}}{0.5\text{ ml (sample aliquot)}} \times \frac{100}{1000\ \mu\text{g/mg}}$$

$$= \mu\text{g ALA (from calibration curve)} \times 0.2 \quad ,$$

$$\text{or ALA, mg/L} = \mu\text{g ALA (from calibration curve)} \times 2 \quad .$$

9.0 Reference

9.1 Davis, J. R. and Andelman, S. L.; "Determination of Lead Poisoning by Measuring Urinary Delta-aminolevulinic Acid"; Arch. Environ. Health, 15, 53-59 (1967).

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-420
DATE	Nov. 27, 1979
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FLUORIDE IN URINE, SELECTIVE ION ELECTRODE METHOD

Analyte:	Fluoride	Method No.:	IHA-420
Matrix:	Urine	Range:	Lower Limit Urine 0.19 mg/L
Procedure:	Selective Ion Electrode	Precision:	25% RSD at 0.8 mg/L
		Bias:	-5% at 0.8 mg/L

1.0 Principle of the Method

1.1 Urine samples are diluted with an equal volume of a pH-activity coefficient buffer solution.

1.2 A fluoride sensitive selective ion electrode and a reference electrode are inserted into the buffered sample. The observed potential difference between the electrodes can then be related to the fluoride concentration in the sample by calibration curves prepared with the same buffer and electrodes.

2.0 Range and Sensitivity

The range and sensitivity of this method have not been established at this time. The electrode recommended range is 0.19-1900 mg/liter urine.

3.0 Interferences

Hydroxide is the only positive interference in the measurement and is eliminated by use of the pH buffer. Negative interferences, which may result from complexing of fluoride by cations such as calcium, are minimized by the complexing agent in the buffer mixture. The buffer also yields a solution of high ionic strength in which the activity coefficient of fluoride is relatively constant.

4.0 Precision and Accuracy

4.1 The 95% confidence limits are ±50% of the value (25% RSD) at the 0.8 mg/L level.

4.2 The recovery on synthetic (spiked urine) samples is 95% of the added value at the 0.8 mg/L level.

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APPROVED BY PGDP	LAB R. E. Simmons	APPROVED BY ORNL	LAB W R Laing	NUMBER IHA-420
	IH C. H. Turak		IH J. A. Ely	

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5.0 Advantages and Disadvantages of the Method

5.1 Advantages over previous methods include simplicity, accuracy, speed, selectivity, and elimination of ashing, distillation, or diffusion steps.

5.2 Interfering ions are complexed by the buffer mixture.

5.3 No significant disadvantages are known.

6.0 Apparatus

6.1 Fluoride sensitive selective ion electrode, Model 94-09, Orion Research Corporation (Cambridge, Massachusetts), or equivalent.

6.2 Reference electrode, calomel or silver/silver chloride, sleeve junction preferable but not necessary.

6.3 pH/Millivolt meter, capable of measuring ±0.5 millivolt.

6.4 Magnetic stirrer, equipped with small stirring bars which can spin freely in the sample beakers.

6.5 Glass beakers (50-ml) and sample collection bottles (200-ml capacity).

6.6 Laboratory glassware.

7.0 Reagents

All chemicals used should be ACS Reagent grade, or equivalent. After being prepared in clean glassware, all fluoride-containing solutions should be stored in plastic beakers and bottles.

7.1 Double distilled water.

7.2 1,2-Cyclohexylenedinitrilotetraacetic acid (CDTA).

7.3 Glacial acetic acid.

7.4 Sodium chloride, crystals.

7.5 Sodium hydroxide solution, 5 M: Dissolve 20 g of sodium hydroxide pellets in 70 ml of distilled water and dilute to 100 ml.

7.6 Total Ionic Strength Adjustment Buffer (TISAB): Place 500 ml of double distilled water in a 1-liter beaker. Add 57 ml of glacial acetic acid, 58 g of sodium chloride, and 2.0 g of CDTA. Stir to dissolve. Place beaker in a water bath (for cooling). Slowly add 5 M sodium hydroxide until the pH is between 5.0 and 5.5. Cool to room temperature and pour into a 1-liter volumetric flask; add double distilled water to the mark.

7.7 Sodium fluoride, for preparation of standards.

7.8 Standard fluoride solutions. All solutions should be stored in plastic bottles. The 0.1 M fluoride standard is reported to be stable for at least two months. All other dilutions should be prepared fresh weekly.

7.8.1 Fluoride standard solution, 1900 mg/L: Dissolve 4.200 g of sodium fluoride in water and dilute to 1000 ml. This solution can also be purchased from Orion Research, Inc., Cambridge, Massachusetts.

7.8.2 Fluoride standard solution, 190 mg/L: Dilute 10 ml of 7.8.1 to 100 ml with water.

7.8.3 Fluoride standard solution, 19 mg/L: Dilute 10 ml of 7.8.2 to 100 ml with water.

7.8.4 Fluoride standard solution, 1.9 mg/L: Dilute 10 ml of 7.8.3 to 100 ml with water.

7.8.5 Fluoride standard solution, 0.19 mg/L: Dilute 10 ml of 7.8.4 to 100 ml with water.

8.0 Procedure

8.1 Cleaning of equipment

8.1.1 All plastic and glassware must be washed free of any fluoride before use.

8.2 Storage of Samples

8.2.1 Samples that cannot be analyzed within 48 hours should be refrigerated. (Do not freeze.)

8.3 Analysis of Urine Samples

8.3.1 Transfer 20 ml of well-mixed urine sample and 20 ml of TISAB buffer solution into a 50-ml beaker, and add a magnetic stirring bar.

8.3.2 Immerse the electrodes in the solution. Adjust stirring speed and positions of the stirrer and electrodes to avoid splashing and hitting the electrodes.

8.3.3 After the EMF (voltage) reading stabilizes (that is, EMF drift is less than 0.5 millivolt per minute) record the EMF to the nearest millivolt.

For most samples, the EMF will stabilize in a minute or two if the fluoride concentration is 2 μg/ml or more. Stabilization may take longer at lower concentrations.

8.3.4 Rinse the electrodes with double distilled water and wipe dry with a clean tissue before proceeding with the next aliquot.

9.0 Calibration and Standards

9.1 Use the standard fluoride solutions prepared in 7.8 and treat them in the same way as the samples, Section 8.3. Start with the most dilute standard solution (0.19 mg/L) and proceed to 190 mg/L.

9.2 Prepare a calibration curve by plotting the concentration vs EMF data on semi-log paper with the fluoride concentration on the log axis.

9.3 Calibrations should be repeated or confirmed at least twice daily.

10.0 Calculations

10.1 The concentration of fluoride is obtained by converting the millivolt reading directly into concentration, using the calibration curve.

10.2 The concentration is reported as mg F per liter of urine.

11.0 References

11.1 *Instruction Manual for Fluoride Electrode Model 94-09*, Orion Research Incorporated, Cambridge, Massachusetts.

11.2 Sun, Mu-Wan; *Fluoride Ion Activity Electrode for Determination of Urinary Fluoride*; Amer. Ind. Hyg. Assoc. J., 30, 133, 1969.

11.3 NIOSH Manual of Analytical Methods, Second Edition, Vol. 1, U. S. Department of Health, Education, and Welfare, Method 114, 1977.

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

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MERCURY IN URINE AND BLOOD, FLAMELESS AA METHOD

Analyte:	Mercury	Method No.:	IHA-450
Matrix:	Urine, Blood	Range:	0.010-0.200 μg/ml urine 0.025-0.500 μg/ml blood
Procedure:	Oxidative digestion; mercury reduction and liberation; flameless atomic absorption	Precision:	∿ 6% RSD urine

1.0 Principle of the Method

1.1 Whole blood and urine samples are digested with HNO_3, H_2SO_4, and potassium permanganate at room temperature, and lastly with potassium persulfate at 95°C for 2 hours.

1.2 After reduction of excess permanganate, elemental mercury is liberated by reduction with $SnSO_4$ solution and measured by flameless atomic absorption at 253.7 nm.

2.0 Range and Sensitivity

2.1 The actual range and sensitivity of the procedure have not been established. However, the lowest concentrations reported are 0.010 μg/ml for urine using a 5-ml aliquot, and 0.025 μg/ml for blood using a 2-ml aliquot, with the practical upper limit at 20 times these values.

2.2 The working range may be extended by decreasing the sample size.

3.0 Interferences

3.1 Organic vapors absorb at the 253.7-nm Hg line and must be absent.

4.0 Precision and Accuracy

4.1 Samples of NBS SRM 2672, Freeze-Dried Urine Certified for Mercury, were analyzed according to this procedure with the following results:

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APPROVED BY PGDP	LAB R. E. Simmons IH C. W. Turak	APPROVED BY ORNL	LAB W. R. Laing IH J. A. Eaf	NUMBER IHA-450

UCN-13234
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Level	Found, µg/ml	Certified, µg/ml
Low	0.0453 ± 0.0024	0.0498 ± 0.0042
Elevated	0.291 ± 0.018	0.294 ± 0.024

The values (Found) are the means obtained in the measurement of seven samples while the uncertainties represent the 95 percent confidence limits.

4.2 No similar statistics are available for blood. No certified mercury-in-blood standards are available.

5.0 Apparatus

5.1 Atomic absorption spectrophotometer, with an absorption cell at least 10-cm long x 2-cm I.D. with quartz end-windows.

5.2 Mercury hollow cathode lamp.

5.3 Strip-chart recorder.

5.4 Reagent bottles, 250-ml.

5.5 Gas supply: air, N_2, or argon.

5.6 Flowmeter, to deliver gas at 1 liter per minute.

5.7 Aerating tubing: a straight cylindrical flat-end glass frit of coarse porosity.

5.8 Drying tube: a 15-cm x 19-mm O.D. tube packed with magnesium perchlorate desiccant. The apparatus is assembled as shown in Figure 1.

5.9 Heparinized vacutainers, mercury-free, 3-ml, equipped with sterilized stainless steel needles.

5.10 Water bath, capable of maintaining 95°C.

6.0 Reagents

All reagents are reagent-grade and water is double-distilled or deionized.

6.1 Sulfuric acid, conc.

6.2 Sulfuric acid, 0.5 N: Add 14.0 ml of conc sulfuric acid to about 900 ml of water and dilute to 1.0 liter.

6.3 Nitric acid, conc: Reagent grade of low mercury content. Transistor-grade Mallinckrodt appears to be suitable. If this grade is not used, and a reagent blank of $\geq$ 0.05 μg is obtained, it will be necessary to distill the nitric acid.

6.4 Stannous sulfate suspension: Add 25 g of stannous sulfate to 250 ml of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

6.5 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100.0 ml. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

6.6 Potassium permanganate: 5% solution, w/v: Dissolve 5 g of potassium permanganate in 100 ml of distilled water.

6.7 Potassium persulfate: 5% solution, w/v: Dissolve 5 g of potassium persulfate in 100 ml of distilled water.

6.8 Stock mercury solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of distilled water. Add 10 ml conc nitric acid and adjust the volume to 100.0 ml (1 ml = 1 mg Hg).

6.9 Working mercury solution: Make successive dilutions of the stock mercury solution to obtain a working standard solution of 1 ml = 0.1 μg. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

7.0 Procedure

7.1 Cleaning of Equipment. Acid-clean all glassware by soaking in 1:1 HNO_3 for 30 minutes and rinsing with deionized water.

7.2 Collection and Shipping of Samples

7.2.1 Urine samples are collected in Hg-free plastic bottles and preserved by the addition of 0.1 g potassium persulfate per 100 ml of urine. Urine preserved in this manner is stable at room temperature for two weeks.

7.2.2 Blood samples are collected in Hg-free heparinized vacutainers equipped with sterilized stainless steel needles. Refrigerated samples are stable for two weeks. (Do not freeze.)

7.3 Sample Preparation

7.3.1 Pipet 5 ml of urine or 2 ml of blood into a 250-ml reagent bottle, dilute to 100 ml with deionized water and mix.

7.3.2 Add 5 ml of conc H_2SO_4 and 2.5 ml of conc HNO_3 to each bottle and mix.

7.3.3 Add 15 ml of $KMnO_4$ solution (6.6) to each bottle, mix, and allow to stand for 15 minutes.

7.3.4 Add 8 ml of $K_2S_2O_8$ solution (6.7) to each bottle, mix, and heat in a water bath at 95°C for 2 hours.

7.3.5 Cool and add 6 ml of sodium chloride-hydroxylamine sulfate solution (6.5) to each bottle to reduce the excess permanganate.

7.4 Analysis of Sample

7.4.1 Add 5 ml of the stannous sulfate suspension (6.4) and immediately attach the bottle to the aeration assembly (See Figure 1).

7.4.2 Set the bypass valves to allow the gas (@ 1 liter/min) to sweep the elemental mercury from the bottle to the absorption cell. The absorbance will increase and reach maximum within 30 seconds.

7.4.3 As soon as the absorbance begins to decrease, open the bypass valves and continue aeration until the recording returns to baseline.

7.4.4 Repeat Steps 7.4.1 through 7.4.3 for each sample.

8.0 Calibration and Standards

8.1 Transfer 0 (Blank), 1.0, 2.0, 5.0, and 10.0-ml aliquots of the 0.1-μg/ml working mercury solution (6.9) to a series of 250-ml reagent bottles. Note: Reagent blank values should not exceed 0.05 μg.

8.2 Dilute to 100 ml with deionized water, mix, and treat as samples, beginning with 7.3.2.

8.3 Plot peak heights vs. μg mercury as a calibration curve.

9.0 Calculations

9.1 Hg in sample, μg/ml = $\frac{A - B}{V}$.

Where A = Hg (μg) found in sample (calibration curve),

B = Reagent blank, μg, and

V = Volume of sample, ml.

10.0 Reference

10.1 *NIOSH Manual of Analytical Methods*, 2nd edition, Vol. 1, April 1977; P & CAM 165 and 167.

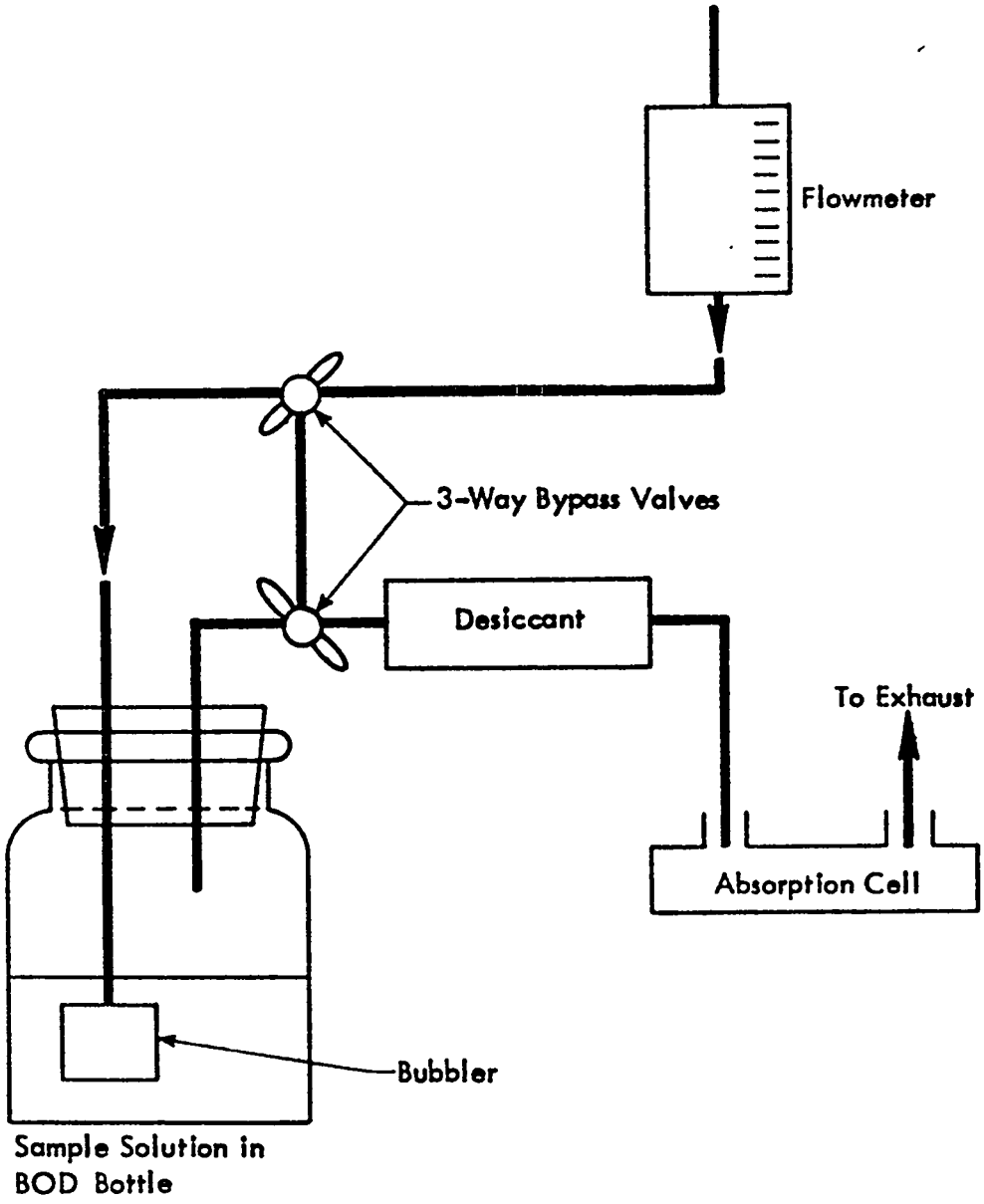

Figure 1. APPARATUS FOR FLAMELESS MERCURY DETERMINATION.

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-460
DATE	March 16, 1981
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METALS (SELECTED, HEAVY) IN WHOLE BLOOD, FURNACE ATOMIC ABSORPTION METHOD

Analyte:	Lead, cadmium, nickel	Method No.:	IHA-460
Matrix:	Whole blood	Range:	See Section 2.2
Procedure:	Graphite furnace atomic absorption spectrophotometry	Precision:	6% RSD Pb
		Accuracy:	No bias for Pb; others not evaluated

1.0 Principle of the Method

1.1 Whole, venous blood is diluted with water and analyzed by atomic absorption spectroscopy using graphite furnace atomization.

1.2 Background correction is necessary to correct for nonatomic absorption and the method of standard additions is necessary to correct for matrix interferences.

2.0 Range and Sensitivity

2.1 The method is suitable over the entire range of lead, cadmium, and nickel blood levels encountered in industrial workers.

2.2 The concentration range of the method is shown in the following table:

	Lower Limit mg/100 g	Upper Limit mg/100 g
lead	0.010	0.100
cadmium	0.002	0.020
nickel	0.020	0.200

The upper limit may be extended by simple dilution.

3.0 Interferences

3.1 The principal interferences are due to the inability to completely ash the sample in the furnace prior to atomization of the metal. The background correction removes the "smoke" contribution to

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absorbance during atomization; and calibration by the method of standard additions eliminates interferences due to variable matrices.

4.0 Precision and Accuracy

4.1 Repeated measurements of lead in spiked blood samples, using the method of standard additions, showed an average relative standard deviation of about 6%. Precisions for cadmium and nickel have not been determined but are expected to be about the same as for lead.

4.2 An informal comparison was made between the lead measurements by this method and those by an isotopic-dilution spark-source mass spectrometric method. Results were within the observed experimental errors of the methods and indicate no significant bias for lead.

5.0 Advantages and Disadvantages of the Method

5.1 The method is simple, fast, and inexpensive.

5.2 The method determines the total metal present and provides no information about its form in the blood media.

6.0 Apparatus

6.1 Atomic absorption spectrophotometer, with automatic background compensation and a graphite furnace atomizer.

6.2 Vacutainer collection tube: 3-cc heparinized or 20-cc nonheparinized tubes.

6.3 Microliter pipets: various sizes for standards preparation and sample injection.

7.0 Reagents

7.1 Nitric acid, ACS.

7.2 Lead stock solution, 1000 μg/ml: Dissolve 1.599 g of reagent grade $Pb(NO_3)_2$ in deionized water, add 10 ml of HNO_3, and dilute to 1000 ml. Commercially prepared standards are available; e.g., Fisher Scientific Co.

7.3 Cadmium stock solution, 1000 μg/ml: Dissolve 1.000 g of cadmium in a minimum volume of 1:1 HNO_3 and dilute to 1000 ml. Commercially prepared standards are available; e.g., Fisher Scientific Co.

7.4 Nickel stock solution, 1000 µg/ml: Dissolve 1.000 g of nickel in 1:1 HNO_3 and dilute to 1000 ml. Commercially prepared standards are available; e.g., Fisher Scientific Co.

7.5 Standard solutions are prepared using one of the following methods:

7.5.1 Standard working solutions: Make successive dilutions of the stock solutions to obtain an appropriate working solution for each element.

7.5.2 Combined standard solution: Combine the stock solutions in a 1-L volumetric flask according to the following schedule:

	ml of Stock	µg/ml in Standard
Pb	10.0	10
Cd	2.0	2
Ni	20.0	20

7.6 Heparin (ammonium salt), for 20-cc Vacutainers.

8.0 Procedure

8.1 Collect venous blood using a 3-cc heparinized Vacutainer or a 20-cc Vacutainer containing 1 ml of heparin, and mix gently. Refrigerate until ready for analysis.

8.2 Weigh 1.0 g of the sample into a 10-ml volumetric flask, dilute to volume with deionized water, and mix.

8.3 Inject a 10-to-50-µl aliquot into the graphite furnace; operate the spectrophotometer and furnace according to the manufacturer's recommendations for the given element.

8.4 Record the peak height or area from the instrument readout or accessory recorder.

9.0 Calibration and Standards

9.1 Calibration is accomplished by the method of standard additions. A typical sample is chosen as the standard and is spiked with appropriate levels of the element(s) of interest from the standard solutions.

9.2 On a plot of total metal signals (peak heights or areas) versus spike levels, a parallel line is drawn through "zero," thus constructing a calibration curve. This is used to determine the metal content in each sample.

9.3 Calibration may also be accomplished using the conventional method of standard additions, in which each sample analyzed is spiked with appropriate levels of the element(s) of interest from the standard solutions.

10.0 Calculation

10.1 Blood metal levels are usually reported in units of mg/100 g. The general formula for converting µg/ml (in the measured solution) to mg/100 g (in the blood sample) is:

$$\text{mg/100 g} = \mu\text{g/ml} \times \frac{\text{diluted-sample volume (ml)}}{\text{blood sample weight (g)}} \times \frac{100}{1000\ \mu\text{g/mg}}$$

10.2 Therefore, when 1 g of blood is diluted to 10 ml, the formula becomes:

Metal, mg/100 g (in the blood sample) = Metal, µg/ (in the measured solution)

11.0 Reference

11.1 Ealy, J. A., Bolton, N. E., McElhaney, R. J., and Morrow, R. W.; "Determination of Lead in Whole Blood by Graphite Furnace Atomic Absorption Spectrophotometry"; American Industrial Hygiene Association Journal; Vol. 35, No. 9, p. 556 (1974).

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-463
DATE	March 16, 1981
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METALS (SELECTED, HEAVY) IN URINE, FURNACE ATOMIC ABSORPTION METHOD

Analyte:	Lead, cadmium, nickel	Method No.:	IHA-463
Matrix:	Urine	Range:	See Section 2.2
Procedure:	APDC-MIBK extraction; furnace atomic absorption	Precision:	7 to 10% RSD
		Accuracy:	No bias for Pb; Others not evaluated

1.0 Principle of the Method

1.1 Urine samples are acidified and the heavy metals extracted using APDC-MIBK. The metals are determined using atomic absorption with graphite furnace atomization.

1.2 Background correction and calibration by the method of standard additions are necessary to achieve a useful analysis.

2.0 Range and Sensitivity

2.1 The method is suitable over the entire range of urinary lead concentrations normally encountered in industrial workers.

2.2 The concentration range of the method is shown in the following table:

	Lower Limit µg/ml	Upper Limit µg/ml
lead	0.010	0.100
cadmium	0.002	0.020
nickel	0.005	0.200

The upper limit may be extended by simple dilution.

3.0 Interferences

3.1 The principal interferences arise from the inability to completely ash the sample in the furnace prior to atomization of the metal. The background correction removes the "smoke" contribution to

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APPROVED BY PGDP	LAB R.E. Simmons	APPROVED BY ORNL	LAB W.R. Laing	NUMBER IHA-463
	IH C.H. Turoke		IH James A. Ealy	

absorbance during atomization; and calibration by the method of standard additions eliminates interferences due to variable matrices.

4.0 Precision

4.1 Precision expressed as percent Relative Standard Deviation is as follows:

9.5% for Pb determined at 0.05 μg/ml
7.0% for Cd determined at 0.01 μg/ml
10.0% for Ni determined at 0.01 μg/ml

5.0 Advantages and Disadvantages of the Method

5.1 The method is simple, fast, and inexpensive.

5.2 The extracted metal complexes are unstable and analysis must be completed without delay.

6.0 Apparatus

6.1 Atomic absorption spectrophotometer, with automatic background compensation and a graphite furnace atomizer.

6.2 Microliter pipets, various sizes for standards preparation and sample injection.

6.3 Glass centrifuge cones, 15-ml capacity with Teflon-lined screw caps.

6.4 pH meter, with a semi-micro combination electrode.

6.5 Laboratory centrifuge.

7.0 Reagents

7.1 Nitric acid, ACS.

7.2 Hydrochloric acid, 1 N.

7.3 Acetic acid, ACS.

7.4 Lead stock solution, 1000 µg/ml: Dissolve 1.599 g of reagent grade $Pb(NO_3)_2$ in deionized water; add 10 ml of HNO_3, and dilute to 1000 ml. (Commercially available solutions* may be used.)

7.5 Cadmium stock solution, 1000 µg/ml: Dissolve 1.000 g of cadmium in a minimum volume of 1:1 HNO_3 and dilute to 1000 ml. (Commercially available solutions* may be used.)

7.6 Nickel stock solution, 1000 µg/ml: Dissolve 1.000 g of nickel in 1:1 HNO_3 and dilute to 1000 ml. (Commercially available solutions* may be used.)

7.7 Standard solutions are prepared using one of the following methods:

7.7.1 Standard working solutions: Make successive dilutions of the stock solutions to obtain an appropriate working standard solution for each element.

7.7.2 Combined standard solution: Combine the stock solutions in a 1-L volumetric flask according to the following schedule:

	ml of Stock	µg/ml in Standard
Pb	10.0	10
Cd	2.0	2
Ni	5.0	5

7.8 Ammonium pyrolidine dithiocarbamate (APDC) solution, 3%: Weigh 0.3 g of APDC into a 50-ml beaker, add 10 ml of deionized water, and swirl vigorously. Prepare fresh daily.

7.9 Methyl isobutyl ketone (MIBK).

8.0 Procedure

8.1 Upon receipt, all samples should be preserved by acidifying with acetic acid to about 1%.

8.2 Transfer 5.0 ml of the sample to a 15-ml centrifuge cone.

8.3 Adjust the pH to 2.8 ± 0.2 with dropwise addition of 1 N HCl.

8.4 Add 0.2 ml of 3% APDC solution and mix thoroughly.

8.5 Pipet 5.0 ml of MIBK into the cone; cap, and shake vigorously for 2 min.

8.6 Centrifuge at ~2800 rpm for 10 min.

* Suggested Vendor: Fisher Scientific Co.; 711 Forbes Ave.; Pittsburgh, PA 15219

8.7 Inject a 10- to 50-µl aliquot of the extract into the graphite furnace, operating the spectrophotometer and furnace according to the manufacturer's recommendations for the given element.

8.8 Record the peak height or area from the instrument readout or accessory recorder.

Calibration and Standards

9.1 Calibration is accomplished by the method of standard additions. A fresh urine sample is obtained and 5-ml aliquots are spiked with appropriate levels of the element(s) of interest from the standard solutions.

9.2 The standards are treated as samples, beginning with Section 8.3.

9.3 On a plot of total metal signals (peak heights or areas) versus spike levels, a parallel line is drawn through "zero," thus constructing a calibration curve. This is used to determine the concentration of the metal in each sample.

9.4 Calibration may also be accomplished using the conventional method of standard additions, in which each sample analyzed is spiked with appropriate levels of the element(s) of interest from the standard solutions.

10.0 Calculation

10.1 Urine metal levels are usually reported in units of µg/ml. Since there is no change in concentration involved in the extraction step and standards are treated the same as samples, the concentration as determined from the calibration curve is reported as µg/ml of the element of interest.

11.0 References

11.1 McElhaney, R. J. and Morrow, R. W.; *Determining Lead in Urine by Flameless Atomic Absorption Spectrophotometry*; Y/DK-90 (1972).

11.2 Hamilton, L. G. and Farrar, R. B.; *Determination of Cadmium, Chromium, Nickel, and Lead in Urine using Graphite Furnace Atomic Absorption Spectrophotometry*; K-2019 (December, 1980).

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-470
DATE	Nov. 27, 1979
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TECHNETIUM-99 IN URINE, RADIOCHEMICAL METHOD*

Analyte:	Technetium-99	Method No.:	IHA-470
Matrix:	Urine	Range:	Lower Limit In Urine 10 dpm/ml
Procedure:	Beta counting, without chemical separation from the sample	Precision:	Not determined

1.0 Principle of the Method

1.1 The beta activity of the urine sample is determined.

1.2 The sample activity is compared to the beta activity of urine spiked with a known level of ^{99}Tc standard solution.

2.0 Range and Sensitivity

2.1 The lower limit of measurement in urine, using a 2.0-ml sample, is approximately 10 dpm/ml with a proportional counter, and 3 dpm/ml using a liquid scintillation spectrometer.

2.2 The upper limit has not been determined; however, spiked samples with activity > 25,000 dpm/ml have been measured.

3.0 Interferences

3.1 The technique is non-specific for ^{99}Tc; other low-energy beta-emitting nuclides will give a positive bias.

4.0 Precision and Accuracy

4.1 The precision and accuracy of this method have not been statistically determined.

4.2 Duplication tests of spiked samples yield an estimate of ± 20% near the lower limit of measurement.

*Because it is not specific for the analyte, this procedure is not appropriate for samples at ORNL, where many radioactive interferences might be present.

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APPROVED BY PGDP	LAB R. E. Simmons IH O. W. Turak	APPROVED BY ORNL	LAB W. R. Laing IH J. A. Eaby	NUMBER IHA-470

UCN 13234
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5.0 Advantages and Disadvantages of the Method

5.1 The advantages of this method include speed, simplicity, and absence from chemical separation techniques. When a liquid-scintillation beta counter is available, it is particularly adaptable to large scale screening of samples.

5.2 The disadvantages of the method arise from its non-specificity. Since the interferences will bias results high, this does not restrict its usefulness as a screening tool. If significant beta activity is detected, confirmatory techniques can be used to positively identify the emitter.

6.0 Apparatus

6.1 Suitable beta counter: planchet gas proportional counter or liquid-scintillation spectrometer.

6.2 Miscellaneous laboratory glassware and volumetric pipets.

6.3 Stainless steel counting planchets, $\geq$ 51 mm diameter.

6.4 Liquid-scintillation counting bottles.

6.5 High velocity fume hood with heat lamps.

7.0 Reagents

7.1 Distilled water.

7.2 Standard ^{99}Tc solutions: 10,000 and 150,000 dpm/ml.

7.3 Liquid-scintillation mix: Insta Gel, Packard Instrument Co.

8.0 Procedure

8.1 Cleaning of Equipment. All glassware, beakers, pipets, etc., must be thoroughly cleaned. Pipets and containers used for ^{99}Tc standard solutions must not be allowed to contact samples. Sample containers, counting vials or planchets must be discarded after use.

8.2 Collection and Handling of Samples.

8.2.1 Urine samples representing potential exposure, as well as samples from personnel not exposed to ^{99}Tc, should be collected.

8.2.2 Samples are collected in glass, plastic, or waxed fiberboard specimen bottles.

8.3 Analysis of Urine Using Proportional Counter

8.3.1 Transfer 2.0 ml of sample to a stainless steel counting planchet (6.3).

8.3.2 Place the planchet under a heat lamp (6.5) and slowly dry the sample. The residual deposit should be fairly uniform.

8.3.3 Determine counts/min per milliliter of sample, using a low background gas proportional counter.

8.3.4 Prepare a comparison control for determining counter efficiency for ^{99}Tc by spiking an aliquot of urine with approximately 1000 dpm of standard ^{99}Tc per milliliter of urine. If the dried sample is unusually heavy with deposit, the efficiency is best determined using a spiked portion of the actual sample.

8.3.5 Measure the counts per min for the control, in the gas proportional counter.

8.3.6 The count contribution from high energy beta emitters (e.g., ^{40}K) can be corrected for, if they are present: the sample planchet is covered with an aluminum sheet of 70-mg/cm^2 density, and counted. No ^{99}Tc beta particles are transmitted. The ^{40}K contribution is reduced to about 57% of its unshielded value.

8.4 Analysis of Urine Using Liquid Scintillation Spectrometer

8.4.1 Transfer 2.0 ml of sample to a liquid-scintillation bottle.

8.4.2 Add 15 ml of liquid-scintillation mix (7.3) and shake.

8.4.3 Place the sample in the beta liquid-scintillation spectrometer.

8.4.4 Count the sample using an energy channel of 0.05-0.3 MeV. High energy beta emitters will not generally contribute significantly to the count.

8.4.5 Add 15,000 dpm of standard ^{99}Tc (100 µl of the 150,000-dpm/ml solution) and count the sample again.

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9.0 Calculations

Sample activity (R) is expressed in dpm/ml:

$$R = \frac{A - B}{C} ,$$

where R = activity in dpm/ml,

A = measured count per minute per ml of the sample.

C = counter efficiency for ^{99}Tc =

$$\frac{\text{additional counts/min measured on the urine control}}{\text{dpm actually added to the control}} .$$

For Proportional Counters:

B = count contribution from high energy betas; treated as ^{40}K, the

$$\text{contribution} = \frac{\text{Al-shielded count per ml of sample}}{0.57} .$$

For Liquid Scintillation Counting:

B = 0.

If desired, R may be expressed in pCi/ml:

Conversion factor = 1 pCi/2.22 dpm .

10.0 REFERENCES

10.1 *Technical Procedures Manual*, Technical Services Division, Paducah Gaseous Diffusion Plant, Procedure No. R-16 (1978).

10.2 Anders, Edward; *The Radiochemistry of Technetium*; National Academy of Sciences; November 1960 (NAS-NS-3021).

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-475
DATE	Nov. 27, 1979
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TRICHLOROACETIC ACID IN URINE, SPECTROPHOTOMETRIC METHOD

Analyte:	Trichloroacetic acid	Method No.:	IHA-475
Matrix:	Urine	Range:	2-120 mg/L, using 25 ml of urine
Procedure:	Acetone extraction; pyridine addition; spectrophotometric measurement	Precision:	RSD of 4.2% at 60 mg/L
		Accuracy:	Not determined

1.0 Principle of the Method

1.1 Trichloroacetic acid is extracted by acetone from a strongly alkaline sample of urine.

1.2 An aliquot of the extract solution is mixed with pyridine and heated.

1.3 The solution transmittance is measured at a wavelength of 500 nm.

2.0 Range and Sensitivity

2.1 The range is from 2 to 120 mg/L trichloroacetic acid in urine when a 25-ml sample is used.

2.2 The limit of sensitivity of the method is 2 mg/L trichloroacetic acid.

3.0 Precision and Accuracy

3.1 Precision expressed as standard deviation is 2.5 mg/L, determined at the 60-mg/L trichloroacetic acid level.

3.2 The accuracy of the overall sampling and analytical method has not been established.

4.0 Apparatus

4.1 Spectrophotometer, Bausch & Lomb Spectronic 20, or equivalent.

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APPROVED BY PGDP	LAB R. E. Simmons IH C. W. Turak	APPROVED BY ORNL	LAB W. R. Laing IH J. A. Eaby	NUMBER IHA-475

UCN 13234
(1235 1 79)

4.2 Graduates, 50-ml, with ground-glass stoppers.

4.3 Test tube, 15-ml, Pyrex or Kimax; with regular stopper, and a special one-hole stopper equipped with a small drying tube containing KOH pellets.

4.4 Constant temperature bath, capable of maintaining a temperature of 70 ± 1°C.

5.0 Reagents

5.1 Sodium hydroxide solution, 12.5 N; dissolve 500 g of pellets in about 800 ml of water and dilute to 1 liter.

5.2 Sodium hydroxide solution, 4.5 N; dilute 360 ml of 12.5 N NaOH (5.1) to 1 liter.

5.3 Pyridine mixture: 25 ml of pyridine, 10 ml of water, and 0.1 ml of 4.5 N sodium hydroxide.

6.0 Procedure

6.1 Pour 25 ml of urine into a 50-ml graduate and add 10 ml of 12.5 N sodium hydroxide and 10 ml of acetone.

6.2 Stopper the graduate, shake for 2 minutes, and allow the layers to separate.

6.3 Pipet 2 ml of the acetone layer into a 15-ml test tube containing 4 ml of pyridine mixture (5.3). Stopper and shake well.

6.4 Replace the stopper with the specially equipped stopper (4.3) and maintain the solution at 70°C for 7 minutes in a constant temperature bath.

6.5 Measure the absorbance of the solution at 500 nm in a 1-cm cell against a distilled water blank which has been processed through the entire procedure.

6.6 Once each week perform a test of recovery from a standard addition.

6.6.1 Prepare a composite sample from four urine samples.

6.6.2 Aliquot 25 ml of the composite into each of two 50-ml graduates.

6.6.3 Add 0.200 ml of 3000-mg/L standard TCA solution (7.1.2) to one of the aliquots.

6.6.4 Process the two samples through steps 6.1 through 6.5 and determine the mg of TCA in both samples.

6.6.5 The addition spike should increase the amount of TCA by 0.6 mg.

7.0 Calibration and Standards

7.1 Preparation of standard TCA stock solution:

7.1.1 Weigh 3.00 g of reagent grade trichloroacetic acid, anhydrous.

7.1.2 Dissolve in 1 liter of distilled water. (3000 mg TCA/liter)

7.1.3 Dilute 10 ml of solution 7.1.2 to 100 ml with distilled water. (300 mg TCA/liter)

7.2 Preparation of standards

7.2.1 Pipet aliquots of 2, 4, 6, 8, and 10 ml of the 300-mg/L TCA solution (7.1.3) into individual 50-ml volumetric cylinders.

7.2.2 Adjust each cylinder to 25-ml volume with distilled water. Add 25 ml of distilled water to an empty cylinder to serve as a blank.

7.2.3 The prepared standards contain the equivalent of 0.6, 1.2, 1.8, 2.4, and 3.0 mg of TCA in a 25-ml sample.

7.3 Calibration

7.3.1 Follow steps 6.1 through 6.5 of the procedure for each standard.

7.3.2 Plot the absorbance vs. the mg of TCA to make a calibration graph.

7.3.3 Verify the calibration with each lot of pyridine.

8.0 Calculations

8.1 The amount of trichloroacetic acid in the sample is determined from the calibration graph.

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8.2 The concentration of TCA in urine may be expressed as:

$$\text{TCA, mg/L} = \frac{\text{mg of TCA in sample}}{\text{volume (in liters) of urine sample}}$$

9.0 Reference

Frant, R. and Westendorp, J.; *Medical Control on Exposure of Industrial Workers to Trichloroethylene*; Arch. Ind. Hyg. Occ. Med., 1, 308 (1950).

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-485
DATE	Nov. 27, 1979
SUPERSEDES	
PAGE	1 OF 7

URANIUM ALPHA ACTIVITY IN URINE, TOPO EXTRACTION
RADIOCHEMICAL METHOD*

Analyte:	Uranium alpha activity	Method No.:	IHA-485
Matrix:	Urine	Range:	Any level ≥ 0.3 alpha dpm/100 ml
Procedure:	TOPO extraction; evaporation; alpha counter	Precision:	15% RSD in the range of 2.5 to 10 alpha dpm/100 ml

1.0 Principle of the Method

1.1 Urine samples are wet-ashed with nitric acid to destroy the organic matrix.

1.2 The sample ash is dissolved in 1:4 nitric acid.

1.3 The dissolved ash is passed through a column of glass beads coated with tri-n-octylphosphine oxide (TOPO), which extracts the uranium.

1.4 Uranium and TOPO are removed from the column by stripping with alcohol.

1.5 The stripped sample is evaporated, ignited, and counted for alpha activity.

2.0 Range and Sensitivity

2.1 The lowest reported level is 0.3 alpha dpm/100 ml of sample.

3.0 Interferences

3.1 Accumulation of solids on counting dish decreases counts by self-absorption.

3.2 Any alpha-emitting nuclide on the counting dish will give a positive bias to the uranium measurement.

*Because it is not specific for the analyte, this procedure is not appropriate for samples at ORNL, where many radioactive interferences might be present.

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(1235 1 79)

4.0 Precision and Accuracy

4.1 At a level of 10.0 alpha dpm/100 ml of sample (a spike of 6.67 μg of natural uranium), the relative standard deviation is 14%.

4.2 At a level of 2.6 alpha dpm/100 ml of sample (a spike of 0.016 μg of 93% enriched uranium), the relative standard deviation is 15%.

4.3 In the above tests of precision, the average recoveries were 88 and 92%, respectively; the reason for low bias has not been established but could involve chemical inefficiency and self-absorption in counting.

5.0 Advantages and Disadvantages of the Method

5.1 The method can easily be semiautomated, thereby increasing production and efficiency.

5.2 Counting bias can be introduced by at least two factors: see sections 3.1 and 3.2.

6.0 Apparatus

6.1 Semiautomatic apparatus for extraction and stripping (Figure 1).

6.2 Muffle furnace, capable of maintaining 650°C.

6.3 Asbestos blocks machined to hold 40-mm watch glasses.

6.4 Hot plate, with an added 1/4-inch steel plate having 38-mm diameter holes for holding the watch glasses.

6.5 Water bath controlled at 40°C.

6.6 Automatic gas proportional counter.

6.7 Adsorption tube, 4.0-mm I.D. glass tubing, 20 cm long.

6.8 Microbeads, glass, 40-mesh.

6.9 Glass wool.

6.10 Watch glasses, 40-mm.

7.0 Reagents

7.1 Tri-n-octylphosphine oxide (TOPO), 2% (w/v) in reagent-grade benzene: Dissolve 20 g of TOPO in benzene and dilute to 1 liter with benzene.

7.2 Nitric acid, concentrated.

7.3 Rinse acid, 3 N nitric acid: Add 188 ml of conc HNO_3 to 500 ml of water and dilute to 1 liter.

7.4 Ethyl alcohol, 95% EtOH.

8.0 Procedure

8.1 Preparation of TOPO Bead Column

8.1.1 Wash 900 g of 40-mesh microbeads with 1:1 nitric acid; rinse with distilled water, followed by 95% ethyl alcohol.

8.1.2 Dry the beads and transfer them to a shallow dish to a depth of 1 nch. Cover the beads with a solution of 2% (w/v) T 'O in benzene. The operation is performed in a properly functioning fume hood.

8.1.3 Evaporate the benzene from the beads at a temperature below 52°C. Transfer the dry, coated beads to a suitable jar for storage. The coated beads should contain 9.5-10.5 mg TOPO per gram of beads.

8.1.4 Place a plug of glass wool in one end of an adsorption tube and fill to within 1/4 inch of the top with coated beads. The beads are lightly packed as they are inserted; control of sample stripping flow is partially dependent upon how tightly the beads are packed. Close the tube with another glass wool plug.

8.2 Sample Digestion and TOPO Adsorption

8.2.1 Transfer 100 ml of a urine sample to a 250-ml beaker. Add 100 ml of concentrated nitric acid. Caution: Take appropriate care in use and handling of this hazardous chemical.

8.2.2 Place the beaker on a hot plate located in a fume hood and evaporate carefully to dryness.

8.2.3 If the residue is not nearly white, add a 25-ml portion of concentrated nitric acid and boil to dryness. Repeat until the residue is nearly white.

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8.2.4 Add 75 ml of distilled water and 25 ml of conc nitric acid and heat on a hot plate until the residue is dissolved.

8.2.5 Remove the sample from the hot plate, cool, and place in a water bath, regulated at 40°C.

8.2.6 Set the semiautomatic apparatus (6.1) to provide a sample aspiration rate of 2 ml/min.

8.2.7 Attach the adsorption tubes to the aspiration system, place a digested urine specimen under each tube, and start the peristaltic pump.

8.2.8 When an entire sample has been aspirated, rinse the inside of the beaker with a few ml of 3 N nitric acid. Continue to aspirate until the beaker is dry.

8.3 Stripping and Ignition

8.3.1 Set the alcohol stripping flow to 0.3 ml/min and the stripping timer to 45 min. The temperature on the ring heater is preset and maintained at 40°C to evaporate the sample at the same rate as it is stripped from the column.

8.3.2 Remove the adsorption tube from the aspiration system and connect it to the stripping system. Place a 40-mm watch glass on the ring heater, position it under the adsorption tube, and strip for 45 minutes. The liquid flow should match the rate of evaporation so that the watch glass will not overflow and thus lose some of the sample.

8.3.3 Remove the empty beakers and stripped columns from the adsorption system. Place a new set of adsorption tubes in place, position another set of digested urine samples, and start another TOPO adsorption cycle.

8.3.4 Remove each watch glass from the ring heater when stripping is complete and dry on a hot plate. Place the watch glasses on an asbestos block and ignite in a muffle furnace at 650°C for 30 minutes.

8.3.5 Remove the holder and watch glasses from the furnace and place where they can cool to a safe handling temperature.

8.4 Counting

8.4.1 Cover the prepared watch glasses to avoid contamination and transfer them to the room where the counting is to be performed.

8.4.2 Uncover each glass and place in a holder that fits the gas proportional counter.

8.4.3 Start the counting and proceed for 10 counts or 30 minutes, whichever occurs first.

8.4.4 If the counter does not shut off before 30 minutes, the activity is $\leq$ the limit of detection (background level) and does not need to be counted again.

8.4.5 If the 10-count is reached before 30 minutes, the sample should be recounted. Perhaps several counting periods will be necessary; acceptable statistics are achieved with at least 50 counts, noting the accumulative time to the nearest 0.01 minute.

9.0 Calibration and Standards

9.1 Calibrate the counting instrument with a standard uranium source, prepared by electrodeposition onto a nickel disk.

10.0 Calculations

10.1 Calculate the dpm/100 ml of urine from the automatic counter.

dpm/100 ml of urine = counts/min x G.F.

Note: Geometry factor (G.F.) is nominally 0.5, but is dependent on system design.

11.0 References

11.1 Dietrich, W. L., Caylor, J. D., and Johnson, E. L.; *Separation of Uranium from Urine by a Tri-n-octylphosphine Oxide Column and an Automation of the Procedure*; Union Carbide Corporation-Nuclear Div., Y-12 Plant, September 15, 1960 (Y-1322).

11.2 Horton, C. A. and White, J. C.; "Separation of Uranium by Solvent Extraction with Tri-n-octylphosphine Oxide; *Anal. Chem.*, 30, 1779 (1958).

11.3 Whitson, T. C. and Kwasnoski, T.; *A Semiautomatic Apparatus and Method for Alpha Activity Determination in Urine*; UCC-ND, ORGDP, April 10, 1963 (TID-16090, Microcard).

LEGEND:

A — SAMPLE HANDLING SYSTEM
B — ASPIRATION SYSTEM
C — ELUTION SYSTEM
D — TWO-STAGE HEATER
E — CONTROL PANEL
F — POWER SWITCHES
G — ELUTION TIMER AND SWITCH
H — HEATER VARIACS
I — PERISTALTIC PUMP
J — AIR PRESSURE REGULATOR

DWG. NO. K/G-79-1192 (U)

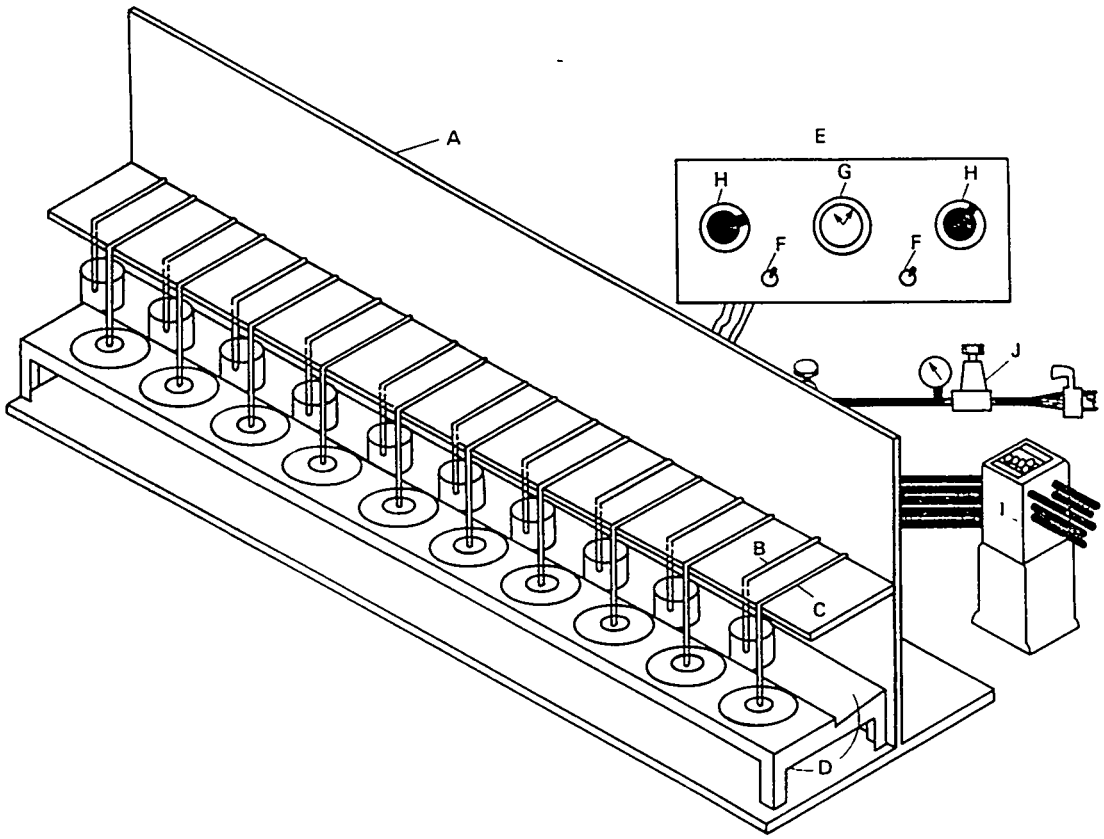

Figure 1
SEMI-AUTOMATIC TOPO APPARATUS

UCN-10766B (12 8-78)

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-510
DATE	October 27, 1982
SUPERSEDES	
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ASBESTOS IN INSULATING MATERIALS, POLARIZED LIGHT MICROSCOPY (QUALITATIVE) METHOD

Analyte:	Asbestos	Method:	IHA-510
Matrix:	Insulation Materials	Range:	0.1% to 100% by wt
Procedure:	Representative sampling of fibers; examination with polarized light microscopy.	Precision and Accuracy:	Method is qualitative only.

1.0 Scope and Application

1.1 This procedure is used to identify the presence of asbestos fibers in insulation materials such as fabrics, pipe wrapping, bulk fibers, hard composites, etc. Fibrous asbestos of concern to EPA and OSHA, assumes an aspect ratio (length:width) of $\geq$ 3:1. Asbestos, if found in insulation is generally at least 10:1 to 50:1 in aspect ratio.

1.2 For the purpose of this procedure, asbestos is defined as consisting of the fibrous minerals chrysotile, amosite, crocidolite, or anthophyllite. These are also the minerals which are available as standard asbestos samples. The Environmental Protection Agency (EPA) includes actinolite and tremolite in their definition and some data for these minerals are included in this procedure. However, during several years of experience at ORGDP, the asbestos in insulation has been either chrysotile or amosite.

1.3 The procedure is used to support the health and safety standards for personnel and environmental protection. EPA has issued regulations for control of asbestos; the Occupational Safety and Health Administration (OSHA) has adopted similar control measures. This analytical procedure provides the Industrial Hygiene departments of the four UCC-ND plants a basis for control of "asbestos material", as defined by EPA (i.e., material containing more than 1% asbestos by weight). If more quantitative results are needed, the laboratory must resort to special ignition techniques and perhaps chemical analyses, to complement microscopic examination.

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1.4 As a qualitative procedure, the technique permits the identification of asbestos as a contaminant in other materials.

2.0 Principle of the Method

2.1 Fibrous portions of the sample are obtained.

2.2 Morphology, appearance with crossed polarizers, and indices of refraction are determined and compared with the characteristics of standard asbestos samples.

2.3 The investigator decides whether asbestos is present and makes a qualitative judgment of whether the content exceeds 1% by weight.

3.0 Range and Sensitivity

3.1 Chrysotile, the most common form of asbestos, can be detected in samples containing as little as 0.1%, if the fibers are larger than 0.5 μm thick and 5 μm long.

3.2 The other forms can be detected at the same concentration, but it may be necessary to spend more time. It should be realized that sensitivity is dependent on the time devoted to viewing the sample.

4.0 Interferences

4.1 Certain finely divided organic fibers (espec. wood or cotton) might resemble chrysotile in optical properties, but comparison of refractive indices, perpendicular and parallel to the plane of polarization, will usually permit positive identification. An intact cotton fiber is normally recognized by its morphology. If identification is not certain, ashing can be used to destroy the organic material.

4.2 It will be necessary to ash samples which contain high percentages of organic fibers in order to determine whether or not asbestos is also present.

4.3 Fibers in the sample might be coated with carbonized material or a fine powder, which will prevent the determination of optical properties. Cleaning by ultrasonics in water will usually remove enough of the coating so that the fibers can be identified.

5.0 Precision and Accuracy

5.1 The method is not quantitative although estimates of content can be made by a trained microscopist.

5.2 As presently applied by experienced microscopists, the method permits a judgment of mass % of asbestos, using the low-power stereo microscope, the polarized microscope techniques, and the general evidence of the mode of fiber incorporation in the sample.

5.3 If asbestos is detected by the application of this procedure, without applying special additional efforts, the analytical report generally will indicate that the asbestos is at least 1% by weight. This approach gives the Industrial Hygiene programs an extra margin of asbestos control.

6.0 Advantages and Disadvantages

6.1 The method is rapid, sensitive, and capable of distinguishing types of asbestos which are difficult to distinguish by other methods. Operators can be trained in a few days and the equipment is relatively inexpensive.

6.2 Important disadvantages are the difficulty of making the method quantitative and the fact that operator judgment cannot be eliminated.

7.0 Apparatus

7.1 Polarized light microscope with a revolving stage, a first-order red retardation plate, and a McCrone disperion staining objective: Olympus BHP, or equivalent.

7.2 Low-power stereo microscope.

7.3 Asher, preferably low-temperature oxygen plasma.

7.4 Ultrasonic bath, e.g., Heat Systems, Inc., 5 x 9 inches, with 125 watts power.

7.5 Miscellaneous laboratory equipment (tweezers, microscope slides and cover glasses, beakers, petri dishes, etc.).

8.0 Reagents

8.1 Cargille high disperson (HD) index of refraction liquids set (N_D^{25} 1.500 to 1.640) and standard liquids (N_D^{25} 1.642 to 1.700).

8.2 U.I.C.C* reference asbestos samples (chrysotile, crocidolite, amosite, and anthophyllite distributed by Duke Standards Co., Palo Alto, CA 94306).

9.0 Procedure

9.1 Sampling. Insulation is usually non-uniform, and considerable care should be taken to remove representative fibers for examination from several regions. Take samples from regions which vary in color or texture, from surfaces and the interior, in a fabric from the warp and the weft, etc. Fibers can usually be obtained with tweezers while observing with a stereo microscope. If fibers are not visible, crush the sample and examine the resulting powder.

9.2 Place the fibers on a clean microscope slide, add a cover glass, and place a drop of 1.550 HD index of refraction liquid on the slide in contact with the cover glass so that the liquid will be drawn under the cover glass. Press lightly with a pencil eraser to expel most of the air.

9.3 Examine for birefringence. Insert the analyzer and check that the analyzer and the polarizer are crossed (on the Olympus BHP, both are in the "0" position). If no fibers are visible, no asbestos is present and the analysis can be terminated. To be certain that there are no birefringent fibers, a high level of illumination should be used (8 on the intensity scale with the Olympus BHP), with a 10X objective so that the preparation can be examined completely, with a 40X objective so that small fibers will not be overlooked, and at 2 positions of the rotating stage (45° apart) so that fibers oriented in the extinction positions will not be missed.

9.4 Determine the sign of elongation. With crossed polarizers select a birefringent fiber showing a first-order gray color and position this fiber near the center of the field. Insert the first-order red plate (R1) and observe the colors when the fiber

*Union Internationalle Contre le Cancer.

is oriented parallel and perpendicular to the slow direction of R1 (the slow direction is marked with a Z on the Olympus R1). If the fiber is blue when parallel to the slow direction, the sign of elongation is +; if yellow when parallel, the sign is -. Examination when the fiber is perpendicular to the slow direction should give the confirmatory opposite color. Crocidolite has a negative sign of elongation. All other forms of asbestos are positive. (See Table 1.)

9.5 Color and morphology. Remove the analyzer and observe the fibers. Crocidolite is blue or blue-gray; the other asbestos types are lightly colored and usually appear white in the microscope. Chrysotile fibers are frequently curved or wavy, crocidolite is sometimes curved, and amosite and anthophyllite are straight. (See Table 2.)

9.6 Dispersion Staining. Rotate the lens turret to position the disperson staining objective, move the central stop into position, and adjust the field diaphragm to obtain a dark field. Chrysotile will appear magenta or blue depending on orientation of the fiber relative to the plane of polarization. To identify other forms of asbestos, it is necessary to mount the fibers in other index of refraction liquids. Table 2 lists the liquids to use and the colors obtained.

9.7 Indices of Refraction. The magenta to blue-magenta colors obtained with dispersion staining indicate a close match of the liquid and fiber indices of refraction, and it is usually unnecessary to measure the indices more precisely. However, a skilled microscopist can develop more precise data. To make this measurement, obtain axial illumination and observe the movement of the Becke line as the focus is raised; if the Becke (white) line moves into the fiber, try a liquid with a higher index of refraction; if the Becke line moves into the liquid, try a liquid with a lower index of refraction. Repeat until matching liquids are found for fiber orientations parallel and perpendicular to the plane of polarization. Refer to Table 1 for correlation of indices of refraction with asbestos type.

9.8 Useful information about non-asbestos fibers present in the sample can be obtained while looking for asbestos. With a little practice and reference to the "Particle Atlas", glass fibers, mineral wool, cellulosic fibers (wood, cotton, etc.), and many synthetic fibers can be identified.

UCN-10766B (12 8-78)

10.0 References

10.1 Hartshorne, N. H., and Stuart, A.; *Crystals and the Polarizing Microscope*, Third Edition; Pitman Press, Bath, England; 1960.

10.2 McCrone, W. C., Delly, J. G., and Palenik, S. J.; *The Particle Atlas*, Second Edition; Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan; 1973 to 1980.

10.3 Bartlett, T. W.; "Detection of Asbestos by Polarized Light Microscopy and by Transmission Electron Microscopy"; Union Carbide Corporation-Nuclear Division, Oak Ridge Gaseous Diffusion Plant, Oak Ridge, Tennessee; presented at 24th Conference on Analytical Chemistry in Energy Technology, Gatlinburg, Tennessee, October 9, 1980.

10.4 McCrone, W. C.; "The Asbestos Particle Atlas"; Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan; 1980.

TABLE 1

REFRACTIVE INDICES OF ASBESTOS

Asbestos Type	Crystallographic Direction*	N_D^{25}	Range of N_D^{25}	Sign of Elongation
Chrysotile	γ	1.558	1.545-1.559	+
Chrysotile	α	1.544	1.531-1.555	
Amosite	γ	1.696	1.655-1.730	+
Amosite	α	1.670	1.635-1.695	
Crocidolite	γ	1.711	1.670-1.715	-
Crocidolite	α	1.691	1.655-1.700	
Anthophyllite	γ	1.634	1.630-1.655	+
Anthophyllite	α	1.610	1.610-1.640	
Actinolite	γ	1.647	1.600-1.630	+
Actinolite	α	1.633	1.625-1.655	
Tremolite	γ	1.630	1.595-1.630	+
Tremolite	α	1.599	1.590-1.675	

*All types of asbestos have three refractive indices, $\alpha < \beta < \gamma$. Except for crocidolite, the N_D^{25} parallel to plane of polarization will approximate the γ index; perpendicular will approximate the α index. This is reversed for crocidolite.

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TABLE 2

DISPERSION STAINING CHART FOR ASBESTOS

Asbestos Type	Index of Refraction Liquid	Color (Central Stop)	Remarks
Chrysotile* Chrysotile**	1.550	Magenta Blue	Fibers are frequently curved or wavy with splayed ends.
Amosite* Amosite**	1.680	Golden Magenta Blue	Fibers are straight.
Crocidolite* Crocidolite**	1.696	Magenta Blue	Color is blue-gray; can interfere with perception of dispersion staining color.
Anthophyllite* Anthophyllite**	1.620	Blue Light Blue	Fibers are straight.

*Fiber oriented parallel to plane of polarized light passed by polarizer.
**Fiber oriented perpendicular to plane of polarized light passed by polarizer.

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-515
DATE	June 15, 1983
SUPERSEDES	
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BENZO(A)PYRENE(BaP) IN FOSSIL FUEL PRODUCTS AND WASTE, HPLC METHOD

Analyte: Benzo(a)pyrene [BaP]

Matrix: Petroleum, shale oil, coal oil products and waste by-products

Procedure: HPLC (semi-preparative) isolation; HPLC quantitation, with fluorescence detector.

Method No: IHA-515

Range: 0.02 to 500 µg/g

Precision: 10% RSD

Accuracy: No bias observed

1.0 Principle of the Method

1.1 After dissolving the sample as completely as possible in benzene or methylene chloride, the BaP-enriched fraction is isolated using a semi-preparative scale polar aminocyano (PAC) HPLC column.

1.2 The eluate obtained in 1.1 is changed stepwise in polarity from 10% v/v methylene chloride in hexane, to methylene chloride, and finally to 66% v/v acetonitrile in methylene chloride. The column is re-equilibrated by reversing the sequence.

1.3 Recovery corrections are achieved by using a radioactive ^{14}C-BaP tracer, activity 5×10^5 dpm.

1.4 Final quantitation is accomplished using a reversed-phase (C_{18}) analytical scale HPLC column equipped with a fluorescence detector. The eluent is 75% acetonitrile/25% water (v/v).

1.5 A set of five BaP standards in acetonitrile fit to a linear least-squares line is used to calibrate the instrument in 1.4.

2.0 Range and Sensitivity

2.1 BaP may be measured routinely at concentrations of 1 to 500 µg/g of sample.

2.2 The sensitivity is readily extended as low as 0.02 µg/g by either concentrating the final extract, injecting the undiluted sample onto the isolation HPLC column (sec. 1.1), or taking a larger sample.

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3.0 Interferences

3.1 Principal potential interferences such as three benzofluoranthenes, perylene, and benzo(e)pyrene are either chromatographically resolved from BaP or else do not respond to the fluorescence wavelengths specified.

3.2 The commercially available compound, 6-methyl BaP, has been examined as a potential interference. This compound does not interfere with the quantitation of BaP.

3.3 Interferences from other alkylated BaP species have not been studied because of the commercial unavailability of such compounds.

4.0 Precision

4.1 Precision expressed as percent Relative Standard Deviation is as follows:

2% at 179 µg/g ..., average of 4 samples of a coal oil,
7% at 11 µg/g ..., average of 4 samples of a shale oil,
13% at 1.2 µg/g ..., average of 3 samples of a petroleum crude c

5.0 Advantages and Disadvantages of the Method

5.1 The method permits facile isolation and determination of BaP in many varied fossil fuel matrices.

5.2 The use of the labeled ^{14}C-BaP tracer enables an accurate recovery measurement which takes only a few minutes of the operator's time.

5.3 The initial cost of setting up the equipment (two HPLC units) and the recovery measurement (labeled tracer and counter) is considerable.

6.0 Apparatus

6.1 Isolation HPLC system, equipped with a loop injector (1000 µL and 250 µL loops), semi-preparative scale (10 mm O.D. x 25 cm) polar amino-cyano HPLC column (PAC, 10 µm particle diameter), and UV detector (analytical scale, 8 µL flow cell, 254 nm absorbance). The system should also be capable of selecting one of three eluants. A guard column with an amino cartridge is strongly recommended.

6.2 Analytical scale HPLC system, equipped with a loop injector (20 µL), reverse-phase analytical scale (4.6 mm I.D. x 10 or 25 cm) HPLC column (C_{18}, 5 µm or smaller particles), and a filter fluorescence detector (365 nm excitation, 425 nm emission). A single eluant is used. A guard column equipped with a reverse-phase C_{18} cartridge is strongly recommended.

6.3 Microliter pipets, various sizes.

6.4 Roundbottom flasks, 300-mL with standard socket joints or ₹ 24/40 joints.

6.5 Apparatus for removing solvent with dry, flowing nitrogen and vacuum. (see reference 12.2).

6.6 Stripchart recorders.

6.7 Apparatus for removing solvent with dry, flowing nitrogen alone, such as Silli-Vap.® (Pierce Chemical Co., Rockford, IL)

6.8 Volumetric flasks, with capacities of 10, 1, 0.5, 0.3, 0.1 mL, commercially available.*

6.9 Syringes with capacities of 5, 1, and 0.1 mL.

6.10 Magnetic stirrer and oversize stirring bars.

6.11 Rotary evaporator.

6.12 Packard C-2425 Tricarb Liquid Scintillation Counter or equivalent.

6.13 Filtering flasks, 250 mL.

6.14 Sintered glass Buchner funnel, medium porosity frit, 60 mL capacity.

7.0 Reagents

7.1 Methylene chloride, "Distilled in Glass" grade, residue-free.

7.2 Acetonitrile, non-spectro grade, "Distilled in Glass", residue-free.

7.3 Hexane, non-spectro grade, "Distilled in Glass", residue-free.

7.4 Benzene, spectro grade, "Distilled in glass", residue-free.

7.5 10% v/v methylene chloride/balance hexane, using 7.1 and 7.3 above.

*Volumetric flasks, volume 1 mL and less: SGA Part No. JM-6180, specify capacity; SGA Scientific, Inc., Bloomfield NJ, 07003.

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7.6 75% v/v acetonitrile/balance water, using 7.2 above. Degas before use.

7.7 ^{14}C-BaP radiolabeled tracer in benzene solution. Activity ~ 5 x 10^5 dpm/mL, and ~ 1 µg/mL. (Nominal specific activity = 30 mCi/mmol.)

7.8 Benzo(a)pyrene, stock solution, 25 mL, 100 µg/mL. Dissolve 2.5 mg of 99%+ benzo(a)pyrene in 25 mL of acetonitrile. Store in refrigerator.

7.9 BaP working standard solutions of 1.0, 0.5, 0.25, 0.1, and 0.05 µg/mL BaP in acetonitrile, prepared from 7.8 by serial dilution. Store in refrigerator.

7.10 Pyrene, 99+% purity.

7.11 Phenanthrene, 99+% purity.

7.12 Standard solution of pyrene, phenanthrene, and BaP, 100 µg/mL each, in 50% v/v methylenechloride in hexane.

7.13 Supply of toluene scintillator cocktail solution.

7.14 Tetrahydrofuran, THF, "Distilled in glass" grade, residue-free.

8.0 Procedure

8.1 It should be established upon receipt of the sample whether it is a (a) highly refined shale oil product, (b) petroleum crude or highly refined coal oil product, (c) crude shale oil or low-boiling coal oil product, (d) high-boiling coal oil product, or (e) solid residue. Each of these materials has a typical expected BaP concentration, and each is prepared separately for analysis.

8.1.1 If the sample is a highly refined shale oil product, add no ^{14}C-tracer solution to the sample (recovery assumed to be 100%). Sample weight is established by the (PAC) HPLC loop volume and the liquid sample density.

8.1.2 If the sample is a highly refined coal oil product or petroleum crude, add no ^{14}C-tracer solution to the sample (recovery assumed to be 100%). Sample weight is established by the (PAC) HPLC loop volume and the liquid sample density.

8.1.3 If the sample is a crude shale oil or low-boiling coal oil product, accurately weigh 1.00 g of sample into a 10 mL volumetric flask and add 1 mL of ^{14}C-BaP tracer solution. Dilute to volume with benzene.

8.1.4 If the sample is a high-boiling coal oil product, accurately weigh 0.050 g into a 10 mL volumetric flask and proceed as for 8.1.3.

8.1.5 If the sample is a solid product, e.g. a flaked bottom product, grind to a fine powder using a mortar and pestle, and weigh 1.00 g

8.1.5.1 Dissolve the sample as completely as possible with 50 mL of THF in a 1 L beaker.

8.1.5.2 Add 1 mL ^{14}C-BaP tracer solution.

8.1.5.3 Add, with magnetic stirring, 400 mL of pentane to the solution in 8.1.5.1. Stir for ten minutes.

8.1.5.4 Permit the solution to remain undisturbed for thirty minutes.

8.1.5.5 Filter the solution through a medium porosity sintered glass funnel using vacuum filtration.

8.1.5.6 Take the filtrate of 8.1.5.5 to dryness by rotary evaporation.

8.1.5.7 Redissolve the residue in exactly 10 mL of methylene chloride.

8.2 Elute a 250 µL aliquot of the standard three-component mixture (7.12) through the PAC column (see 6.1) using 10% methylene chloride/hexane as the eluant, flow rate 3 mL/min.

8.2.1 Locate the retention time of BaP.

8.2.2 The volume of eluant eluting ± 10 minutes of the BaP retention time is the "BaP enriched fraction", and should be collected for real samples.

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8.3 Inject the sample prepared in section 8.1 onto the PAC column as follows, depending on the sample type:

8.3.1 Inject 1.00 mL of the highly refined shale oil product by loop injection without dilution.

8.3.2 Inject 0.250 mL of the highly refined coal oil product or petroleum crude without dilution by loop injection.

8.3.3 Inject 0.250 mL of the solution of crude shale oil (8.1.3), high-boiling coal oil(8.1.4), or solid product (8.1.5) by loop injection.

8.4 Collect the BaP-enriched fraction, using 10% v/v methylene chloride/hexane as the eluant.

8.5 Remove the solvent from the BaP-enriched fraction using either the rotary evaporator or the concentration apparatus of 6.5.

8.6 Redissolve the BaP-enriched fraction as follows:

8.6.1 For highly-refined shale oil or highly-refined coal oil products, redissolve in 0.1 mL of acetonitrile.

8.6.2 For all other samples, redissolve in 1.0 mL of acetonitrile.

8.7 Determine the isolation recovery of BaP by counting 100 µL of the solution in 8.6.2 mixed with 10 mL of scintillation cocktail using the scintillation counter.

8.8 Flush and re-equilibrate the PAC column as follows:

8.8.1 Elute polar material, but do not collect, from the column for 30 minutes with methylene chloride at a rate of 3 mL/min.

8.8.2 Elute polar material, but do not collect, from the column for 30 minutes with 2/1 v/v acetonitrile/methylene chloride at a rate of 3 mL/min.

8.8.3 Repeat step 8.8.1.

8.8.4 Flush and re-equilibrate the column for 30 min with 10% v/v methylene chloride in hexane at a rate of 3 mL/min.

8.8.5 The entire isolation and three-component standard chromatograms should resemble those in Figure 1. The figure also shows how the BaP fraction is obtained.

8.9 Degas by vacuum one liter of 75% v/v acetonitrile (balance water) for 30 min, to be used as the eluant in the analytical HPLC. Flow rate should be 1 mL/min.

8.10 Inject a 20-µL aliquot of the BaP-enriched fraction prepared in 8.6.

8.11 Record the peak height or area from the instrument readout or recorder.

8.12 BaP typically elutes in 25 min under the conditions specified. A sample chromatogram is given in Figure 2.

9.0 Calibration and Standards

9.1 Calibration is established by injecting the BaP standards given in 7.9 onto the analytical scale HPLC column and recording the peak heights or areas.

9.2 The peak heights or areas are plotted against the standard concentrations and are fitted to a linear least squares line. The correlation coefficient typically exceeds 0.99.

9.3 The least squares line is used to determine the concentration of BaP in the BaP-enriched fraction.

10.0 Calculations

10.1 The concentration of BaP in the original sample on a weight/weight basis (typically µg/g) may be expressed:

$$\text{BaP, } \mu g/g = \frac{C\ V_i}{W(v_l/V_o)Y} - \frac{w_s\ Y}{W}$$

where:
- C = BaP in the BaP-enriched isolate, µg/mL
- V_i = volume of the BaP-enriched isolate, mL
- W = sample mass, g
- v_l = volume of the sample loop for injection to (PAC) HPLC column, mL.
- V_o = total sample solution volume (8.1.3, 8.1.4, 8.1.5), mL
- Y = overall recovery (fraction) of the ^{14}C-labeled BaP
- w_s = mass of BaP tracer added to the sample, µg

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When analyzing all types of samples except highly refined products or petroleum crudes, v_l is a constant (v_l = 0.250 mL), which simplifies the major expression to:

$$\text{BaP, } \mu g/g = \frac{4CV_iV_o}{WY} - \frac{w_s\ Y}{W}$$

10.2 In the cases where the sample is injected directly into the (PAC) HPLC, with no tracer added, a recovery of 100% is assumed and the equation becomes:

$$\text{BaP, } \mu g/g = \frac{C\ V_i}{W}\ ,$$

or

$$\text{BaP, } \mu g/g = \frac{C\ V_i}{v_l\ \rho}\ ,$$

where ρ = density of the liquid sample, g/mL

11.0 Quality Assurance

11.1 The quality assurance standard for this procedure is NBS SRM 1580, "Organics in Shale Oil,"available from the Office of Standard Reference Materials, National Bureau of Standards, Washington, D.C. The certified value for BaP is 21 ± 6 µg/g. The ORNL analytical results on this standard, collected from November 1981 through January 1982, averaged 20.8 µg/g.

11.2 SRM 1580 should be analyzed monthly as a quality assurance check.

12.0 References

12.1 Tomkins, B. A., Reagan, R. R., Caton, J. E., and Griest, W. H.; "Liquid Chromatographic Determination of Benzo(a)Pyrene in Natural, Synthetic, and Refined Crudes," Anal. Chem., 53, 1213-17 (1981).

12.2 Higgins, C. E. and Guerin, M. R., "Recovery of Naphthalene during Evaporative Concentration," Anal. Chem., 50, 1984-87 (1980).

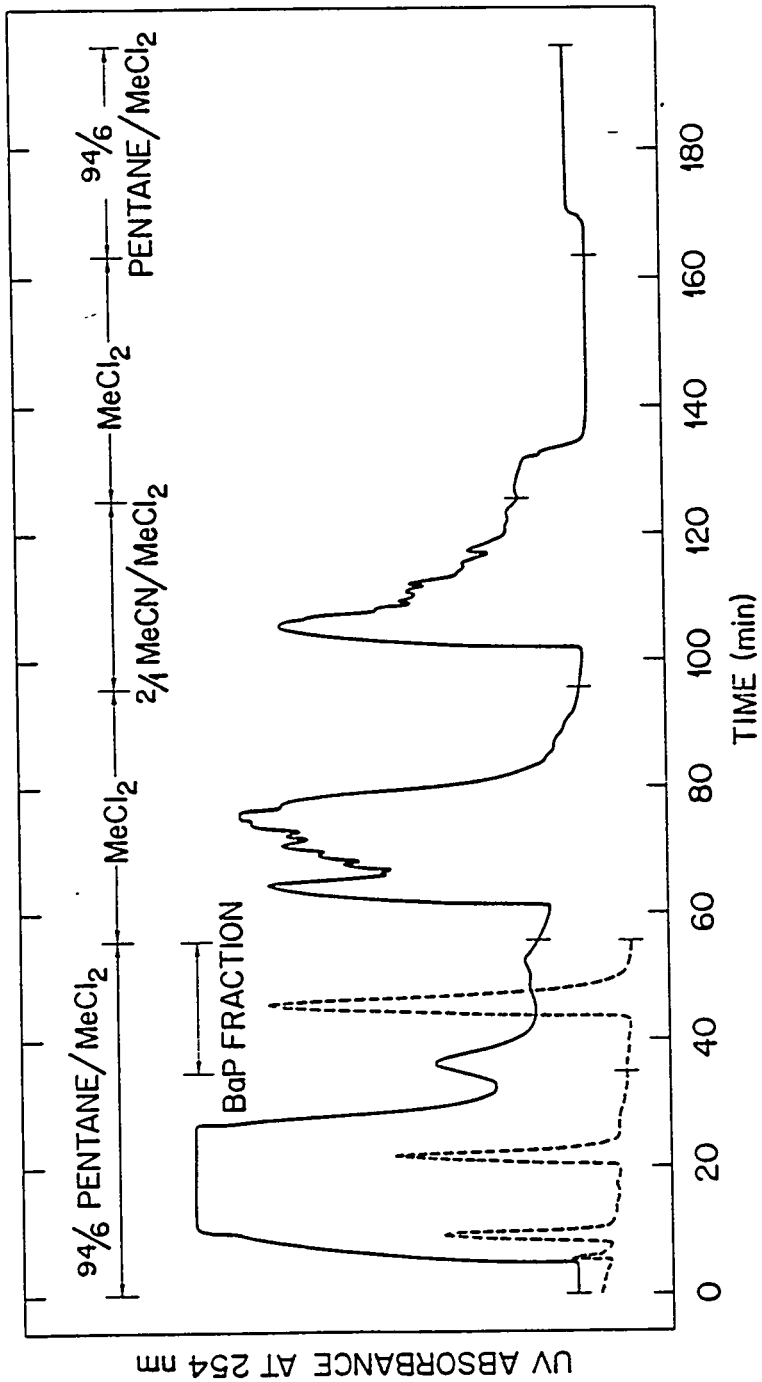

Figure 1. Isolation chromatogram of a coal oil.

The dotted lines show the three-component standard. BaP-enriched fraction collected in the region noted.

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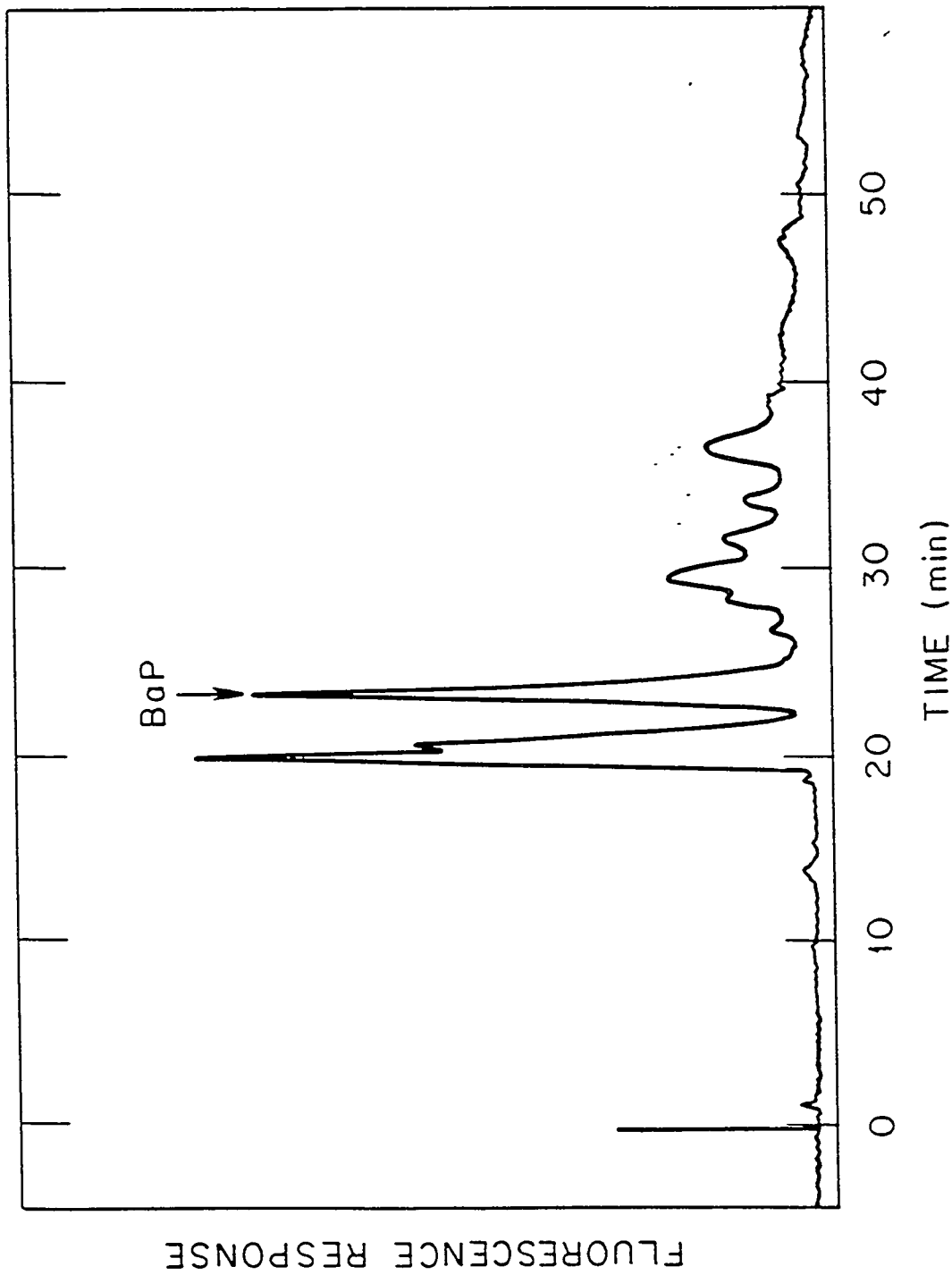

Figure 2. Quantitative HPLC chromatogram of the BaP-enriched fraction of a coal oil, collected in Figure 1.

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-520
DATE	August 27, 1980
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COLIFORM BACTERIA (TOTAL) IN DRINKING WATER, MEMBRANE FILTER METHOD

Analyte:	Total Coliform Bacteria	Method No.:	IHA-520
Matrix:	Drinking Water	Range:	Lower - 1 colony/100 ml Upper - Depends on dilution
Procedure:	Collection on membrane filter; incubation on culture medium; counting colonies at 10-15X magnification	Precision:	See Section 4.0

1.0 Principle of Method

1.1 This test determines the total coliform density in various types of water samples, as an indication of potability.

1.2 A water sample (normally 100 ml) is filtered through a membrane filter and the filter is incubated in contact with a pad saturated with M-Endo culture medium at 35 ± 0.5°C for 22 to 24 hours.

1.3 The coliform colonies are counted directly under a microscope or other optical device. The coliform density is reported as colonies per 100 ml.

1.4 The presence of coliform bacteria in water is a warning sign that other dangerous bacteria may be present. Their absence, however, does not rule out the presence of other harmful bacteria.

2.0 Range and Sensitivity

2.1 This procedure is designed to cover the range of 1-80 coliform colonies per 100 ml when the usual 100-ml sample of drinking water is filtered. The high end can be extended, however, by reducing the amount of sample filtered (by dilution if necessary - see Section 8.2.6.2) as long as the sample size selected produces approximately 50 coliform colonies (20-80 is ideal) and not more than 200 colonies of all types on the membrane filter to be tested.

3.0 Interferences

3.1 Low coliform estimates may be caused by the presence of high numbers of noncoliforms, or by substances toxic to the procedure, such as zinc, copper, heavy metals, and phenols.

APPROVED BY Y-12	LAB A. F. McElhaney IH W. S. Emmett, Jr.	APPROVED BY ORGDP	LAB T. Kwasowski IH D. J. Duncan	APPROVED BY UCCND-COORD'R C. W. Weber
APPROVED BY PGDP	LAB R. E. Simmons IH C. N. Turuk	APPROVED BY ORNL	LAB W. R. Laing IH James A. Ealy	NUMBER IHA-520

4.0 Precision and Accuracy

4.1 Although the statistical reliability of the membrane filter technique is greater than that of the Most Probable Number (MPN) procedure (see Reference 10.1), membrane counts are not really absolute numbers. No accuracy data are available. The precision data in Table 1 illustrate some 95% confidence limits.

Table 1

95% CONFIDENCE LIMITS FOR MEMBRANE FILTER RESULTS USING A 100-MILLILITER SAMPLE

Number of Coliform Colonies Counted	95% Confidence Limits Lower	Upper
1	0.05	3.0
2	0.35	4.7
3	0.81	6.3
4	1.4	7.7
5	2.0	9.2

5.0 Advantages and Disadvantages

5.1 Widespread use of the membrane filter technique has confirmed its high degree of reproducibility, its acceptability to testing larger sample volumes, and its ability to yield definite results more rapidly than the MPN procedure.

5.2 The procedure is extremely useful in emergencies and in the examination of most waters as an indication of potability.

5.3 Turbidity caused by algae or other interfering material may not permit testing of a sample volume large enough to yield significant results. (Normally this is not a problem with drinking water.)

5.4 The presence of high numbers of noncoliforms or substances toxic to colony growth (see Section 3.1) may cause low coliform estimates.

6.0 Apparatus

6.1 Sterile membrane filter, grid-marked, such as Millipore filter type HA, 47-mm diameter, 0.45-micron pore size (see Section 8.2.1.3).

6.2 Sterile absorbent pads for nutrient (see Section 8.2.1.3).

6.3 Sterile culture container (15 x 60-mm diameter petri dishes): glass, borosilicate, or equivalent grade; or 12 x 50-mm diameter plastic, disposable sterile petri dishes with tight fitting lids.

6.4 Sterile pipets, 10-ml, graduated in 1 ml.

6.5 Sterile pipets, 1-ml, graduated in 0.1 ml.

6.6 Pipet boxes, stainless steel or aluminum; or autoclavable glass trays.

6.7 Polypropylene bottles, autoclavable, 500-ml: Nalge #2006, or equivalent.

6.8 Milk dilution bottle, Pyrex brand, graduated at 99 ml for dilution water, preferably screw-cap type.

6.9 Sterile funnel apparatus, Millipore 47-mm filter assembly No. xx1004700, or equivalent.

6.10 Dissecting microscope with 10X or 15X magnification, or other suitable optical device, such as an illuminated magnifying lens.

6.11 Steam autoclave, with approved gauges.

6.12 Source of vacuum.

6.13 Burner, alcohol or gas.

6.14 Forceps with smooth flat inner surface, not sharp on edges or corners, Millipore Filter Corporation Cat. No. xx6200006, or equivalent.

6.15 Sterilizing oven, with thermostat and thermometer; it should reach and maintain a temperature of at least 170°C. Alternatively, an autoclave or an ultraviolet sterilizer can be used.

6.16 Sample bottles with penny-head ground-in glass stoppers, autoclavable, 250-ml wide-mouth, clear reagent glass, Curtin Matheson Scientific Co. Cat. No. 033-720, or equivalent.

6.17 Incubator, Thelco Model 2, or equivalent; or incubation water bath with cover; to maintain a temperature of 35 ± 0.5°C.

6.18 Kraft paper.

6.19 Ultraviolet sterilizer (optional): Millipore XX6370000, or equivalent.

7.0 Reagents

7.1 Dehydrated M-Endo broth culture medium (BBL), or M-Endo broth medium prepared ready for use in 2-ml glass ampules. Both are available from Fisher Scientific Co.--Cat. Nos. B11205 and 9-730-108, respectively.

7.2 Ethyl alcohol, 95%.

7.3 Sodium thiosulfate solution, 10% (w/v): Dissolve 100 g of $Na_2S_2O_3$ in 800 ml of distilled water, and dilute to 1 liter.

7.4 Potassium phosphate, monobasic (KH_2PO_4).

7.5 Sodium hydroxide solution, 1 N: Dissolve 40 g of NaOH in distilled water and dilute to 1 liter.

7.6 Magnesium sulfate ($MgSO_4 \cdot 7H_2O$).

7.7 EDTA Reagent, 15% (w/v): 15 g of the disodium salt of ethylenediamine-tetraacetic acid (EDTA) is dissolved in 80 g of water and diluted to 100 ml.

8.0 Procedure

8.1 Water Sampling and Preservation

8.1.1 Containers

8.1.1.1 Samples for bacteriologic examination must be collected in bottles that have been cleansed and rinsed with great care, given a final rinse with distilled water, and sterilized.

8.1.2 Dechlorination

8.1.2.1 A dechlorinating agent should be added to bottles intended for the collection of water samples containing residual chlorine. Sodium thiosulfate is a satisfactory dechlorinating agent. Its presence at the instant of collection of a sample from a chlorinated supply will neutralize any residual chlorine and will prevent a continuation of the bactericidal action of the chlorine during the time the sample is in

transit to the laboratory. The bacteriologic examination will then indicate more probably the true bacterial content of the water at the time of sampling.

8.1.2.2 The sodium thiosulfate should be added to the clean sample bottle before sterilization, in an amount sufficient to provide an approximate concentration of 100 mg/liter in the sample. This can be accomplished by adding 0.1 ml of a 10% solution of sodium thiosulfate to a 120-ml (4-oz) bottle (this will neutralize a sample containing about 15 mg of residual chlorine/liter). The bottle is then stoppered, capped, and sterilized by either dry or moist heat as described in Section 8.2.1.2.

8.1.3 Metal Chelation (Normally not necessary for drinking water)

8.1.3.1 Water samples high in copper or zinc, and wastewater samples high in heavy metals, should be collected in sample bottles containing a chelating agent that will reduce metal toxicity. This is particularly important when such samples are in transit for 24 hours or more. Ethylenediaminetetraacetic acid (EDTA) is a satisfactory chelating agent. A concentration of 372 mg/liter has been found adequate. The EDTA may be added separately to the sample bottle before bottle sterilization (0.3 ml of a 15% solution in a 120-ml bottle) or it may be combined with the sodium thiosulfate (dechlorinating) solution before addition to the sample bottle.

8.1.4 Sample Collection and Storage

8.1.4.1 When the sample is collected, leave ample air space in the bottle (at least 2.5 cm or 1 inch) to facilitate mixing of the sample by shaking preparatory to examination.

8.1.4.2 Exercise care to take samples that are representative of the water being tested and to avoid contamination of the sample at the time of collection or in the period before examination.

8.1.4.3 The sampling bottle shall be kept unopened until the moment it is to be filled. Then remove the stopper, taking care to avoid soiling.

8.1.4.4 During sampling, hold the bottle near the base; fill it without rinsing, and replace the stopper immediately. Do not handle the neck of the bottle, or unnecessarily handle the stopper.

8.1.4.5 The volume of sample should be sufficient to carry out the tests required, preferably not less than 100 ml.

8.1.4.6 All samples should be accompanied by complete and accurate identifying and descriptive data.

8.1.4.7 If the samples cannot be processed within 1 hour after collection, the use of iced coolers is recommended for storage during transport to the laboratory.

8.1.4.8 If refrigeration of individual potable water samples sent to the laboratory by mail service is not possible, the use of a thermos-type insulated sample bottle that can be sterilized is recommended as an option.

8.1.4.9 The bacteriological examination of a water sample should be started promptly after collection to avoid unpredictable changes, but in no case should the time elapsing between collection and examination exceed 30 hours.

8.1.4.10 The time and temperature of storage of all samples should be recorded and should be considered in the interpretation of data.

8.2 Determination of Total Coliform Density

8.2.1 Sterilization of Equipment

8.2.1.1 Wash all glassware and filtering equipment using a suitable detergent. Rinse thoroughly with tap water followed with distilled water, and dry. The surfaces should be free of any residue.

8.2.1.2 Sterilize glassware not in metal containers by dry heating for not less than 60 minutes at 170°C. Sterilize glassware in metal containers for not less than 2 hours at 170°C. As an alternative, sterilization can be done in an autoclave at 121°C for 15 minutes, for items not in closed containers. Also, sterilization can be done in an ultraviolet sterilizer, following manufacturer's instructions.

8.2.1.3 Membrane filters are commercially available, conveniently packaged in units of 10, sterilized, and ready for use. The packets also contain 10 sterilized absorbent pads.

8.2.1.4 Autoclave 500 ml of buffered dilution water (see Section 8.2.2) in a 500-ml sample bottle for rinsing and dilution purposes. If sample dilution is necessary, autoclave the 99-ml dilution bottles, after filling to 102 ml with buffered dilution water.

8.2.1.4.1 Screw caps on loosely and place bottles upright in a basket or suitable holder. Cover with heavy brown Kraft paper, unless they are to be used immediately after sterilization.

8.2.1.4.2 Autoclave for 20 minutes at 121°C and 15 psig. Start timing when autoclave has reached the proper temperature and pressure.

8.2.1.4.3 Turn off steam supply after 20 minutes and allow autoclave to cool <u>slowly</u>.

8.2.1.4.4 When the gauge pressure reaches zero, remove the bottles from the autoclave.

8.2.1.5 Sterilize funnel and base. If they are to be stored before use, wrap separately in Kraft paper and autoclave for 15 minutes at 121°C and 15 psig. Alternatively, use an ultraviolet sterilizer. Wrapping may be omitted if the equipment is to be used immediately after sterilization.

8.2.1.6 Sterilize the forceps used for handling sterile filter.

8.2.1.6.1 Place the tip of the forceps into a 50-ml beaker containing a one-inch level of 95% ethyl alcohol.

8.2.1.6.2 Light the alcohol or gas burner.

8.2.1.6.3 Remove the forceps from the beaker and place the tip over the flame source just long enough to ignite the alcohol. Do <u>not</u> prolong heating.

8.2.1.6.4 The forceps are sterile and ready to use as soon as the alcohol on the forceps is consumed and the flame is out.

8.2.2 Preparation of Buffered Dilution Water

8.2.2.1 Weigh 34.0 grams of potassium phosphate, monobasic (KH_2PO_4) into 500 ml of distilled water.

8.2.2.2 Adjust the pH to 7.2 with 1 N NaOH and dilute to 1 liter with distilled water. This is the stock phosphate buffer solution and should be refrigerated.

8.2.2.3 Prepare magnesium sulfate solution: 50 g of $MgSO_4 \cdot 7H_2O$ dissolved in distilled water and diluted to 1 liter.

8.2.2.4 Add 1.25 ml of the stock phosphate buffer solution and 5.0 ml of magnesium sulfate solution to 1 liter of distilled water. (When sample dilution is necessary, dispense 102 ml of this buffered water into a dilution bottle to provide 99 ml after autoclaving for 20 minutes.)

8.2.3 Preparation of M-Endo Culture Medium

8.2.3.1 A commercially prepared dehydrated M-Endo culture medium may be purchased from Fisher Scientific Co. (Section 7.1).

8.2.3.2 Rehydrate the M-Endo culture medium in 1 liter of distilled water containing 20 ml of 95% ethyl alcohol.

8.2.3.3 Heat the medium to the boiling point, promptly remove the medium from the heat, and cool it to below 45°C. Do not sterilize by autoclaving. Final pH should be between 7.1 and 7.3.

8.2.3.4 The finished medium should be stored in the dark at 2 to 10°C and any unused medium discarded after 96 hours.

8.2.3.5 Alternatively, commercially prepared M-Endo culture medium, packaged and ready for use in 2-ml glass ampules, may be purchased from Fisher Scientific Co. (Section 7.1).

8.2.4 Preparation of Petri Dishes for Receiving Membranes

8.2.4.1 Being careful to avoid contamination, label the sterile petri dishes with sample numbers corresponding to those on a worksheet.

8.2.4.2 Place a sterile absorbent pad into each labeled dish and deposit 1.8 - 2.0 ml of prepared culture medium onto the pad.

8.2.5 Preparation of Filter Apparatus

8.2.5.1 Connect two suction flasks in series, using one for the filter receptacle and the other to protect the vacuum system from water being pulled in accidentally. Connect the train to a source of vacuum with a length of vacuum hose.

8.2.5.2 Place a sterile filter on the sterile filter receptacle, center it properly, and then place the funnel on the filter receptacle (see Section 6.9).

8.2.6 Preparation of Sample

8.2.6.1 Depending on the expected bacterial density and degree of turbidity, select the proper water sample size and transfer to the filter apparatus. When testing drinking water, a 100-ml sample is normally used.

8.2.6.2 Sample Dilution

8.2.6.2.1 Sample dilution is normally not necessary for drinking water, but can be used to extend the upper end of the procedure range if the degree of contamination requires it.

8.2.6.2.2 Shake the bottle containing the sample 25 times to ensure adequate mixing; remove the top and flame the mouth of the bottle to sterilize it.

8.2.6.2.3 Remove the screw cap from a sterile dilution bottle containing 99 ml of sterile dilution water and flame the mouth of the bottle.

8.2.6.2.4 Using a sterile pipet, transfer exactly 1 ml of sample into the 99 ml of dilution water. Flame the mouth of the dilution bottle and carefully replace the cap.

8.2.6.2.5 Shake the bottle 25 times. Remove the cap and flame the mouth of the bottle again.

8.2.6.2.6 With the vacuum turned off, pour 25-30 ml of sterile buffered water into the funnel to provide a better distribution of the sample over the surface of the filter.

8.2.6.2.7 Using a sterile 1-ml pipette, transfer exactly 1 ml of diluted sample from the dilution bottle onto the filter. At this point, 0.01 ml of the original sample has been processed.

8.2.6.2.8 If additional dilution is required, transfer 1 ml of solution from the first dilution bottle to a second sterile dilution bottle and proceed from Step 8.2.6.2.4. This will result in 0.0001 ml of the original sample having been processed.

8.2.6.2.9 Carefully remove the filter paper from the funnel and place it into a prepared petri dish (8.2.4). Ensure that good contact is made between the filter paper and the sterile absorbent pad.

8.2.6.2.10 Between samples, sterilize the funnel and base by immersing in boiling water for 1 minute, or by flaming with a gas burner, or by placing the unit under a UV lamp for 2 minutes. Cool before use.

8.2.7 Incubation

8.2.7.1 Place all prepared cultures (8.2.6.2.9) upside down in an incubator or above a hot water bath within 30 minutes after filtration.

8.2.7.2 Incubate at 35 ± 0.5°C for 22-24 hours.

8.2.8 Counting

8.2.8.1 Place the filter membrane in the field of a 10-15X microscope or other suitable optical device. Adjust the light source (daylight fluorescent is best) from above and approximately perpendicular to the plane of the membrane.

8.2.8.2 Count all colonies having a pink to dark red color with a metallic sheen. The sheen may vary in size from a small pinhead to complete coverage of the colony surface.

8.2.8.3 Record on an appropriate data sheet the number of colonies counted on each filter.

9.0 Calculation

9.1 Calculate the total coliform density as follows:

$$\text{Total coliform colonies/100 ml} = \frac{A \times 100}{B}$$

where:

A = total coliform colonies counted, and

B = volume of original sample filtered, ml.

10.0 References

10.1 Standard Methods for the Examination of Water and Wastewater, 14th Edition; Method No. 908A, p. 916 (1975).

10.2 Ibid., Method No. 909A, p. 928.

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-555
DATE	June 15, 1983
SUPERSEDES	
PAGE	1 OF 5

N-NITROSODIETHANOLAMINE IN MACHINING COOLANTS, HPLC METHOD

Analyte:	N-Nitrosodiethanolamine (NDELA)	Method No.:	IHA-555
Matrix:	Water-soluble machining coolants	Range:	10 to 100 µg/mL
Procedure:	Resolution by high performance liquid chromatography (HPLC); detection by UV.	Precision:	± 6% RSD

1.0 Principle of the Method

1.1 Most samples of used water-soluble machining coolants can be analyzed as received. Samples of water-soluble machining coolant concentrates must be diluted to put the NDELA within the analytical range or to reduce their viscosity.

1.2 An aliquot of the aqueous sample is injected into the liquid chromatograph, which is equipped with a UV detector (254 nm).

1.3 The peak height or area is compared with a calibration curve to determine the NDELA concentration.

2.0 Working Range, Sensitivity, and Detection Limit

2.1 The working range for most coolants will be between 10 and 100 µg NDELA/mL. The range can be extended by using a different detector sensitivity and/or injection volume, or by changing the dilution factor of the sample.

2.2 The sensitivity of the analytical method, with a fixed injection volume of 0.020 mL and a detector sensitivity of 0.2 AUFS, is approximately 0.5 µg per mm chart deflection.

2.3 The detection limit of NDELA is dependent on the operating parameters. Levels of less than 1 µg NDELA/mL have been quantitated at 0.050 mL injection volume and detector sensitivity of 0.005 AUFS.

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UCN-13234
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3. Interferences

3.1 It must be emphasized that any compound which has the same retention time as the analyte under the operating conditions of this method is an interference. Without further corroborating analyses, retention time data cannot be considered as proof of chemical identity.

3.2 For machining coolants not previously analyzed and for samples where "positive" proof of chemical identity is needed, the "NDELA" peak is fractionated, concentrated, derivatized and analyzed by GC/MS in the EI (electron impact) mode.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($C\overline{V}_t$) for the total analytical method in the range of 10-100 µg/mL is 0.060. This corresponds to ± 6% relative standard deviation(RSD).

4.2 No bias has been recognized in this method, when properly calibrated.

5. Advantages and Disadvantages

5.1 An advantage of the method is the specificity of the HPLC procedure ... the absence of recalcitrant interferences. The Y-12 analytical laboratory has not encountered any false positive results, during application of this procedure.

5.2 An advantage of this method is that it can be done in any laboratory with a high performance liquid chromatograph with an ultraviolet absorption detector (a fairly standard configuration) and does not require extremely expensive or specific detectors unless very low levels of quantitation are necessary.

5.3 The method is not readily applicable to very low levels (<< 1 µg NDELA/mL), because no practical method of concentrating or extracting the analyte has been found.

5.4 Certain machining coolants have components that are very strongly retained on the HPLC column. This requires either waiting for them to elute (~ 25 minutes under analysis conditions) or flushing the column with a stronger solvent and waiting for the reequilibration of the system.

6. Apparatus

6.1 HPLC and Accessories.

6.1.1 A high performance liquid chromatograph equipped with an ultraviolet absorption detector capable of operating at 254 nm.

6.1.2 A prepacked octadecyl silane reverse phase column, 3.9 mm ID x 300 mm long, Waters Associates μBondapak C18, or equivalent.

6.1.3 Potentiometric strip chart recorder, 10 mV.

6.1.4 An electronic integrator, if desired or available.

6.2 Glassware

6.2.1 A 25-μL glass syringe for sample injection.

6.2.2 A 2-mL (minimum) glass syringe for flushing solvent.

6.2.3 Appropriate pipettes and volumetric flasks for the preparations of samples and standards.

6.3 Analytical balance, 0.1 mg resolution.

7. Reagents

7.1 Water, deionized, (Milli-Q or equivalent).

7.2 Acetonitrile, distilled-in-glass, UV-grade (Burdick and Jackson Laboratories, or equivalent).

7.3 N-Nitrosodiethanolamine for the preparation of standards.

CAUTION: This material is a carcinogen and should be treated with care. Gloves should be worn at all times.

8. Procedure

8.1 Cleaning of equipment. Wash all glassware to be used in the analysis with detergent; rinse with tap water, then distilled water, and dry thoroughly.

8.2 Analysis of Samples

8.2.1 Preparation of samples. Coolants, new or used, that have been diluted to the operating level can usually be analyzed as received. Coolant concentrates must be diluted with distilled water 25-to 50-fold prior to analysis. Some coolants may need dilution to lower their visosity for proper syringe operation.

8.2.2 Mobile phase preparation. The mobile phase for the HPLC is pure deionized, distilled water. Acetonitrile is used to flush strongly retained components from the column, which must then be reequilibrated with water.

8.2.3 Liquid chromatographic conditions.

8.2.3.1 The following are basic operating conditions:

Mobile phase - 100% H_2O
Flow Rate - 1.0 mL/min
Chart Speed - 1.0 cm/min
Detector Wavelength - 254 nm

8.2.3.2 The following conditions may be altered as the situation warrants:

Detector sensitivity - 0.2 AUFS
Injection volume - 0.02 mL

8.2.4 Inject a 20-µl aliquot of the sample solution into the liquid chromatograph and determine the size of the peak corresponding to NDELA. Under the above conditions, NDELA elutes in about 5 minutes.

8.2.5 Measure peak heights or peak areas.

9. Calibration

9.1 A stock solution of NDELA is prepared by accurately weighing 0.05 g of NDELA in a 100-mL volumetric flask. The flask is diluted to the mark with deionized water. This stock solution (500 µg NDELA/1mL) is

diluted as needed to give appropriate standard concentrations. The following are dilutions suggested for use with the instrumental conditions as stated in 8.2.3:

Dilution	Concentration
Stock	500 µg/mL
10:50	100 µg/mL
7:50	70 µg/mL
5:50	50 µg/mL
3:50	30 µg/mL
1:50	10 µg/mL

9.2 Each standard concentration (20-µL aliquot) is injected into the HPLC three times. Measurements should agree to within 5%.

9.3 A calibration curve is generated by plotting the concentration of NDELA in each standard versus the peak height (or peak area). The plot should be linear.

10. Calculations

10.1 The concentration of NDELA corresponding to the peak height (or peak area) in each sample is obtained from the calibration curve. If the sample was diluted the final answer is corrected for the dilution factor. Report the result in units of µg/mL or mg/L.

11. References

11.1 Anselme, J. P. (editor), N-Nitrosamines, ACS Symposium Series #101, American Chemical Society, Washington, DC (1979).

11.2 Scanlan, R. A., and Tannenbaum, S. R., (editors), N-Nitroso Compounds ACS Symposium Series #174, American Chemical Society, Washington, DC (1981).

11.3 Lijinsky, W., Reuber, M. D., and Manning, W. B.; Nature, 288, 589-590 (1980).

11.4 Habs, M., Preussmann, R., and Schmahl, P. J.; Cancer Res. Clin. Oncol., 99, A27 (1981).

UCN-10766B (12 8-78)

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-570
DATE	March 16, 1981
SUPERSEDES	
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POLYCHLORINATED BIPHENYLS (PCBs) IN SMEAR SAMPLES, GAS CHROMATOGRAPHIC METHOD

Analyte:	PCBs	Method No.:	IHA-570
Matrix:	Filter paper smears	Sensitivity:	0.5 μg
Procedure:	Surface wiped with filter paper; desorption with hexane; gas chromatography with electron capture detection	Precision:	25% RSD
		Accuracy:	Within 25% relative (analytical)

1.0 Principle of the Method

1.1 The surface to be checked is wiped with a piece of filter paper.

1.2 The filter is leached with hexane to dissolve any PCBs present.

1.3 A one-μl portion of the hexane leachate is injected into a gas chromatograph equipped with an electron capture detector.

1.4 Identification and quantitation are accomplished by comparison with PCB standards. The most common PCBs are Aroclor 1248, 1254, 1260, and mixtures of these. Specific identification may be made in the analysis.

1.5 This is a general procedure and is applicable to all types of PCBs, by using appropriate standards and identification chromatograms.

2.0 Sensitivity

2.1 The lowest concentration reported is 0.5 μg of PCB.

3.0 Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete analytical interferences and/or elevated baselines, causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis. Used glassware should be cleaned thoroughly with hexane and chromic acid, rinsed with distilled water, and dried in an oven (400°C for 1 hour or 150°C overnight) before reuse.

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3.2 The sample itself may contain compounds that seriously interfere in the detection and measurement of PCBs. Chromatographic column (Florisil) cleanup may be necessary to remove these interferences; however, detection and measurement of PCBs may be impossible on samples with interfering compounds that cannot be eliminated.

4.0 Precision and Accuracy

4.1 Recovery of PCBs from filter paper is fairly quantitative; precision is approximately 25% (Relative Standard Deviation).

4.2 Accuracy of the analysis is at least ± 25% relative.

5.0 Advantages and Disadvantages of the Method

5.1 The method of sampling is quick and easy, but not quantitative or reproducible. This procedure is used primarily to determine if an area cleanup operation is necessary or has been completed.

6.0 Apparatus

5.1 Gas chromatograph, with glass-lined injection port, glass column, electron capture detector, and strip chart recorder.

5.2 Chromatographic column, glass, 2-m (6-ft) x 6.4-mm (1/4-in.) x 2-mm ID, packed with Chromosorb WHP, 80/100 mesh, coated with 3% OV-101, or equivalent.

5.3 Microsyringe, 10-µl.

7.0 Reagents

7.1 Hexane, ACS; if not adequately pure, use pesticide grade, available commercially.

7.2 Benzene, ACS; if not adequately pure, use pesticide grade, available commercially.

7.3 PCB Standards

7.3.1 Stock solutions. Dissolve 20 mg each of the Aroclor 1248, 1254, and 1260 PCB material in benzene and dilute each to 100 ml with benzene. Each stock solution contains 200 µg/ml of the respective PCB. These solutions will be stable for 6 months if kept frozen while not in use.

7.3.2 Standard solutions. Dilute 5 ml of each stock solution to 100 ml with benzene. Each standard solution contains 10 µg/ml of the respective PCB. These solutions will remain stable for 6 months if kept frozen while not in use.

7.3.3 Working standards. Prepare a set of working standards for each PCB type by diluting the standard solutions with hexane. The working standards should cover the range of 0 to 1.0 µg/ml; e.g., blank, 0.1, 0.4, 0.7, and 1.0 µg/ml. These standards will be stable for 1 month if kept refrigerated while not in use.

8.0 Procedure

8.1 Place the filter paper sample in a screw-cap glass vial and add 10 ml of hexane.

8.2 Cap the vial and allow it to stand at least 30 min with frequent agitation.

8.3 Inject 2-µl portions of the hexane solution into the gas chromatograph and identify the PCB peaks using Figures 1, 2, or 3.

8.4 Determine the amount of PCB from the calibration curve, or using the summation of either peak heights or areas (see Section 9.2).

9.0 Calibration and Standards

9.1 Inject 2-µl portions of the working standards into the gas chromatograph sequentially with aliquots of the sample.

9.2 Construct a calibration curve of PCB concentration versus peak height (or area) using the same peaks in the standards that will be used in the samples. In more routine practice, calibrations are conducted with the summation of peak heights (or areas), which is used to generate a calibration factor related to the injected amount of the specific PCB.

10.0 Calculations

10.1 The total amount of PCB in the sample is found using the following formula:

$$\text{PCB, } \mu g = C \times 10$$

where C = PCB found in the hexane solution, μg/ml,

10 = volume of hexane solution, ml.

10.2 Always report the type of PCB present--Aroclor 1248, 1254, or 1260--where possible.

11.0 References

11.1 Polychlorinated Biphenyls in Water; ASTM Standard D3534-76T; Annual Book of ASTM Standards, Part 31, p. 664 (1978).

11.2 Procedure IHA-270, this manual.

DWG. NO. K/G-80-207
(U)

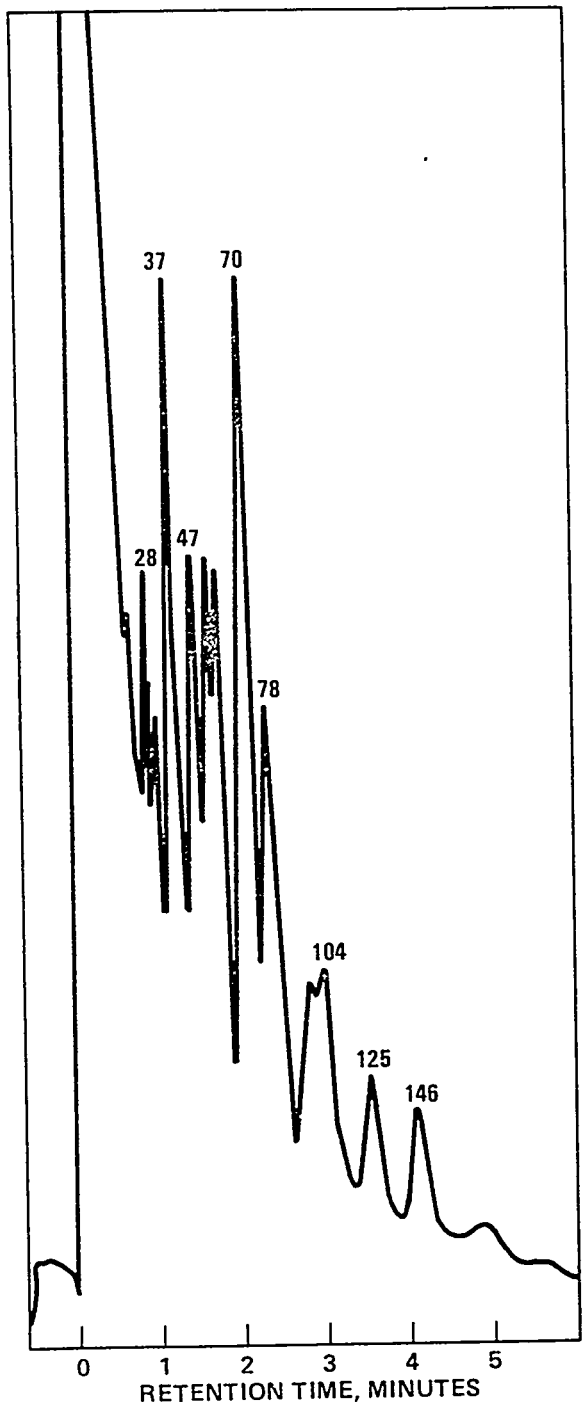

Figure 1. AROCLOR 1248

PEAK LABELS ARE RRT'S (RELATIVE RETENTION TIMES);
RRT = RT RELATIVE TO p, p' –DDE = 100

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(U)

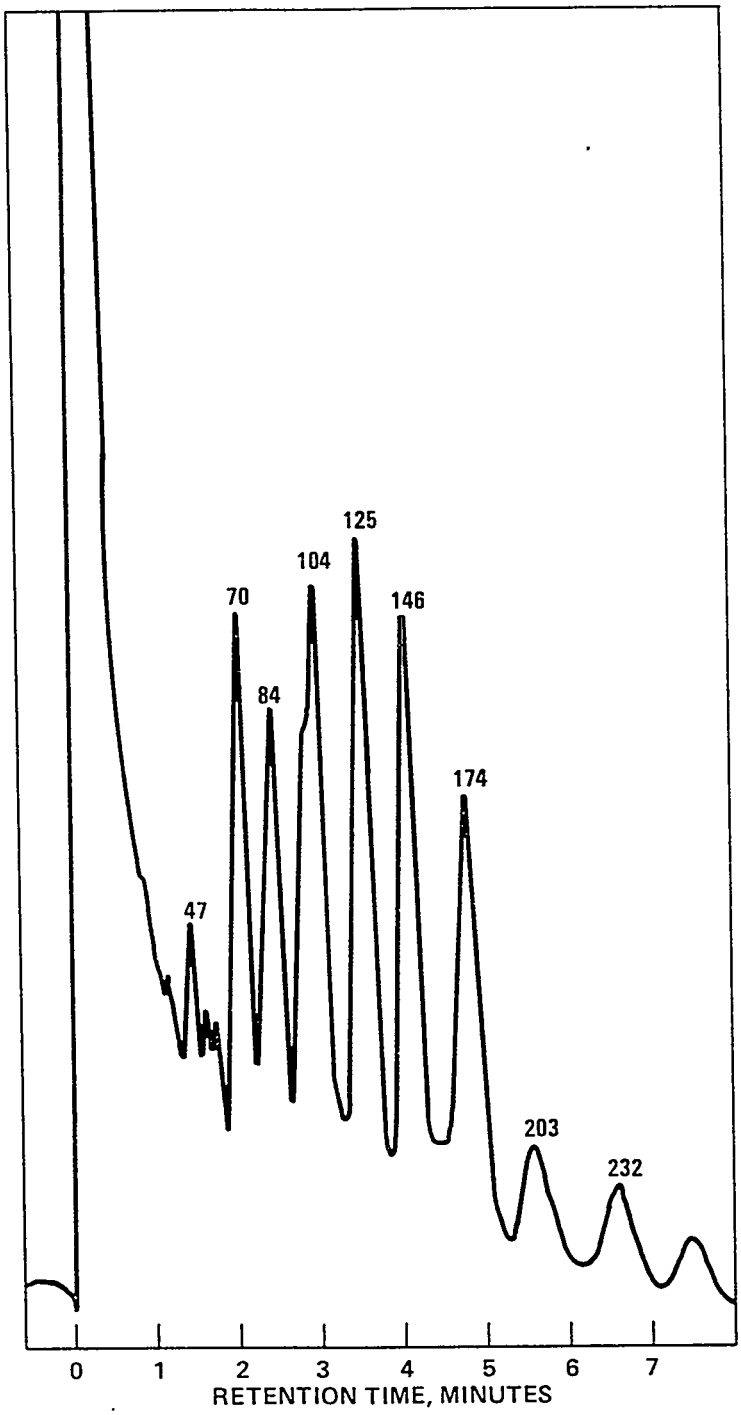

Figure 2. AROCLOR 1254

PEAK LABELS ARE RRT'S (RELATIVE RETENTION TIMES);
RRT = RT RELATIVE TO p, p' – DDE = 100

DWG. NO. K/G-80-205
(U)

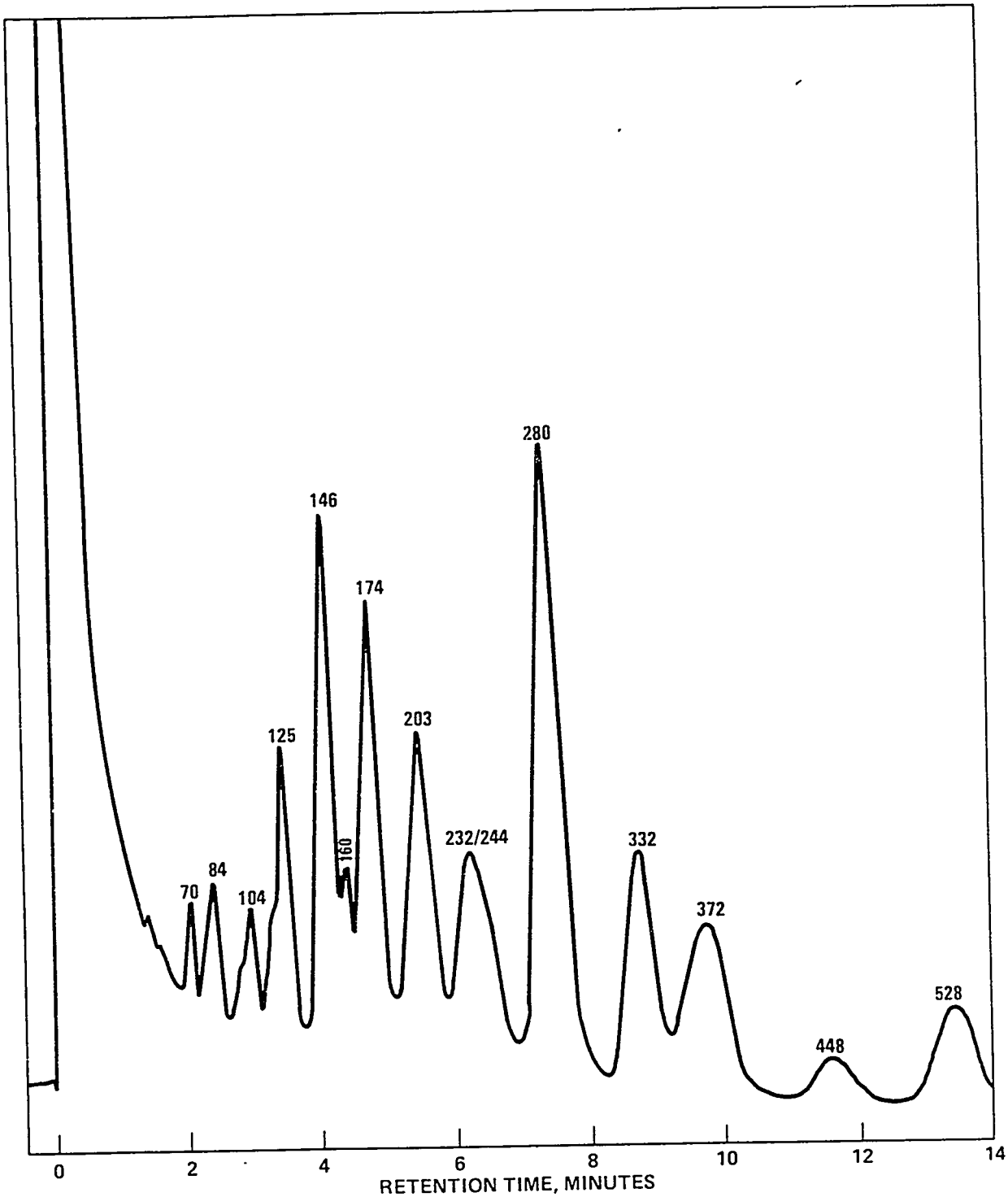

Figure 3. AROCLOR 1260

PEAK LABELS ARE RRT'S (RELATIVE RETENTION TIMES);
RRT = RT RELATIVE TO p, p' – DDE = 100

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	
DATE	March 16, 1981
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APPROVED BY Y-12	LAB / IH	APPROVED BY ORGDP	LAB / IH	APPROVED BY UCCND-COORD R C W Weber
APPROVED BY PGDP	LAB / IH	APPROVED BY ORNL	LAB / IH	NUMBER

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*This radiochemical procedure is principally applied to samples and programs administered by the Health Physics functions of UCC-ND; however, the analytical results are also of interest to industrial hygienists, as confirmation of potential chemical toxicological problems.

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*This radiochemical procedure is principally applied to samples and programs administered by the Health Physics functions of UCC-ND; however, the analytical results are also of interest to industrial hygienists, as confirmation of potential chemical toxicological problems.

1.0 SCOPE AND APPLICATION

1.1 Each laboratory uses appropriate practices and methods for measured parameters to ensure that the reported data are reliable and meet the needs of the responsible monitoring organizations.

1.2 Analytical methods, programs, and services are employed which will ensure that reliable data are available in a timely and cost-effective manner to demonstrate that plant operations involving potentially hazardous emissions are being controlled within the guidelines of the Industrial Hygiene Departments and the National Institute for Occupational Safety and Health (NIOSH).

2.0 SUMMARY OF PROGRAM

Laboratory management at each installation determines and implements, as needed, specific quality assurance and quality control programs. In addition to using external control programs, each laboratory adopts those internal controls and calibration procedures necessary to provide day-to-day confidence in the reported data.

3.0 DESCRIPTION OF PROGRAM

3.1 Organization

Each laboratory has a documented organizational structure to establish functional responsibilities. Laboratory management will work with the Industrial Hygiene groups to ensure that organization, facilities, and methods are adequate to provide the necessary analyses in a timely and cost-effective manner.

3.2 Quality Assurance Program

A written statement should be prepared that describes the quality assurance requirements for the organization. Quality Assurance procedures should be written as needed. A periodic review of the program by management should be established.

3.3 Training and Qualification

3.3.1 A method of training and qualifying personnel will be established. The type and complexity of the program will be determined by each laboratory and approved by management.

3.3.2 A documented training program should include periodic reviews and upgrading based on personnel advancement and changes in work situations.

3.4 Control of Equipment, Materials, and Samples

3.4.1 Adequate control is exercised to ensure that analytical instrumentation is performing in an acceptable manner. Instruments and equipment are calibrated on a regular basis. Records of calibration should be maintained.

3.4.2 Chemicals used in the preparation of reagents and standards should be of reagent-grade quality or better. Standards should be traceable to NBS or other established sources when possible.

3.4.3 Adequate labeling and sample handling procedures will be followed. Proper storage conditions are observed as directed by the procedures or regulatory agencies.

3.4.4 Expiration dates on reagents, standards, samples, and instrument calibration will be monitored and respected.

3.5 Use of Procedures

3.5.1 A process for preparing and approving formal procedures has been established. The process provides for technical and editorial review, with final approval by the Energy Systems Industrial Hygiene Analysis Committee.

3.5.2 Adequate control shall be exercised to ensure that procedures are used correctly and that unauthorized changes are avoided. An evaluation of the procedures will be conducted to verify their validity. Spikes, blanks, duplicates, and internal controls will be used for this purpose.

3.5.3 Laboratories use procedures approved by NIOSH when these are available. Internal procedures are referenced to NIOSH procedures when possible. NIOSH also acknowledges the validity of the OSHA Analytical Methods Manual, issued by the Salt Lake City Laboratory of the Occupational Health and Safety Agency.

3.6 Internal Control of Measurements

3.6.1 Quality control includes those activities that have been established to control the measurement quality so that the reported results meet the needs of the customer. This quality should be dependable, of adequate level, and economic, and it should result in a measurement process that is stable, reproducible, and well documented.

3.6.2 Each laboratory will determine the internal control program needed for its particular situation. When appropriate, laboratory management may work with the Industrial Hygiene groups to determine the needed program types. Some basic techniques are listed in this section. Each group may establish other programs as needed.

3.6.3 Measurement Calibration

Method or instrument calibrations will be performed according to instructions given in the procedures. Check points on the calibration chart will be confirmed as required. Sample readings shall fall within the area of calibration.

3.6.4 Standards

Standards used in calibration and analysis will be prepared using the appropriate procedures. Proper labeling and record techniques will be followed so that retrievable documentation is established.

3.6.5 Blanks

Appropriate blanks will be used both in calibration and in sample analysis. Reagent blanks measure the signal contribution from chemicals or solvents that are used in preparing samples for analysis. Media blanks measure the contribution from collection media when such media are used. Field blanks measure any contamination that may have occurred during the collection and storage process. Field blanks and, perhaps, media blanks are usually submitted by the sampling group. The number of blanks and their type will be determined by each installation.

3.6.6 Internal Controls and Check Standards

This type of method control is used to verify that the equipment is properly calibrated and that the reagents have been prepared correctly. These standards will have a known or accepted value. The results will be plotted on a chart that shows the established control limits. The analyst will bring any out-of-control points to the attention of the supervisor, and appropriate documented corrective actions will begin on both standard and accompanying samples.

3.6.7 Blind Controls

3.6.7.1 These samples are prepared by someone other than the analyst performing the measurement. Such controls provide an independent check on accuracy and precision. The analyst may or may not recognize the samples as controls; in either case, the true value will be unknown to the analyst. In some situations, the group preparing these controls will be in an organization other than the analytical laboratory.

3.6.7.2 The types of controls required will depend on the particular needs of each installation laboratory. Typical parameters that will be measured are fluoride in air; uranium, technetium, lead or mercury in urine; organics in air; metals on air filters; and mercury in air.

3.6.8 Duplicates

Duplicate measurements are made at a predetermined frequency to assist in the evaluation of measurement variance. Measurement of duplicate samples would also include the sample variance.

3.6.9 Recovery Study

The use of spiked samples will be employed when feasible. The analyte of interest is added to a portion of the sample at a level within the range generally expected in the original sample. Recovery amounts can be determined, and possible interferences will be noted. Consideration must be given to the possibility that the original sample contains the analyte in a form different from that in the spike.

3.7 Laboratory Records and Records Control

3.7.1 A records system is used that gives adequate documentation of work done in the laboratory. These records provide traceability of results, indicate which individuals did the work, and identify the procedures and quality control data used.

3.7.2 Any special conditions, procedure deviations, or special treatments are noted on the analytical record. Unusual matrices, supervisory approval, and any communication with the customer should also be indicated.

3.7.3 Systems for recording and handling data vary among installations. Data entries should be in ink, and any changes will be made by drawing a line through the old data and then recording and initialing the corrected value. Sufficient data should be recorded that will enable another trained person to arrive at the same results as the original analyst, with no other source of information.

3.7.4 Storage facilities are established so that records are properly protected, identified, and easily retrieved. Retention times are established by management, by regulatory agencies, or by the DOE.

3.8 Corrective Actions

3.8.1 Each laboratory will implement a system to detect and correct deficiencies before they become large enough to result in serious consequences. The methods used will depend on the needs of the particular laboratory. Such practices could include internal controls, check standards, control charts, and audits.

3.8.2 Evaluation of reported deficiences should include appropriate actions needed for correction. The final disposition should be documented and reported to management.

4.0 REFERENCES

4.1 ASTM C-1009-85 Standard Guide for Establishing a Quality Assurance Program, American Society for Testing and Materials, Philadelphia, PA, 1985.

4.2 NBSIR 85-3105, Principles of Quality Assurance of Chemical Measurements, National Bureau of Standards, Gaithersburg, MD, 1985.

4.3 Standard Methods for the Examination of Water and Wastewater, 16th Ed., American Public Health Association, Washington, DC, 1985.

4.4 Methods of Air Sampling and Analysis, 2nd Ed., American Public Health Association, Washington, DC, 1977.

4.5 Handbook for Analytical Quality Control in Water and Wastewater Laboratories, U.S. Environmental Protection Agency, Cincinnati, OH, 1972.

4.6 NIOSH Manual of Analytical Methods, 3rd Ed., U.S. Department of Health and Human Services, Cincinnati, OH, 1984.

NIOSH #7400
Asbestos Procedure

FIBERS

FORMULA: various

M.W.: various

METHOD: 7400
ISSUED: 2/15/84
REVISION #2: 5/15/86

PROPERTIES: solid, fibrous

OSHA: 0.2 asbestos fibers (> 5 µm long)/mL
NIOSH: 0.1 asbestos f/mL [1]; 3 glass fibers (>10 µm x <3.5 µm)/mL [2]
ACGIH: 0.2 crocidolite; 0.5 amosite; 2 chrysotile and other asbestos, f/mL

SYNONYMS: actinolite asbestos [CAS #13768-00-8], grunerite asbestos (amosite) [CAS #12172-73-5], anthophyllite asbestos [CAS #17068-78-9], chrysotile asbestos [CAS #12001-29-5], crocidolite asbestos [CAS #12001-28-4], tremolite asbestos [CAS #14567-73-8]; fibrous glass.

SAMPLING

SAMPLER: FILTER
(0.8 to 1.2 µm cellulose ester membrane, 25-mm diameter; conductive cowl on cassette)

FLOW RATE*: 0.5 to 16 L/min (see step 4)

VOL-MIN*: 400 L @ 0.1 fiber/mL (see step 4)
-MAX*: (see step 4)
*Adjust for 100 to 1300 fibers/mm² (step 4)

SHIPMENT: routine (securely packed to reduce shock)

SAMPLE STABILITY: stable

FIELD BLANKS: 10% (≥2) of samples

ACCURACY

RANGE STUDIED: 80 to 100 fibers counted

BIAS: see EVALUATION OF METHOD

OVERALL PRECISION (s_r): 0.115 to 0.13 (A Rules) [3] (see Appendix C)

MEASUREMENT

TECHNIQUE: LIGHT MICROSCOPY, POSITIVE PHASE CONTRAST

ANALYTE: fibers (manual count)

SAMPLE PREPARATION: acetone/triacetin "hot block" method [4]

COUNTING RULES: Set A (P&CAM 239 [3,4]) or Set B (modified CRS [5])

EQUIPMENT:
1. positive phase-contrast microscope
2. Walton-Beckett graticule (100 µm field diameter): A Rules use G-22; B Rules use Type G-24
3. phase-shift test slide (HSE/NPL)

CALIBRATION: HSE/NPL test slide

RANGE: 100 to 1300 fibers/mm² filter area

ESTIMATED LOD: 7 fibers/mm² filter area

PRECISION: 0.10 to 0.12 (A Rules) [3] (see Appendix C)

APPLICABILITY: The method gives an index of airborne asbestos fibers in workplace atmospheres but may be used for other materials such as fibrous glass by inserting suitable parameters into the counting rules. Phase contrast microscopy will not differentiate between asbestos and other fibers and should not be used for this purpose. Fibers less than ca. 0.25 µm diameter will not be detected by this method [6].

INTERFERENCES: Any other airborne fiber may interfere since all particles meeting the counting criteria are counted. Chain-like particles may appear fibrous. High levels of non-fibrous dust particles may obscure fibers in the field of view and increase the detection limit.

OTHER METHODS: This method introduces changes for improved sensitivity and reproducibility. It also replaces P&CAM 239 [3,7] and Method 7400 (dated 5/15/85).

REAGENTS:

1. Acetone*
2. Triacetin (glycerol triacetate), reagent grade.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: field monitor, 25-mm, three-piece cassette with 50-mm extension cowl with cellulose ester filter, 0.8- to 1.2-µm pore size and backup pad.
   NOTE 1: Analyze representative filters for fiber background before use and discard the filter lot if a mean of more than 5 fibers/100 fields are found. These are defined as laboratory blanks.
   NOTE 2: An electrically conductive extension cowl is required to reduce electrostatic effects on fiber sampling. The cowl should be grounded whenever possible during sampling, especially for area sampling.
2. Personal sampling pump, 0.5 to 16 L/min (see step 4 for flow rate), with flexible connecting tubing.
3. Microscope, positive phase contrast, with green or blue filter, 8 to 10X eyepiece, and 40 to 45X phase objective (total magnification ca. 400X); numerical aperture = 0.65 to 0.75.
4. Slides, glass, single-frosted, pre-cleaned, 25 x 75 mm.
5. Cover slips, 22 x 22 mm, No. 1-1/2, unless otherwise specified by microscope manufacturer.
6. Lacquer or nail polish.
7. Knife, #10 surgical steel, curved blade.
8. Tweezers.
9. Heated aluminum block for clearing filters on glass slides (see ref. [4] for instructions on manufacture).
10. Micropipet, 100- to 500-µL.
11. Micropipets, 5-µL.
12. Graticule, Walton-Beckett type with 100-µm diameter circular field at the specimen plane (area = 0.00785 mm^2) (Type G-22 for A Rules; Type G-24 for B Rules). Available from PTR Optics Ltd., 145 Newton Street, Waltham, MA 02154 (Telephone [617] 891-6000) and from McCrone Accessories and Components, 2506 S. Michigan Ave., Chicago, IL 60616 (Telephone [312] 842-7100).
    NOTE: The graticule is custom-made for each microscope. Specify disc diameter needed to fit exactly the ocular of the microscope and the diameter (mm) of the circular counting area (see APPENDIX A).
13. HSE/NPL phase contrast test slide, Mark II. Available from PTR Optics Ltd.
14. Telescope, ocular phase-ring centering.
15. Stage micrometer (0.01-mm divisions).

SPECIAL PRECAUTIONS: Acetone is an extremely flammable liquid and precautions must be taken not to ignite it. Heating of acetone in volumes greater than 1 mL must be done in a ventilated laboratory fume hood using a flameless, spark-free heat source.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line [3].
2. For personal sampling, fasten the sampler to the worker's lapel as close as possible to the worker's mouth. Remove the top cover from the end of the cowl extension (open face) and orient face down. Wrap the joint between the extender and monitor body with shrink tape to prevent air leaks.

   NOTE: Use a conductive cowl and, if possible, ground the cassette to remove any surface charge. Grounding should consist of a lead wire held in contact with the conductive cowl and attached to a non-electrical metal fixture.
3. Submit at least two field blanks (or 10% of the total samples, whichever is greater) for each set of samples. Remove the caps from the field blank cassettes and store the caps and cassettes in a clean area (bag or box) with the caps from the sampling cassettes during the sampling period. Replace the caps in the cassettes when sampling is completed.
4. Sample at 0.5 L/min or greater [8]. Adjust sampling flow rate, Q (L/min), and time, t (min), to produce a fiber density, E (fibers/mm^2), of 100 to 1300 fibers/mm^2 [$3.85 \cdot 10^4$ to $5 \cdot 10^5$ fibers per 25-mm filter with effective collection area (A_c= 385 mm^2)] for optimum counting precision and quantitation (step 20). If more than 50% of the filter surface is covered with particles, the filter may be too overloaded to count. These variables are related to the action level (one-half the current standard), L (fibers/mL), of the fibrous aerosol being sampled by:

$$t = \frac{(A_c)(E)}{(Q)(L)10^3}.$$

   NOTE: A sampling flow rate of 1 to 4 L/min for 8 hrs is appropriate in non-dusty atmospheres containing ca. 0.1 fiber/mL. Dusty atmospheres require smaller sample volumes; ambient, clean atmospheres require larger air samples for optimum counting precision. The primary consideration in calculating sampling times is to obtain optimum loading on the filter. The sample volumes needed to achieve optimum loadings will vary considerably between atmospheres of high and low fiber concentrations. It is conceivable that in dusty areas, sample volumes of less than 400 L may be needed to obtain countable samples. In such cases it may be necessary to take short, consecutive samples and average the results over the total collection time. For documenting episodic exposures, high flow rates (around 7-16 L/min) may be needed over shorter sampling times. Also, in relatively clean atmospheres, where targeted fiber concentrations are much less than 0.1 fibers/mL, much larger sample volumes (on the order of 2000, to 10000L) may be needed to achieve quantifiable fiber loadings on the filters. Care should be taken, however, not to overload the filter with background dust.
5. Remove the field monitor at the end of sampling, replace the plastic top cover and small end caps, and store the monitor.
6. Ship the samples in a rigid container with sufficient packing material to prevent jostling or damage.

   NOTE: Do not use untreated polystyrene foam in the shipping container because electrostatic forces may cause fiber loss from the sampler filter.

SAMPLE PREPARATION:

Mounting Procedure:

NOTE: The object is to produce samples with a smooth (non-grainy) background in a medium with a refractive index equal to or less than 1.46. The method below collapses the filter for easier focusing and produces permanent mounts which are useful for quality control and

inter-laboratory comparison. The aluminum "hot block" technique is also a method for mounting MCE filters outside the laboratory. Other mounting techniques meeting the above criteria may also be used (e.g., the laboratory fume hood procedure for generating acetone vapor as described in Method 7400 - revision of 5/15/85, or the non-permanent field mounting technique used in P&CAM 239 [1,3,7]). A videotape of the mounting procedure is available from the NIOSH Publication Office [19].

7. Ensure that the glass slides and cover slips are free of dust and fibers.
8. Plug in and turn on the heat source to the aluminum "hot block" clearing device [4]. Adjust the rheostat to heat the block to approximately 70 °C. If the "hot block" is not used in a fume hood, it must rest on a ceramic plate and be isolated from any surface which is susceptible to heat damage.
9. Mount a wedge cut from the sample filter on a clean glass slide.
   a. Cut wedges of ca. 25% of the filter area with a curved blade steel surgical knife using a rocking motion to prevent tearing.
   b. Place the filter or wedge, dust side up, on the slide. Static electricity will usually keep the filter on the slide until it is cleared.
   c. Insert the glass slide into the receiving slot at the base of the heated aluminum block. Place the tip of a micropipet containing ca. 250 µL acetone into the inlet port of the PTFE cap on top of the aluminum block. Inject the acetone into the vaporization chamber with a slow, steady pressure on the plunger button while holding the pipet firmly in place. Remove the pipet and glass slide from their respective ports after waiting 3 to 5 sec for the filter to clear.

      CAUTION: Although the volume of acetone used in this technique is small, it is, nevertheless, incumbent on the user to take the necessary safety precautions to ensure safe use of the mounting technique. It is recommended that the block be used inside a laboratory fume hood when available. If the "hot block" device is used outside of a fume hood, take precautions not to ignite the acetone and to keep the mounting area well ventilated. Continuous frequent use of this device in a closed or unventilated space may produce acetone vapor build-up and is not recommended.
   d. Using the 5-µL micropipet, immediately place 3.0 to 3.5 µL triacetin on the filter. Gently lower a clean cover slip down onto the filter at a slight angle to reduce the possibility of forming bubbles.

      NOTE: If too many bubbles form or the amount of triacetin is insufficient, the cover slip may become detached within a few hours. If excessive triacetin remains in contact with the edge of the filter under the cover slip, fiber migration may occur at the edges.
   e. Glue the edges of the cover slip to the glass slide using a lacquer or nail polish [9].

      NOTE: If clearing is slow, the slide may be warmed on a hotplate (surface temperature 50 °C) for up to 15 min to hasten clearing. Use caution when heating a prepared filter to ensure that gas bubbles do not form in the sample preparation. Counting may proceed immediately after clearing and mounting are completed.

CALIBRATION AND QUALITY CONTROL:

10. Microscope adjustments. With each microscope, keep a logbook which records the dates that microscope cleanings, adjustments, and calibrations are made. Follow the manufacturer's instructions and, each time a sample is examined, do the following:
    a. Adjust the light source for even illumination across the field of view at the condenser iris each time a new sample is examined.

       NOTE: Köhler illumination is preferred, where available.

b. Focus on the particulate material to be examined.

c. Make sure that the field iris is in focus, centered on the sample, and open only enough to fully illuminate the field of view.

d. Use the telescope ocular supplied by the manufacturer to ensure that the phase rings (annular diaphragm and phase-shifting elements) are concentric. Perform this check at least once daily.

11. Check the phase-shift detection limit of the microscope periodically for each analyst/microscope combination:

a. Remove the HSE/NPL phase-contrast test slide from its shipping container and center it under the phase objective.

b. Bring the blocks of grooved lines into focus.

NOTE: The slide consists of seven sets of grooves (ca. 20 grooves to each block) in descending order of visibility from sets 1 to 7. The requirements for asbestos counting are that the microscope optics must resolve the grooved lines in set 3 completely, although they may appear somewhat faint, and that the grooved lines in sets 6 and 7 must be invisible. Sets 4 and 5 must be at least partially visible but may vary slightly in visibility between microscopes. A microscope which fails to meet these requirements has either too low or too high a resolution to be used for ~~asbestos~~ fiber counting.

c. If the image quality deteriorates, clean the microscope optics. If the problem persists, consult the microscope manufacturer.

12. Quality control of fiber counts.

a. Prepare and count field blanks along with the field samples. Report the counts on each blank. Calculate the mean of the field blank counts and subtract this value from each sample count before reporting the results.

NOTE 1: The identity of the blank filters should be unknown to the counter until all counts have been completed.

NOTE 2: If a field blank yields fiber counts greater than 7 fibers/100 fields, report possible contamination of the samples.

b. Perform blind recounts by the same counter on 10% of filters counted (slides relabeled by a person other than the counter).

c. Each laboratory should maintain as an integral part of its quality assurance program a set of reference slides to be used on a daily basis. These slides should consist of filter preparations from a variety of sources including both field and PAT samples. The set of reference slides should be large enough to accommodate a range of loadings and background dust levels typically encountered on a routine basis by the laboratory. The Quality Assurance Officer should maintain custody of the reference slides and ensure that each counter is supplied with a minimum of one reference slide per workday as a quality control procedure. The labels on the reference slides should be changed periodically so that the analyst does not become familiar with the samples. By obtaining records of blind repeat counts on these reference slides, a laboratory can document its internal intra-counter and intra-laboratory s_r (see step 21).

13. Use the following test to determine whether a pair of counts by the same counter on the same filter should be rejected because of possible bias. This statistic estimates the counting repeatability at the 95% confidence level. Discard the sample if the difference between the two counts exceeds 2.77 $(\bar{F})s_r$, where $\bar{F}$ = average of the two fiber counts and s_r = relative standard deviation, which should be derived by each laboratory based on historical in-house data.

NOTE: If a pair of counts is rejected as a result of this test, recount the remaining samples in the set and test the new counts against the first counts. Discard all rejected paired counts. It is not necessary to use this statistic on blank counts.

14. Enroll each new counter in a training course which compares performance of counters on a variety of samples using this procedure.

    NOTE: To ensure good reproducibility, all laboratories engaged in asbestos counting should participate in an asbestos proficiency testing program such as the NIOSH Proficiency Analytical Testing (PAT) Program and routinely participate with other asbestos fiber counting laboratories in the exchange of field samples to compare performance of counters.

MEASUREMENT:

15. Place the slide on the mechanical stage of the calibrated microscope with the center of the filter under the objective lens. Focus the microscope on the plane of the filter.
16. Regularly check phase-ring alignment and Köhler illumination [6].
17. Select one of the following sets of counting rules:

    NOTE: The two sets of rules have been demonstrated to produce equivalent mean counts on a variety of asbestos sample types [5] and must be strictly followed in order to obtain valid results. No hybridizing of the two sets of rules is permitted. The calibration of the microscope with the HSE/NPL test slide determines the minimum detectable fiber diameter (ca. 0.25 µm).

    a. A Rules (same as P&CAM 239 rules [1,3,7]; see APPENDIX B).
       1. Count only <u>fibers</u> longer than 5 µm. Measure the length of curved fibers along the curve.
       2. Count only fibers with a length-to-width ratio equal to or greater than 3:1.
       3. For fibers which cross the boundary of the graticule field, do the following:
          a. Count any fiber longer than 5 µm which lies entirely within the graticule area.
          b. Count as 1/2 fiber any fiber with only one end lying within the graticule area, if the fiber meets the criteria of rules a.1. and a.2.
          c. Do not count any fiber which crosses the graticule boundary more than once.
          d. Reject and do not count all other fibers.
       4. Count bundles of fibers as one fiber unless individual fibers can be identified by observing both ends of a fiber.
       5. Count enough graticule fields to yield 100 fibers. Count a minimum of 20 fields. Stop at 100 fields regardless of fiber count.

    b. B Rules (see APPENDIX B)

       NOTE: The B Rules are preferred analytically because of their demonstrated ability to improve the reproducibility of fiber counts [5].

       1. Count only <u>ends</u> of fibers. Each fiber must be longer than 5 µm and less than 3 µm diameter.
       2. Count only ends of fibers with a length-to-width ratio equal to or greater than 5:1.
       3. Count each fiber end which falls within the graticule area as one end, provided that the fiber meets rules b.1 and b.2. Add split ends to the count as appropriate if the split fiber segment also meets the dimensional criteria in rules b.1 and b.2.
       4. Count visibly free ends which meet rules b.1 and b.2 when the fiber appears to be attached to another particle, regardless of the size of the other particle. Count the end of a fiber obscured by another particle if the particle covering the fiber end is less than 3 µm in diameter.
       5. Count the free ends of fibers emanating from large clumps and bundles up to a maximum of 10 ends (5 fibers), provided that each segment meets rules b.1 and b.2.
       6. Count enough graticule fields to yield 200 ends. Count a minimum of 20 fields. Stop at 100 fields, regardless of the fiber count.
       7. Divide the total end count by 2 to yield fiber count.

18. Start counting from the tip of the filter and progress along a radial line to the outer edge, shift either up or down on the filter, and continue in the reverse direction. Select fields randomly by looking away from the eyepiece briefly while advancing the mechanical stage. Ensure that, as a minimum, each count covers one radial line from the filter center to the outer edge of the filter. When an agglomerate covers ca. 1/6 or more of the field of view, reject the field and select another. Do not report rejected fields in the number of total fields counted.

NOTE 1: When counting a field, continuously scan a range of focal planes by moving the fine focus knob to detect very fine fibers which have become embedded in the filter. The small diameter fibers will be very faint but are an important contribution to the total count. A minimum counting time of 15 seconds/field is appropriate to ensure thorough sample examination.

NOTE 2: This method does not allow for differentiation of fibers based on morphology. Although some experienced counters are capable of selectively counting only fibers which appear to be asbestiform, there is presently no acceptable method for ensuring uniformity of judgment between laboratories. It is, therefore, incumbent upon all laboratories using this method to report total fiber counts. Other techniques such as Polarized Light Microscopy are available which can identify and eliminate fiberglass and other isotropic fibers from the fiber count. If such procedures are used, they should be noted in the report of analytical results. If serious contamination from non-asbestos fibers occurs in samples used to obtain asbestos fiber counts, other techniques such as Transmission Electron Microscopy must be used to identify the asbestos fiber fraction present in the sample (see NIOSH Method 7402).

CALCULATIONS AND REPORTING OF DATA:

19. Calculate and report fiber density on the filter, E (fibers/mm²), by dividing the total fiber count, F, minus the mean field blank count, B, by the number of fields, n, and the field area, A_f (0.00785 mm² for a properly calibrated Walton-Beckett graticule):

$$E = \frac{\left(\frac{F}{n_f} - \frac{B}{n_b}\right)}{(A_f)}, \text{fibers/mm}^2.$$

20. Calculate the concentration, C (fibers/mL), of fibers in the air volume sampled, V (L), using the effective collection area of the filter, A_c (385 mm² for a 25-mm filter):

$$C = \frac{(E)(A_c)}{V \cdot 10^3}.$$

NOTE: Periodically check and adjust the value of A_c, if necessary.

21. Report laboratory relative standard deviation (s_r) with each set of results. (In the absence of other information use s_r = 0.45 [see Appendix C]). Because precision is dependent upon the total number of fibers counted [3,10], it is insufficient to report only a number for fiber air concentration when using either Method 7400 or P&CAM 239. So that the end user can best utilize the data, laboratories are obligated to report both fiber concentrations as a function of filter area and air volume, and the reliability of the reported numbers in terms of precision. Relative standard deviation (also called coefficient of variation) is documented in references [3,10,11,12] for fiber counts up to 100 fibers in 100 fields. In addition, each laboratory should maintain records which document the laboratory's RSD for fiber counts in the quantitative range of 100 to 1300 fibers/mm². This will facilitate control of data within the laboratory, help the

Quality Assurance Officer to identify problems and be useful to the end user of the data (see Step 12c). As a first approximation, use +213% and -49% as the upper and lower confidence limits (see APPENDIX C).

EVALUATION OF METHOD:

This method is a revision of NIOSH Method P&CAM 239 [1,3,7]. A summary of the revisions is as follows:

A. Sampling:

The change from a 37-mm to a 25-mm filter size was incorporated to improve sensitivity for similar air volumes. The change in flow rates allows for 2 m^3 full-shift samples to be taken, providing that the filter is not overloaded with non-fibrous particulates. The collection efficiency of the sampler is not affected by changes in flow rate in the range 0.5 to 16 L/min [8].

B. Sample Preparation Technique:

The acetone vapor-triacetin preparation technique has been incorporated in the method as a faster, more permanent mounting technique than the dimethyl phthalate/diethyl oxalate method of P&CAM 239 [1,3,4,7,13].

C. Measurement:

1. The inclusion of the Walton-Beckett graticule in the method was made to standardize the field area observed through the eyepiece [13,14].
2. The introduction of the HSE/NPL test slide was made to standardize microscope optics for sensitivity to fiber diameter [6,13].
3. An international collaborative study involved 16 laboratories using prepared slides from the asbestos, cement, milling, mining, textile, and friction material industries [5]. The modified CRS (NIOSH B) Rules were found to yield equivalent counts but were more precise than the AIA (NIOSH A)* Rules. The ranges of relative standard deviations (s_r) which varied with sample type and laboratory were:

	s_r		
	Intra-laboratory	Inter-laboratory	Overall
AIA (NIOSH A Rules)*	0.12 to 0.40	0.27 to 0.85	0.46
Modified CRS (NIOSH B Rules)	0.11 to 0.29	0.20 to 0.35	0.25

*Under AIA rules, only fibers having a diameter less than 3 µm are counted and fibers attached to particles larger than 3 µm are not counted. NIOSH A Rules are otherwise similar to the AIA rules.

The B Rules have also been favorably received by analysts as less ambiguous and simpler to use; these rules also showed the least bias relative to AIA rules in the collaborative study. An independent NIOSH laboratory study using amosite fibers reported a relative standard deviation, including within- and between-sample variability, of 0.16 for the B Rules [15]. Another NIOSH study was conducted using field samples of asbestos [18]. This study indicated intra-laboratory s_r's in the range 0.17-0.25 and an inter-laboratory s_r of 0.45. This data agrees well with results reported from other recent studies [5,10,12] (see Appendix C).

4. Because of past inaccuracies associated with low fiber counts, the minimum recommended loading has been increased to 100 fibers/mm^2 filter area (80 fibers total count). This level should yield intra-counter s_r in the range of 0.13 to 0.17 [3,7,15,18]. APPENDIX C discusses inter-laboratory accuracy and precision.

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METHOD REVISED BY: James W. Carter, David G. Taylor, Ph.D., CIH, and Paul A. Baron, Ph.D., NIOSH/DPSE; based on the revised Method P&CAM 239 [1,3,4].

APPENDIX A:

CALIBRATION OF THE WALTON BECKETT-GRATICULE:

Calibration of the Walton-Beckett graticule to obtain a counting area (D) 100 µm in diameter at the image plane. The diameter, d_c (mm), of the circular counting area and the disc diameter must be specified when ordering the graticule.

1. Insert any available graticule into the eyepiece and focus so that the graticule lines are sharp and clear.
2. Set the appropriate inter-pupillary distance and, if applicable, reset the binocular head adjustment so that the magnification remains constant.
3. Install the 40 to 45X phase objective.
4. Place a stage micrometer on the microscope object stage and focus the microscope on the graduated lines.
5. Measure the magnified grid length of the graticule, L_o (µm), using the stage micrometer.
6. Remove the graticule from the microscope and measure its actual grid length, L_a (mm). This can best be accomplished by using a stage fitted with verniers.
7. Calculate the circle diameter, d_c (mm), for the Walton-Beckett graticule:

$$d_c = \frac{L_a}{L_o} \times D.$$

Example: If L_o = 108 µm, L_a = 2.93 mm and D = 100 µm, then d_c = 2.71 mm.

8. Check the field diameter, D (acceptable range 100 µm ± 2 µm) with a stage micrometer upon receipt of the graticule from the manufacturer. Determine field area (mm^2).

APPENDIX B:

COMPARISON OF COUNTING RULES:

Figure 1 represents a Walton-Beckett graticule as seen through the eyepiece of the microscope. Although the graticule design shown accommodates counting rules using the 3:1 aspect ratio definition for a fiber, both the "A" and "B" rules will be discussed as they apply to the labeled fibers in the figure.

FIBER COUNT

Fiber	A Rules	B Rules	DISCUSSION
1	1 fiber	3 ends	(A) No accommodation is made in the "A" rules for split ends; therefore, count one fiber. (B) When using the 'B' rules, first determine whether the fiber meets the necessary dimensional criteria, i.e., >5 µm, >5:1 aspect ratio, <3 µm diameter. Next determine which two ends are the main trunk of the fiber and count as two ends. Finally, count all split ends which are greater than 5 µm as one end. Fiber #1 in this figure is counted as 3 ends under the "B" rules.
2	1 fiber	2 ends	(A) Single fiber with a small particle attached. The particle is not considered by the "A" rules and treated as if it does not exist. (B) The particle is less than 3 µm in diameter and, therefore, ignored under the "B" rules.
3	1 fiber	2 ends	(A) As with Fiber 1, one fiber is counted under "A" rules because it meets the >3:1 aspect ratio, >5 µm criteria. (B) The split end is less than 5 µm long so it is not counted under the "B" rules.
4	1 fiber	5 ends	(A) Fiber ends all are attached to a central large fiber or bundle; therefore, one fiber is counted under "A" rules. (B) Two ends are counted as belonging to the main fiber. Three of the remaining four split ends are >5 µm, giving a total of 5 ends under the "B" rules.
5	1 fiber	Do not count	(A) No diameter limit under "A" rules; therefore this thick fiber is counted because it meets the >3:1, >5 µm counting criteria. (B) The fiber is >3 µm diameter; therefore, it is not counted under the "B" rules.
6	1 fiber	1 end	(A) Non-fibrous particulate matter is treated as nonexistent under the "A" rules; therefore, this fiber is counted as a whole fiber. (B) The short end of the fiber is less <5 µm long and obscured by a particle >3 µm in diameter; therefore, not counted under the "B" rules.

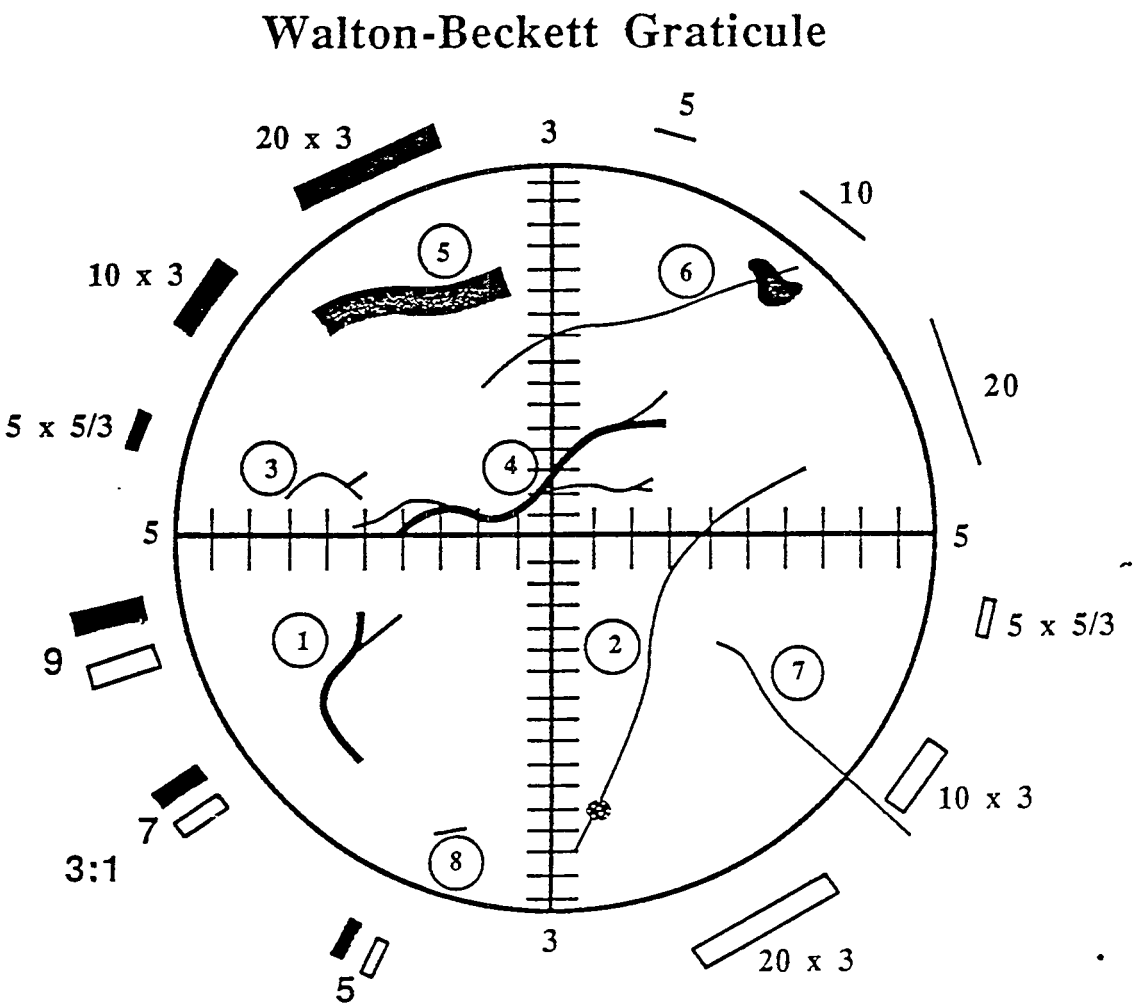

Figure 1. Walton-Beckett graticule with fibers.

Fiber	A Rules	B Rules	DISCUSSION
7	1/2 fiber	1 end	(A) Fibers which meet the definition of a fiber in rules a.1. and a.2. and cross the graticule boundary are counted as 1/2 fiber under the "A" rules unless the fiber crosses the graticule boundary more than once, in which case the fiber is not counted no matter how many ends lie within the graticule area. (B) Fiber ends lying inside the graticule boundary are counted as one end provided that the entire fiber meets the definition of a fiber in rules b.1. and b.2. and each end is longer than 5 µm. The portion of the fiber lying outside the graticule boundary must be considered in order to make this determination. Under "B" rules, it does not matter how often the fiber crosses the graticule boundary.
8	Do not count	Do not count	The fiber is <5 µm long.

APPENDIX C:

INTER-LABORATORY COMPARABILITY:

At this time, there is no independent analytical method for analyzing asbestos so that the overall accuracy of the current method can be determined. Therefore, it is desirable to have some means of estimating the reliability of results determined by this method. One way of assessing this reliability is to estimate how well the count for a single sample agrees with the mean count from a large number of laboratories. The following discussion indicates how this estimation can be carried out based on measurements of the inter-laboratory variability, as well as showing how the results of this technique relate to the theoretically attainable counting precision and to measured intra- and inter-laboratory s_r.

Theoretically, the process of counting randomly (Poisson) distributed fibers on a filter surface will give a coefficient of variation (s_r) that depends on the number (N) of fibers counted

$$1/(N)^{1/2} \qquad (1)$$

This gives s_r of 0.1 for 100 fibers and 0.32 for 10 fibers counted. The actual fiber count s_r found in a number of studies is greater than this (5,10,11,12).

There is an additional component of variability that comes primarily from "subjective" differences from counter to counter, and, more importantly, from laboratory to laboratory. In a study of a group of ten counters that were part of a continuing sample exchange program, Ogden (10) found this subjective component to be approximately 0.2 (subjective component of intra-laboratory s_r) and estimated the overall s_r by the term

$$\frac{(N + (0.2 * N)^2)^{1/2}}{N} \qquad (2)$$

Ogden found that the 90% confidence interval of the individual intra-laboratory counts in relation to the means were 2 s_r and - 1.5 s_r. In this program, one sample out of ten was a quality assurance sample. For laboratories not engaged in an intensive quality assurance program, the subjective component of variability can be higher.

In a study of counting field samples by 46 laboratories, the Asbestos Information Association (12) also found that the variability had both a constant component and one that depended on the fiber count. Their results indicate the subjective s_r (on the same basis as the Ogden analysis) for field samples of approximately 0.45 (subjective component of inter-laboratory s_r). This is the same s_r obtained for 12 PAT laboratories analyzing a set of 24 field samples (18). This value falls slightly above the range of s_r's (0.25 - 0.42 for 1984-85) found for 80 reference laboratories in the NIOSH Proficiency Analytical Testing program (laboratory generated samples) (11).

Obviously, a number of factors come into play in the determination of s_r for a reporting laboratory, such as that laboratory's actual counting performance and the type of samples being analyzed. In the absence of other information, such as from an inter-laboratory quality assurance program using field samples, the value for the subjective component of variability is chosen as 0.45. Note that, though based on at least two studies, this is a somewhat arbitrary choice. It is hoped that by requiring the use of this number in the absence of other information, laboratories will carry out the recommended inter-laboratory quality assurance programs to improve their performance and thus reduce the s_r that they use.

The above s_r's describe the range of counts when the population mean has been determined. It is more useful for laboratories reporting results to estimate the 90% confidence interval on the mean count from a single sample fiber count. Given a single fiber count, Figure 2 shows the range in which it is estimated that 90% of the inter-laboratory means will fall. These curves were calculated assuming that the shape of the count distribution for inter-laboratory results is the same as that for intra-laboratory results. For further details on how these curves were calculated see Ogden (10).

For example, if a sample gives a count of 24 fibers, we can use Figure 2 to determine that the mean inter-laboratory count will fall within the range of 227% above and 52% below that value 90% of the time. We can apply these percentages directly to the air concentrations as well. If, for instance, this sample (24 fibers counted) represented a 500 liter volume, then the measured concentration is 0.1 fibers/cc (assuming 100 fields counted, 25 mm filter, 0.00785 mm^2 counting field area). If this same sample were counted by a group of laboratories, it is estimated that there is a 90% probability that the mean would fall between 0.327 and 0.048 fiber/cc. It is recommended that these limits be reported in any comparison of results between laboratories (see Step 21).

Note that the s_r of 0.45 used in Figure 2 is used as an estimate for a random group of laboratories. If several laboratories belonging to a quality assurance group can show that their inter-laboratory s_r is smaller, than it is more correct to use that smaller s_r. However, the estimated s_r of 0.45 is to be used in the absence of such information. Note also that it has been found that for certain types of samples, such as asbestos cement, that the s_r can be higher. This should be taken into account when comparing results for these types of samples.

Quite often the result of an asbestos analysis is used to compare that result against a limit or standard. For instance, if one is trying to show compliance with an 0.5 fiber/cc limit

using a single sample on which 100 fibers have been counted, then Figure 2 indicates that the 0.5 fibers/cc standard must be 213% higher than the measured air concentration. This indicates that if one measures a fiber concentration of 0.16 fibers/cc (100 fibers counted), then the mean fiber count by a group of laboratories (of which the compliance laboratory might be one) has a 95% chance of being less than 0.5 fibers/cc.

It can be seen from Figure 2 that the Poisson component of the variability is not very important unless the number of fibers counted is small. Therefore, a further approximation is to simply use the upper and lower confidence values of 213% and -49% that are obtained for a 100 fiber count.

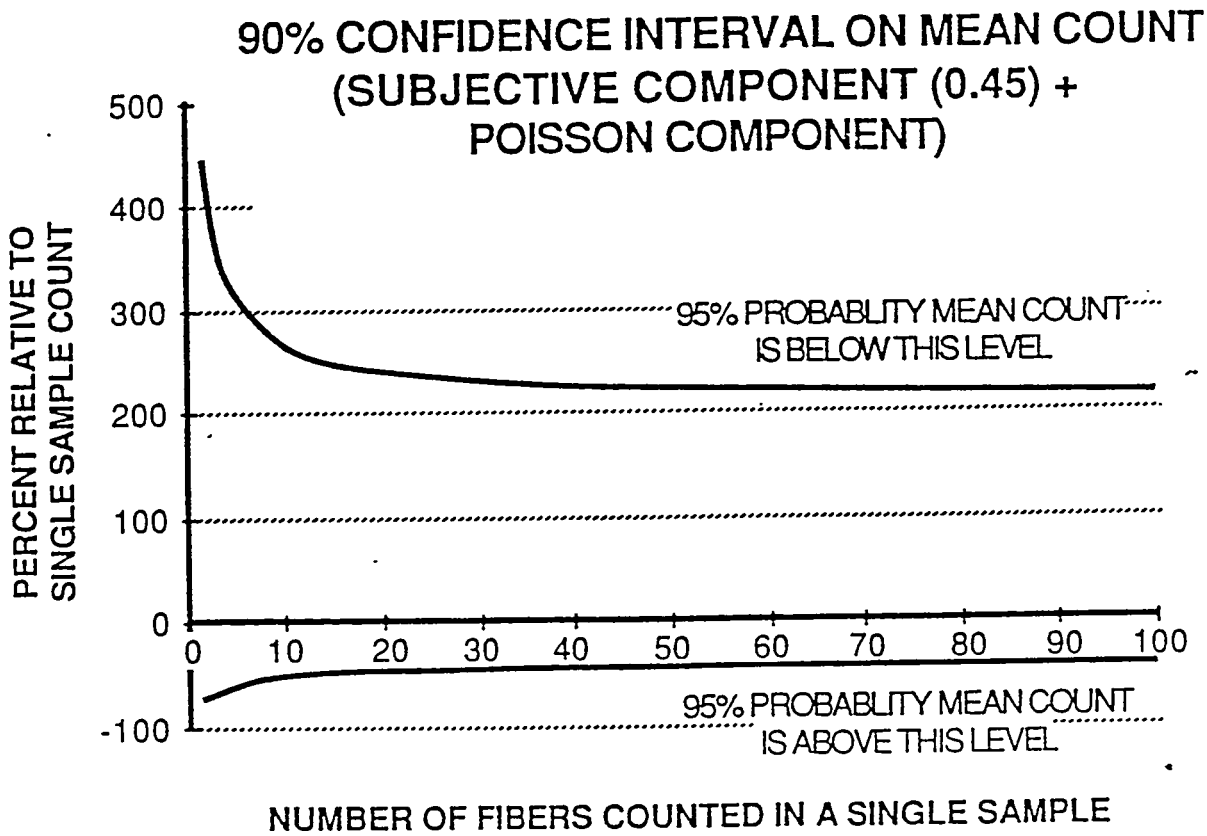

Figure 2.

HOMEWORK NAME _____

MEAN. 373 NUMBER OF COUNTS. 24

COUNT FREQ IN FIBERS/SQ MM

0 - 99		
100 - 199	000	
200 - 299	000	
300 - 399	00000000000	
400 - 499	0000	
500 - 599	00	
600 - 699		
700 - 799		
800 - 899		
900 - 999		
1000 - 1099	0	
1100 - 1199		

DATA	DEV	DEV^2
345		
371		
314		
546		
372		
421		
271		
314		
331		
1049		
503		
306		
420		
592		
460		
324		
489		
195		
381		
320		
255		
223		
161		
184		

$\Sigma x = 8076$

$\bar{x}$ AVERAGE. 336.5

MEDIAN _____

MODE. _____

STD DEV. _____

CV _____

95% BETWEEN _____ & _____

95% LESS THAN _____

95% GREATER THAN. _____

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INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-110
DATE	Nov. 27, 1979
SUPERSEDES	
PAGE	1 OF 22

ASBESTOS FIBERS IN AIR, MICROSCOPIC COUNT METHOD

Analyte:	Asbestos fibers	Method No.:	IHA-110 (NIOSH 239)
Matrix:	Air	Range:	0.1 - 60 fibers/cm^3
Procedure:	Filter collection, slide preparation, fiber count using phase-contrast microscopy	Precision (CV_T): (or RSD):	0.24 to 0.38 24 to 38%

For this analysis, the undersigned committee has approved for inclusion in this manual an existing procedure, exactly as published. Accordingly, the following pages are taken verbatim from the NIOSH Manual of Analytical Methods, Second Edition, Vol. 1, U. S. Department of Health, Education, and Welfare, Method 239, 1977.

APPROVED BY Y-12	LAB R J McUhaney IH W. S. Everett, Jr.	APPROVED BY ORGDP	LAB T. Kuzmoski IH D. J. Duncan	APPROVED BY UCCND-COORD'R C W Weber
APPROVED BY PGDP	LAB R. E. Simmons IH C. W. Turak	APPROVED BY ORNL	LAB W R Laing IH J. A. Ealy	NUMBER IHA-110

UCN-13234
(1235 1-79)

The following procedure is a photocopied excerpt from: NIOSH Manual of Analytical Methods, Second Edition, Vol. 1, U. S. Department of Health, Education, and Welfare, 1977.

ASBESTOS FIBERS IN AIR

National Institute for Occupational Safety and Health

Analytical Method

Analyte:	Asbestos fibers	**Method No.:**	P&CAM 239
Matrix:	Air	**Range:**	0.1-60 fibers/cm^3
Procedure:	Filter collection, microscopic count	**Precision (CV_T):**	0.24 to 0.38
Date Issued:	3/30/77	**Classification:**	D (Operational)
Date Revised:			

1. **Principle of the Method**

1.1 This method describes the equipment and procedures for collecting, mounting, and counting asbestos fibers on cellulose ester membrane filters in the evaluation of personal samples of airborne asbestos fibers. The purpose of the method is to determine an employee's index of exposure to airborne asbestos fibers. The method is primarily a personal monitoring technique, but can be used for area monitoring.

1.2 The sample is collected by drawing air through a membrane filter by means of a battery powered personal sampling pump. The filter is transformed from an opaque solid membrane to a transparent optically homogeneous gel. The fibers are sized and counted using a phase-contrast microscope at 400-450X magnification.

1.3 Definitions. Asbestos fiber, for counting purposes, means a particulate which has a physical dimension longer than 5 micrometers and with a length to diameter ratio of 3 to 1 or greater. Asbestos includes chrysotile, cummingtonite-grunerite (amosite), crocidolite, fibrous tremolite, fibrous anthophyllite, and fibrous actinolite.

1.4 Any laboratory attempting to use this procedure should have at least one counter attend a training course conducted by an experienced, proficient laboratory. Novice, untutored counters, using only published instructions, can easily obtain counts of half those performed by experienced, proficient counters. Large differences between laboratories can be caused by: 1) differences in technique and observing ability among counters and 2) small, but significant, differences between microscopes meeting the basic specifications of Section 6.2. The following procedures are recommended:

1.4.1 All microscopists who perform asbestos counting should meet together for an "asbestos counting workshop" at least quarterly. This is best accomplished with counters from several laboratories using their own microscopes.

1.4.2 Each microscopist should count the same series of slides and with the results being compared.

1.4.3 Differences between counters should be resolved with side-by-side counting of the fields by the different counters.

1.4.4 Individuals who are found to be persistent outliers over several sessions should be encouraged to seek other tasks in their respective laboratories.

2. **Range and Sensitivity**

2.1 The usable range is primarily a function of sample volume, microscope count field area, and background airborne particulates. The influence of these variables is discussed in 8.1.3. For a microscope count field area of 0.003 mm^2 (see Figure 1) and a pump flow rate of 1.7 lpm, the optimal fiber densities would be produced over the range of 0.4 fiber/cm^3 (8-hour sample) to about 60 fibers/cm^3 (15-minute sample). For a field area of 0.006 mm^2 (see Figure 2) and a pump flow rate of 1.7 lpm, the optimal range is 0.2 fiber/cm^3 (8-hour sample) to about 30 fibers/cm^3 (15-minute sample). In each case, the optimal detection limits are inversely proportional to pump flow rate.
The upper detection limit can be extended by using sample times less than 15 minutes or using lower flow rates. The lower detection limit can be extended by increasing the flow rate up to about 2.5 lpm. Filter surface fiber densities less than optimal (less than about 0.5 to 1.0 fiber per count field) are still adequate, but will lead to decreased precision for the method (increased coefficient of variation, see Section 4).
The minimum total fiber count in 100 fields considered adequate for reliable quantitation is 10 fibers. Thus, the lower limit of reliable quantitation is 0.1 fiber/cm^3 (100,000 fibers/m^3). For this level, a flow rate of about 2.5 lpm is recommended. For a field area of 0.003 mm^2, the minimum sample time would be about 2 hours. For a field area of 0.006 mm^2, the minimum sample time would be about 1 hour.

2.2 This method considers only fibers with a length to diameter ratio of 3 to 1 or greater and a length greater than 5 micrometers.

3. **Interferences**

In an atmosphere known to contain asbestos, all particulates with a length to diameter ratio of 3 to 1 or greater, and a length greater than 5 micrometers should, in the absence of other information, be considered to be asbestos fibers and counted as such.

4. **Precision and Accuracy**

4.1 In the past decade, there have appeared a number of articles examining sources of variation in the asbestos sampling and counting procedure. These include: Lynch et al. (11.1), Weidner and Ayer (11.2), Conway and Holland (11.3), Leidel and Busch (11.4), Beckett and Attfield (11.5), and Rajhans and Bragg (11.6). The sources of variation will be discussed by stages in the membrane filter evaluation procedure.

4.2 **Sources of Variation in the Sampling Process.** These include variations in pump flow rate, proximity of the filter to the employee's body, and filter location (left to right) in the employee's breathing zone.

4.2.1 Section 9.1 requires that the personal sampling pump be calibrated with sufficient accuracy such that the 95% confidence limits on the flow rate are ± 10%. This is equivalent to a coefficient of variation (CV) of about 5%. However, this CV makes a negligible contribution to the total CV for the method due to the relatively large CV of the counting procedure.

4.2.2 Conway and Holland (11.3) concluded that positioning of the filter cassette on the wearer (regarding the angular portions of the filter and their proximity to the wearer) is not a significant factor in determining the fiber distribution on filters.

4.2.3 Weidner and Ayer (11.2) concluded that there is no appreciable difference between samples collected on either the right or left sides of a breathing zone or between samples collected side-by-side, especially for samples with concentrations less than 2.5 fibers/cm^3.

4.3 Sources of Variation in the Counting Procedure

4.3.1 Random variations exist in the fiber distribution on a filter wedge (intra-wedge variability). The industrial hygiene literature has seen considerable debate in the last 20 years concerning whether or not the distribution of mineral dust or asbestos fibers on a filter surface is adequately described by a Poisson distribution probability density function. Leidel and Busch (11.4) found excellent agreement between empirical error variance and theoretical variance calculated from the assumption of Poisson distributed true counts. They concluded that there was not excessive variation among count fields for a filter wedge and that clumping of fibers (non-random coalescence) did not occur.

4.3.2 Variations exist in the fiber distribution on the total filter surface (inter-wedge variability) due to the random or non-random distribution of fibers across the total surface of the filter. This type of variation is easily confused with intra-wedge variations. The count procedure does not require counting of multiple sectors of the filter. There may be significant differences between average counts for different wedges, or the fiber distribution variations for the total filter surface may be greater than the variations of the Poisson distribution. If either of these occur experimentally, one must use the experimental variations to estimate the minimum precision of the count procedure. The minimum precision is governed by the variations of the fiber distribution on the total surface of the filter.

Conway and Holland (11.3) concluded the distribution of fibers on filters is not uniform and the distribution of fiber counts is more disperse than Poisson. For their filters which had significant variations in fiber concentrations between sectors (as much as 50-60% of the total filter mean), they described the following relation for the standard deviation of the total number of fibers counted on a wedge (N)

$$\text{empirical } s(N) = 1.6\ (N)^{1/2}$$

where N is about 100. The Poisson standard deviation would be:

$$\text{Poisson } \sigma(N) = (N)^{1/2}$$

Rajhans and Bragg (11.6) in Series I of their study found significant variation between filter segments and rejected the Poisson distribution for the total filter surface. However, in Series II of their study, utilizing various experimental modifications, they found no significant variation between filter segments and no reason to reject the assumption of Poisson distributed fiber counts.

4.3.3 Systematic variations due to differences between microscopes were studied by Leidel and Busch (11.4). In their study using five different brands of microscopes, they found no significant differences among four, but the fifth gave counts approximately 45% higher on the average than the other four.

4.3.4 Variations due to differences between counters should be examined at three levels: experienced counters occasionally counting, experienced counters routinely counting, and inexperienced (new or untutored) counters. Leidel and Busch (11.4) studied five experienced counters, with one counting only occasionally. There were no significant differences among three of the counters, but a fourth was 16% lower than the first three. The fifth, who occasionally counted, averaged 27% higher than the first three. Conway and Holland (11.3) studied three experienced counters and three inexperienced counters. They found statistically significant differences between the means of both the experienced and inexperienced counters that typically were in the range plus or minus 5 to 15%. They concluded that experience as a fiber counter is not a significant parameter affecting intercounter variations.

Rajhans and Bragg (11.6) found no significant differences among means of five experienced counters in Series I of their study. But in their carefully controlled Series II, an analysis of variance showed significant variations between counters that were plus or minus 1 to 15%.

4.3.5 Variations between laboratories are most likely due to systematic biases and are not a significant additional source of random variations. Any additional variations are most likely due to differences in counting technique. Beckett and Attfield (11.5) observed that standard counters improved greatly after personal instruction; also new counters, after instruction, tended to overcompensate and get exceedingly high counts. Additionally, they found that counts from an experienced laboratory that had not had contact with other laboratories performing the same analysis were as far from the standard values as were the counts by new counters.

4.4 Sources of variations between samples taken at different times on one employee during one work shift can affect the exposure estimate for that employee. These are primarily due to a) differences in exposure concentrations during the day, b) differences in location of the employee within the plant, and c) differences in work operation performed by the employee during the day. These sources of variation can be controlled by proper choice of sampling strategy. Refer to Leidel and Busch (11.7) and Leidel, Busch, and Lynch (11.8) for an extended discussion of sampling strategies. Interday temporal variations can affect the exposure estimates obtained on different days. Refer to Leidel, Busch, and Crouse (11.9) for a discussion of this type of variation.

4.5 Until recently, the total coefficient of variation (CV_T) for the sampling and counting procedure was best estimated from the work of Conway and Holland (11.3). The conclusions of their study included:

4.5.1 The precision of their procedure for filters not containing an abundance of fine fibers can be estimated by a coefficient of variation of 16.2%. This value includes variation among counters and observed interaction effects.

4.5.2 The accuracy of the procedure for similar filters may be estimated for a 100-fiber count by a coefficient of variation of 21.4%. This assumes that the contribution of the overall variance from the nonuniform fiber distribution is additive.

4.5.3 A high percentage of very fine fibers on the filter can significantly affect the standard deviation and confidence limits for counts by different counters. After combining variations in fiber concentrations over the entire filter with those for different counters, it was concluded:

a. For filters with a low concentration of fine fibers, the coefficient of variation is estimated at 21% and the 95% confidence interval is ± 43%.
b. For filters with a high concentration of fine fibers, the coefficient of variation is estimated at 25% and the 95% confidence interval is ± 50%.

Lynch, Kronoveter, and Leidel (11.1) have also reported on variations of the method. Their intralaboratory study utilized the data from a large number of dust counts made by different methods by experienced counters over a period of years in an epidemiologic study of the asbestos products industry. They concluded that the standard deviation of counts of fibers longer than 5 micrometers on membrane filters could be estimated from the relation $\sigma = (N)^{0.501}$. Thus for counts of about 100 fibers, the coefficient of variation could be estimated at about 15.2% and the 95% confidence limits at ± 30.4%. These values are lower than the values reported by Conway and Holland (11.3).

Recently, the Johns-Manville Corporation conducted an in-house investigation of the asbestos count method (11.10). The study data contained total fiber counts for over

100 filters with each filter counted by two to five counters. From the Johns-Manville data, NIOSH calculated over 100 estimates of the count CV for the method (11.11). The NIOSH CV estimates included random intrafilter variations and intercounter variations, but did not include random pump flow rate variations. It was found that the count coefficient of variation (all random variations except for pump variations) was a function of the total fiber count. NIOSH then included a CV of 0.05 for random pump variations (see Section 9.1) in the CV-estimator equation to obtain a CV_T-estimator. The CV_T-estimator line is plotted on Figure 3 for total fiber counts in the range 10 to 100 fibers. Or the following equation can be used:

$$CV_T = [\text{antilog}_{10}(-0.215 - 0.203\,(\log_{10}FB)) + 0.0025]^2$$

where FB is total fiber count as discussed in Section 10.

Figure 3 demonstrates that for a total fiber count of 100, the best CV_T is attainable with the appropriate sampling times given in 8.1.3 and the count rules in 8.3.9. When making decisions regarding compliance with the OSHA asbestos exposure standards in 29 CFR 1910.1001, the statistical procedures given in Leidel et al. (11.11) should be followed. The procedures are based on statistical theory and assumptions given in References 11.12, 11.13.

Because of the possibility of systematic biases due to differences between microscopes, counters, and laboratories as discussed above, it is strongly recommended that any laboratory counting asbestos should participate in an interlaboratory quality control program that includes the counting of standard reference filters. These standard filters are available from NIOSH through the Proficiency Analytical Testing (PAT) Program. The PAT Program is used by the American Industrial Hygiene Association (AIHA) as part of its Laboratory Accreditation Program. Each laboratory's quality control program must include protocols for routinely adjusting and calibrating sampling and counting equipment plus training and evaluation programs for counters.

5. **Advantages and Disadvantages of the Method**

5.1 The method is intended to give an index of employee exposure to airborne asbestos fibers of specified dimensional characteristics.

5.2 It is not meant to count all asbestos fibers in all size ranges or to differentiate asbestos from other fibrous particulates.

6. **Apparatus**

6.1 Sampling Equipment

The personal sampling equipment train consists of 1) personal sampling pump, 2) tubing, 3) clothing spring clip, 4) tubing-to-field monitor metal adaptor, and 5) field monitor (filter and holder).

6.1.1 Personal Sampling Pump. The pump must be capable of sampling at 1.0 to 2.5 liters per minute (lpm) against a flow resistance of 7.5 inches of water (1.4 cm Hg) for 8 continuous hours on a fully charged battery.

6.1.2 Tubing. Laboratory tubing such as rubber or plastic with 6-mm bore and about 100 cm length.

6.1.3 Clothing Spring Clip. The clip attaches the rubber tubing to the lapel or shirt of the individual being monitored.

6.1.4 Tubing-to-field Monitor Adaptor. A short metal adaptor with ridges on one end to grip the inside of the tubing. The other end is designed for a pressure fit into the field monitor.

6.1.5 Field Monitor (Filter and Holder). The only field monitor currently considered acceptable by NIOSH is manufactured by the Millipore Corporation. The unit con-

sists of 1) a three section styrene plastic case designated Millipore Aerosol Monitor Case, 2) a 37-mm diameter plain white cellulose ester membrane filter designated Millipore AA (pore size of 0.8 micrometer), 3) a support pad, and 4) two plastic sealing caps. If a large number of samples are to be taken, it may be less expensive to reuse the plastic cases. Great care must be taken in the cleaning and reassembly process. The outside mating surfaces of the field monitors may be covered with a "shrink-fit" band to provide proper sealing and a writing surface for filter identification.

6.2 **Optical Equipment and Microscope Features**

6.2.1 Microscope body with binocular head.

6.2.2 10X Huygenian eyepieces are recommended. Other eyepieces can be substituted if necessary. Wide field eyepieces can be used; however, wide field eyepieces may yield a count field area less than 0.003 mm^2 with the Porton reticle. This is not always desirable from the standpoint of obtaining optimum sampling times (see Section 8.1.3). If wide field eyepieces are used, it is preferable to use the Patterson Globe and Circle reticle to obtain a larger count field area.

6.2.3 Koehler illumination (preferably built-in with provisions for adjusting light intensity).

6.2.4 A Porton reticle is recommended. Others such as the Patterson Globe and Circle can be substituted.

6.2.5 Mechanical stage.

6.2.6 Phase-Contrast condenser with a numerical aperture (N.A.) equal to or greater than the N.A. of the objective.

6.2.7 40-45X phase contrast achromatic objective (N.A. 0.65 to 0.75).

6.2.8 Phase-ring centering telescope or Bertrand lens.

6.2.9 Green or blue filter, if recommended by microscope manufacturer.

6.2.10 Stage micrometer with 0.01 mm subdivisions.

6.2.11 For general guidance on phase contrast microscopy, consult Needham (11.12), Clark (11.15) and McCrone (11.14).

6.3 **Filter Mounting Equipment.** Experience has shown that certain equipment is useful for efficient sample mounting. The following items are recommended for extracting and mounting a portion of the filter for counting.

6.3.1 Microscope slides. 2.5 by 7.5 cm glass slides are most commonly used. Sample number, data, initials, etc., can be conveniently written on a frosted end slide.

6.3.2 Cover Slips. Cover slips are a necessary part of the slide mount and optical system. The shape should be appropriate for the size of the filter wedge. The appropriate cover slip depends upon the objective to be used. Ordinarily, objectives are optically corrected for a #1½ (0.17 millimeter) thickness cover slip. Improper cover glass thickness will detract from the final image quality.

6.3.3 Scalpel. A scalpel is needed to cut out a portion of the filter to be examined. A number-ten curved blade scalpel is recommended.

6.3.4 Tweezers. A pair of fine-tipped tweezers is used to remove the membrane filter slice from the field monitor and place it upon the slide.

6.3.5 Lens Tissue. To insure cleanliness, a lint-free tissue is recommended. This tissue should also be used for wiping mounting tools and for cleaning slides and cover slips.

6.3.6 Glass Rod. A fire-polished glass rod may be used to spread the mounting solution on the slide.

6.3.7 Wheaton Balsam Bottle. This special glass container has a glass top which prevents contamination of the mounting solution. A glass rod is included for dispensing the solution.

7. **Reagents**

Chemicals should be reagent grade, free from particles and color, conforming to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

7.1 Dimethyl phthalate

7.2 Diethyl oxalate

Avoid getting the mounting solution on the skin. Wash skin promptly with soap and water if skin contact occurs.

8. **Procedure**

8.1 **Sampling**

8.1.1 General Information

Guidelines for the monitoring of employee exposures to industrial atmospheres are given in Reference 11.8. The Federal requirements for monitoring employee exposure to airborne asbestos are found in 29 CFR 1910.1001.

8.1.2 Mounting the Sampling Pump on the Worker

Fasten the sampling pump to the worker's belt and fasten the field monitor to the lapel or shirt front (as close to the breathing zone as is practical). Remove the top cover of the plastic monitor, then invert the monitor making certain the exposed filter is facing downward. Turn the pump on and adjust to the calibrated flow rate (1.0 to 2.5 lpm). Record the following information in a logbook.

1. Filter number
2. Pump start time and date
3. Flow rate
4. Subject's name and job title
5. Type of operation or process
6. Ventilation controls and is the worker wearing a respirator approved for asbestos?

The pump should be checked periodically during the sampling period for proper operation and flow rate.

8.1.3 Optimum Sampling Times

The requirement for the minimum count of 100 fibers or 20 fields in 8.3.9 was determined to be the best compromise to achieve adequate precision for the airborne fiber estimate and reasonable counting times. An optimum fiber density of about 1 to 5 fibers per microscope count field is recommended. To estimate appropriate sampling times for feasible counting and optimal counting, one must consider the following constraints:

1. microscope count field area (generally 0.003 to 0.006 mm^2)
2. pump flow rate (typically 2.5 lpm maximum)
3. average airborne fiber concentrations
4. counting rule range of 20 to 100 fields
5. adequate fiber density to obtain a minimum count of 10 fibers in 100 fields, which is the least total fiber count that yields an acceptable count precision
6. background airborne particulate levels that can reduce the count precision due to an obscuring of fibers on the filter surface

The preceding constraints were considered in drawing Figures 1 and 2. These figures were developed from the following relationship:

$$\text{sampling time} = \frac{(FB/FL)\ (ECA/MFA)}{(FR)\ (AC)\ (1000)} \quad \text{minutes}$$

where:

FB/FL = 1 to 5 fibers/field

ECA = effective collecting area of filters (855 mm^2 for 37-mm filter with effective diameter of 33 mm)

MFA = microscope field area (generally 0.003 to 0.006 mm^2)

FR = Pump flow rate (generally 1.0 to 2.5 lpm)

AC = Air concentration of fibers in fibers/cm^3.

Figure 1 (microscope field area = 0.003 mm^2) and Figure 2 (microscope field area = 0.006 mm^2) show optimum and feasible sampling times for a pump flow rate of 1.7 lpm. Each individual responsible for sampling asbestos should prepare a similar chart for his particular pump flow rate and microscope field area before sampling is performed to aid in estimating proper sampling times. On Figures 1 and 2, the areas with solid shading lines are generally the optimum conditions for counting. The broken shading lines are for conditions very close to optimal.

However, feasible counting conditions may extend down to about 0.1 fiber/field and and above 5 fibers/field. Recommended sampling times are most strongly influenced by background airborne particulate levels, once all the other constraints have been estimated. For heavy particulate levels, it may be necessary to limit each filter to about 60 to 180 minutes sampling duration. Each individual responsible for sampling should work closely with the microscopist to attain as high as possible filter surface fiber densities (up to about 5 fibers/field), while avoiding filter surface background particulate levels that create very difficult or impossible counting conditions. If one has very little idea of airborne fiber and particulate levels, the best procedure is to take several long samples (as one 8-hour or two consecutive 4-hour samples) in conjunction with several short samples (as four consecutive 2-hour or eight consecutive 1-hour samples). If the longer samples prove very difficult to count, the microscopist will have the shorter samples to fall back on.

From Figures 1 and 2, it can be seen that there are certain sampling times which will yield optimum fiber densities on the filter for almost all airborne fiber concentrations from 1 to 10 fibers/cm^3. These optimum times have been calculated and are presented in Figure 4. Note that the optimum times given by Figure 4 are approximate and can be varied by as much as ± 25%. The nomogram is intended as a guide to be used where no prior knowledge of the air concentration is available.

8.1.4 End of Sampling Period

Remove the field monitor, replace the plastic top cover and the small end caps, and store the monitor. Always shut off the pump when changing monitors to avoid contaminating or damaging the pump. Record the pump shutoff time and flow rate in the logbook.

8.1.5 Blanks

With each batch (25 to 50 filters) of samples sent for analysis, submit two unopened field monitors which have been subjected to the same treatment as the samples except that they were not exposed to the sampling environment. Label these as blanks. If the blanks yield fiber counts greater than 5 fibers/100 fields, then the entire sampling procedure should be examined carefully for the cause of contamination. The

mounting solution of Section 8.2.1 should also be examined for contamination and/or crystal growth.

8.1.6 Shipping

The field monitors in which the samples are collected should be shipped in a rigid container with sufficient packing material to prevent crushing.

8.1.7 Numbers of Samples

When sampling for the Federal ceiling standard of 10 fibers (>5μm)/cm³, [29 CFR 1910.1001(b) (3), effective July 7, 1972], only one sample (15 minutes maximum duration) is necessary, theoretically. However, several samples should be taken during expected periods of peak air concentrations to allow for detection of gross sampling or counting errors.

When sampling for determination of noncompliance with the Federal 8-hour TWA standard of 2 fibers (>5μm)/cm³, [29 CFR 1910.1001(b) (2)], one should continuously sample as large a portion of the work day as is feasible for airborne concentrations of about 2 to 10 fibers/cm³. However, for a lower airborne concentration such as 0.5 fiber/cm³, one sample might require 4 to 8 hours sampling time in order to get the proper filter fiber density (Section 8.1.3). For this situation, the 8-hour TWA exposure would be determined from one 8-hour or two 4-hour samples as appropriate.

8.2 Sample Preparation

8.2.1 Preparation of Mounting Solution

A very important part of the sample evaluation is the mounting process. This process involves a special mounting medium of prescribed viscosity. The proper viscosity is important in order to expedite filter dissolving and still minimize particle migration. After the sample has been mounted, an elapsed time of approximately sixty minutes is needed before the sample is ready for evaluation.

Combine the dimethyl phthalate and diethyl oxalate in a one to one ratio by volume and pour into a Wheaton balsam bottle. Add approximately 0.05 (± 0.005) grams of new membrane filter per milliliter of solution to reach the necessary viscosity. The mixture must be stirred periodically until the filters have dissolved and a homogeneous mixture is formed. The normal shelf life of the mounting solution is about three months. Twenty milliliters of mounting solution will prepare approximately 300 samples.

8.2.2 Sample Mounting

Cleanliness is important! A dirty working area may result in sample contamination and erroneous counts. The following steps should be followed when mounting a sample.

1. Clean the slides and cover slips with lens tissue. Lay each slide down on a clean surface with the frosted end up. It is a good practice to rest one edge of the cover slip on the slide and the other edge on the working surface. By doing this, you keep the bottom surface (the one which contacts the filter) from becoming contaminated.
2. Wipe all the mounting tools clean with lens tissue and place them on a clean surface (such as lens tissue). All tools should be wiped clean prior to mounting each sample.
3. Using the glass rod supplied with the Wheaton balsam bottle, apply a drop of mounting solution onto the center of the slide. It may be necessary to adjust the quantity of solution so that after the cover slip has been placed on top, the solution extends only slightly beyond the filter boundary. If the quantity is greater than this, particle migration may occur.

4. Using another glass rod, spread the mounting media into a triangular shape. The size of this triangle should coincide with the dimension of the filter wedge.
5. Separate the middle and bottom sections of the field monitor case to expose the filter. Cut a triangular wedge from the center to the edge of the filter using the scalpel. The size of the wedge should approximate one-eighth of the filter surface. The filter can be very carefully removed from the cassette for cutting, but this should only be done with great care.
6. Grasp the filter wedge with the tweezers on the perimeter of the filter which was clamped between the monitor case sections. Do not touch the filter with your fingers. Place the wedge, **sample side up,** upon the mounting medium.
7. Pick up a clean cover slip with tweezers and carefully place it on the filter wedge. Once this contact has been made, **do not reposition the cover slip.**
8. Label the slide with the sample number and current date before proceeding to the next filter. On the bottom (backside) of the slide, trace the perimeter of the filter wedge with a felt tip marking pen. This will enable the counter, after the filter has become transparent, to stay within the filter perimeter when counting.
9. The sample should become transparent within fifteen minutes. If the filter appears cloudy, it may be necessary to press very lightly on the cover slip. This is rarely necessary; however, counting should not be started until an hour after the mounting. This allows the microscopic texture of the filter to become invisible to microscope viewing.
10. Discard the sample mount after two days if it has not been counted. Crystals appearing similar to asbestos fibers may begin to grow at the mounting media/air interfaces. They seldom present any problems if the slide is examined before two days. In any case, stay away from the filter's edges when counting and sizing.

8.3 **Counting of Fibers**

8.3.1 Place the slide on the mechanical stage of the microscope and position the center of the wedge under the objective lens and focus upon the sample. Start counting from one end of the wedge and progress along a radial line to the other end (count in either direction from perimeter to wedge tip). Random fields are selected, without looking into the eyepieces, by slightly advancing the slide in one direction with the mechanical stage control.

8.3.2 It is essential to continually scan over a range of focal planes (generally the upper 10 to 15 micrometers of the filter surface) with the fine focus control during each field count. This is especially necessary for asbestos fibers due to their impaction into the filter matrix.

8.3.3 On most airborne samples, asbestos fibers will generally have fiber diameters less than one micrometer. Therefore, it is necessary to look carefully for faint fiber images.

8.3.4 Regularly check phase ring alignment.

8.3.5 When an agglomerate (mass of material) covers a significant portion of the field of view (approx 1/6 or greater) reject the field and select another. (Do not include it in the number of fields counted.) However, report the fact as it may have meaning on other data collection.

8.3.6 Bundles of fibers are counted as one fiber unless both ends of the fiber can be clearly resolved.

8.3.7 Count only fibers with a length to width ratio greater than or equal to 3:1.

8.3.8 Count only fibers greater than 5 micrometers in length. (Be as accurate as possible in accepting fibers near this length.) Measure curved fibers along the curve to estimate the total length.

8.3.9 Count as many fields as necessary to yield a total count of at least 100 fibers. Exceptions: a) count at least 20 fields even if you count more than 100 fibers, and b) stop at 100 fields even if you haven't reached 100 fibers.

8.3.10 For fibers that cross either one or two sides of the counting field, the following procedure is used to obtain a representative count.
COUNT any fiber greater than 5 micrometers in length, that lies entirely within the counting area. COUNT as "½ fiber" any fiber with only one end lying within the counting area. DO NOT COUNT any fiber crossing any two sides.
Reject and do not count all other fibers. Refer to Figures 5 through 10. Note that the fibers in Figures 5 through 10 **are not representative** of the appearance of most asbestos fibers. Most fibers have a very faint image.

9. Calibration and Standards

9.1 Sampling Train Calibration

The accurate calibration of the sampling pump is essential to the correct calculation of the air volume sampled. The frequency of calibration is dependent on the use, care, and handling to which the pump is subjected. Pumps must be recalibrated if they have just been repaired, misused, or received from the manufacturer. If the pump receives hard usage, more frequent calibration may be necessary. Ordinarily, pumps should be calibrated in the laboratory both before they are used in the field and after they have been used to collect a large number of field samples.

The accuracy of calibration is dependent upon the type of instrument used as a reference. The choice of a calibration instrument will depend largely on where the calibration is performed. For laboratory testing, a 1-liter buret used as a soap bubble flow meter or wet-test meter is recommended. Other standard calibrating instruments, such as a spirometer, Marriott's bottle, or dry gas meter can be used. The calibration should be of sufficient precision that the 95% confidence limits on the flow rate are ± 10% (95% of the flow rates will fall within ± 10% of the calibrated value).

Instructions for calibration with the soap bubble flow meter follow. The sampling train used (pump, hose, filter cassette) in the pump calibration should be the same as the one used in the field.

9.1.1 Check the voltage of the pump battery with a voltmeter both with the pump off and while it is operating to assure adequate voltage for calibration. If necessary, charge the battery to manufacturer's specifications.

9.1.2 Fill a beaker with 10 ml of soap solution.

9.1.3 Connect the filter cassette inlet to the top of the buret with a length of hose.

9.1.4 Turn the pump on and moisten the inside of the soap bubble meter by immersing the open end of the buret into the soap solution and drawing bubbles up the inside of the buret. Perform this task until the bubbles are able to travel the entire length of the buret without breaking.

9.1.5 Adjust the pump rotameter to provide a flow between 1.5 to 2.5 lpm.

9.1.6 With a water manometer, check that the pressure drop across the filter is less than 13 inches of water (about 1 inch of mercury).

9.1.7 Start a soap bubble up the buret and measure the time it takes for the bubble to travel a minimum volume of 1 liter.

9.1.8 Repeat the procedure in 9.1.7 at least three times, average the results, and calculate the calibrated flow rate by dividing the volume traveled by the soap bubble by the elapsed time. If the range between the highest and lowest of the three flow rates is greater than about 0.33 lpm, then the calibration should be repeated since it is likely that the precision is not adequate.

9.1.9 Data required for the calibration include the volume measured, elapsed time, pressure drop, air temperature, atmospheric pressure (or elevation), pump serial number, date, and name of person performing the calibration.

9.1.10 Corrections to the flow rate for pumps with rotameters may be necessary if the pressure (elevation) or temperature where the samples are collected (actual flow rate) differs significantly from that where the calibration was performed (indicated flow rate). Actual flow rates at time of sampling may be calculated for a linear scale rotameter by using the following correction formula:

$$Q_{actual} = Q_{indicated} \sqrt{\frac{P_{cal}}{P_{actual}} \cdot \frac{T_{actual}}{T_{cal}}}$$

where both pressure (P) and temperature (T) are in absolute units such as:

psia = psig + 14.7
deg Rankin = deg Fahrenheit + 460
deg Kelvin = deg Celsius + 273

9.2 **Microscope Setup**

9.2.1 Porton Reticle and the Counting Field
The asbestos fiber count procedure consists of comparing fiber length to the diameters of calibrated circles of a Porton reticle, and counting all fibers greater than 5 micrometers in length lying within a given counting field area. The Porton reticle is a glass plate inscribed with a series of circles and rectangles. The left half of the reticle is divided into six rectangles constituting the counting field. The counting field is illustrated in Figures 5 through 10.

9.2.2 Placement in Eyepiece
The Porton reticle is placed inside the Huygenian eyepiece where it rests on the field-limiting diaphragm. If other types of eyepieces are used, it may be necessary to insert a counting collar for retaining the reticle. The reticle should always be kept clean, since dirt on the reticle is in focus and could complicate the counting and sizing process.

9.2.3 Stage Micrometer
The Porton reticle cannot be used for counting until it has been properly calibrated with a stage micrometer. Most stage micrometer scales are approximately two millimeters long and are divided into units of one-hundredth of a millimeter (ten micrometers).

9.2.4 Microscope Adjustment
When adjusting the microscope, follow the manufacturer's instructions while observing the following guidelines.

1. The light source image must be in focus and centered on the condenser iris or annular diaphragm.
2. The particulate material to be examined must be in focus.
3. The illuminator field iris must be in focus, centered on the sample, and opened only to the point where the field of view is illuminated.
4. The phase rings (annular diaphragm and phase-shifting elements) must be concentric.

9.2.5 Porton Reticle Calibration Procedure
Each eyepiece-objective-reticle combination on the microscope must be calibrated. Should any of the three be changed (disassembly, replacement, zoom adjustment, etc.), the combination must be recalibrated. Calibration may change if interpupillary dis-

tance is changed. For proper calibration, the following procedure should be followed closely.

With a 10X objective in place, place the stage micrometer on the mechanical stage, focus the millimeter scale, and center the image. Change to the 40-45X objective and adjust the first millimeter scale division to coincide with the left boundary of the Porton rectangle. Measure the distance between the left and extreme right boundaries of the Porton rectangle, estimating any portion of the final division. This measurement represents 200 L units. The rectangle is 100 L units on the short vertical dimension. The calculated "L" is inserted into the formula $D = L(2^N)^{1/2}$ where "N" is the circle number (indicated on the reticle) and "D" is the circle diameter. Since the circle diameters vary logarithmically, every other circle doubles in diameter. For example, circle number three is twice the diameter of number one; number four is twice the diameter of number two. When the circle sizes have been determined, the counting field area which consists of the left six smaller rectangles can be calculated from the relation $10{,}000\ L^2$. This completes the reticle calibration for this specific objective-eyepiece-reticle combination.

Example for Porton Reticle

The following calibration was obtained for a pair of 10X Huygenian eyepieces and a 43X objective:

200 L = 0.148 mm = 148 micrometers
100 L = 0.074 mm = 74 micrometers
One L-unit = 0.74 micrometers

Thus Circle #1 has a diameter $D = L(2^N)^{1/2} = 0.74(2^1)^{1/2} = 0.74\ (1.414) = 1.05$ micrometers.

Then our circle diameter calibration table looks like:

Diameter of Circle #1 = 1.05 micrometers
#2 = 1.48
#3 = 2.09
#4 = 2.96
#5 = 4.19
#6 = 5.92

Field area = (10,000) (L^2) = (100 L) (100 L) = (0.074) (0.074) = 0.0055 mm^2

Thus fibers with a length greater than a distance halfway between the diameters of the #5 and #6 circles would be counted.

If a Patterson Globe and Circle reticle is used, a different calculation procedure is required. The circle diameters are related as follows. The #25 circle diameter is (0.1) (reticle length).

The circle diameters are proportional to the ratio of their numbers. Thus the #20 circle diameter is (20/25) or 0.8 times the #25 circle diameter.

10. **Calculations**

10.1 The average airborne asbestos fiber concentration estimated by the filter sample may be calculated from the following formula:

$$AC = \frac{[(FB/FL) - (BFB/BFL)]\ (ECA)}{(1000)\ (FR)\ (T)\ (MFA)}$$

where:

AC = Airborne fiber concentration in (fibers > 5 μm)/cm^3.
BFB = Total number of fibers counted in the BFL fields of the blank or control filters in fibers > 5 μm.
BFL = Total number of fields counted on the blank or control filters.
ECA = Effective collecting area of filter (855 mm^2 for a 37-mm filter with effective diameter of 33 mm).
FR = Pump flow rate in liters/min (lpm).
FB = Total number of fibers counted in the FL fields in fibers > 5 μm.
FL = Total number of fields counted on the filter.
MFA = Microscope count field area in mm^2 (generally 0.003 to 0.006).
T = Sample collection time in minutes.

10.2 Recount criteria. It is very desirable for a counter to conduct a "blind recount" for about 1 in every 10 filter wedges (slides) counted. Alternatively, a second counter could perform the blind recount. In training sessions for novice counters, the trainee should conduct a blind recount for filter wedges counted by an experienced, proficient counter. In all cases, we will observe differences between the first and second counts of the same filter wedge. Most of these differences will be due to chance alone, that is, due to the random variability (precision) of the count method. Statistical recount criteria enable us to decide whether observed differences can reasonably be explained due to chance alone or are probably due to systematic differences between counters or microscopes or due to some other biasing factor.
The following recount criterion is for a pair of counts that estimate some airborne fiber concentration (AC) in fibers/cm^3. The criterion is given at the type-I error level. That is, there is a 5% maximum risk that we will reject a pair of counts for the reason that one might be biased, when the large observed difference is really due to chance.
Reject a pair of counts because one might be biased if:

$$(AC_2 - AC_1) \text{ exceeds } 2.77(\overline{AC})(CV_{FB})$$

where:

AC_1 = lower estimated airborne fiber concentration
AC_2 = higher estimated airborne fiber concentration
$\overline{AC}$ = average of the two airborne concentration estimates
CV_{FB} = average CV for the two concentration estimates which are a function of the total fiber count (FB) in each case. Use the relation in Section 4 or Figure 3.

For a pair of counts on the same filter, reject the pair because one might be biased if:

$$(FB_2 - FB_1) \text{ exceeds } 2.77(\overline{FB})(CV_{\overline{FB}})$$

where:

FB_1 = lower fiber count on the filter (total fibers)
FB_2 = higher fiber count on the filter (total fibers)
$\overline{FB}$ = average of the two total fiber counts
$CV_{\overline{FB}}$ = CV_F for the value FB. Use the relation in Section 4 or Figure 3.

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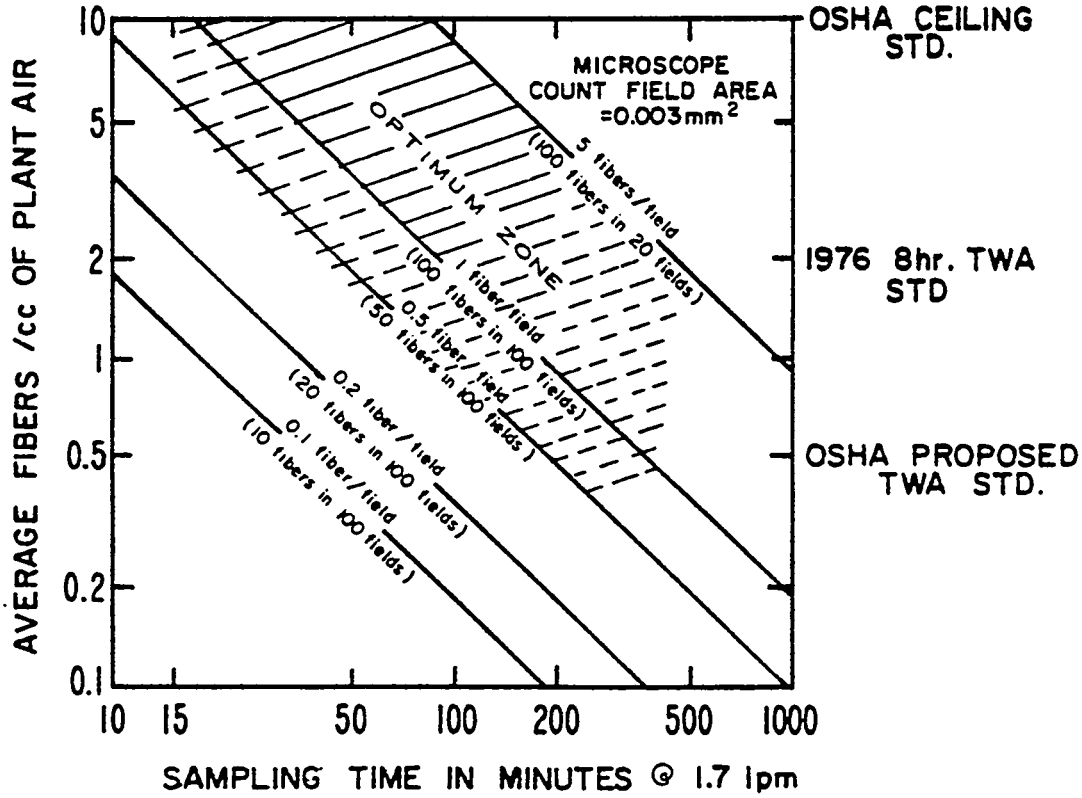

FIGURE 1. Optimum Sampling Times for airborne asbestos where microscopic field area = 0.003 mm²

UCN-1076.6B (12 8-78)

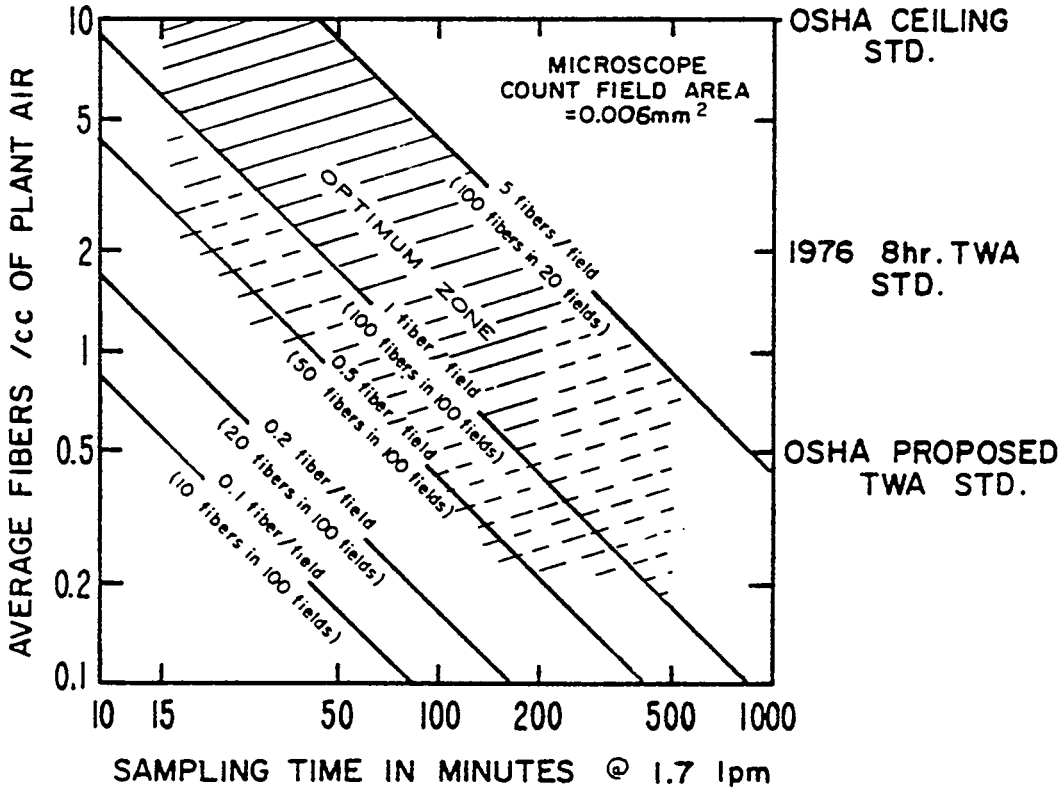

FIGURE 2. Optimum sampling times for airborne asbestos where microscopic field area = 0.006 mm^2

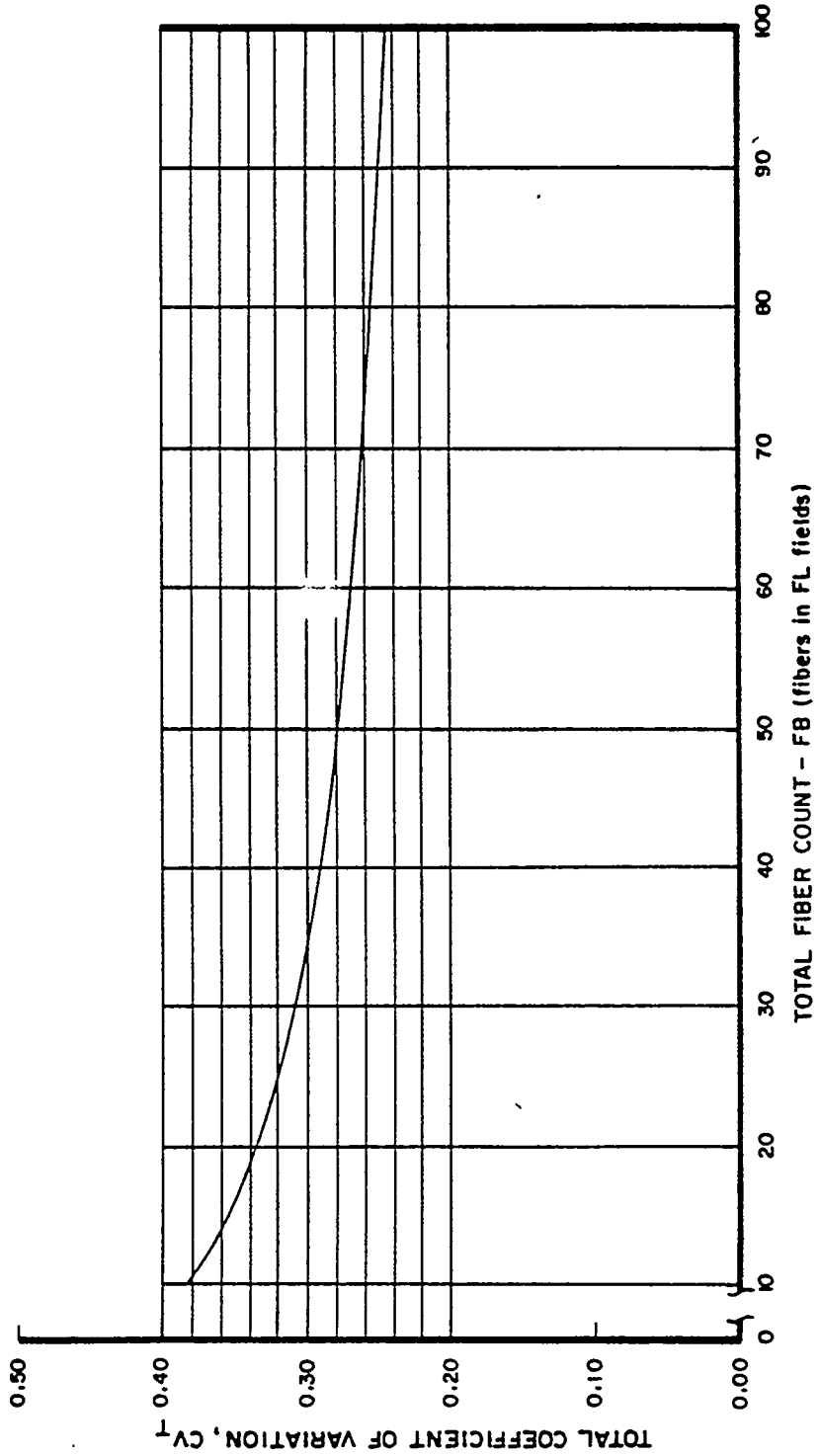

FIGURE 3. Total coefficient of variation as a function of total fiber count

UCN-10766B (12 8-78)

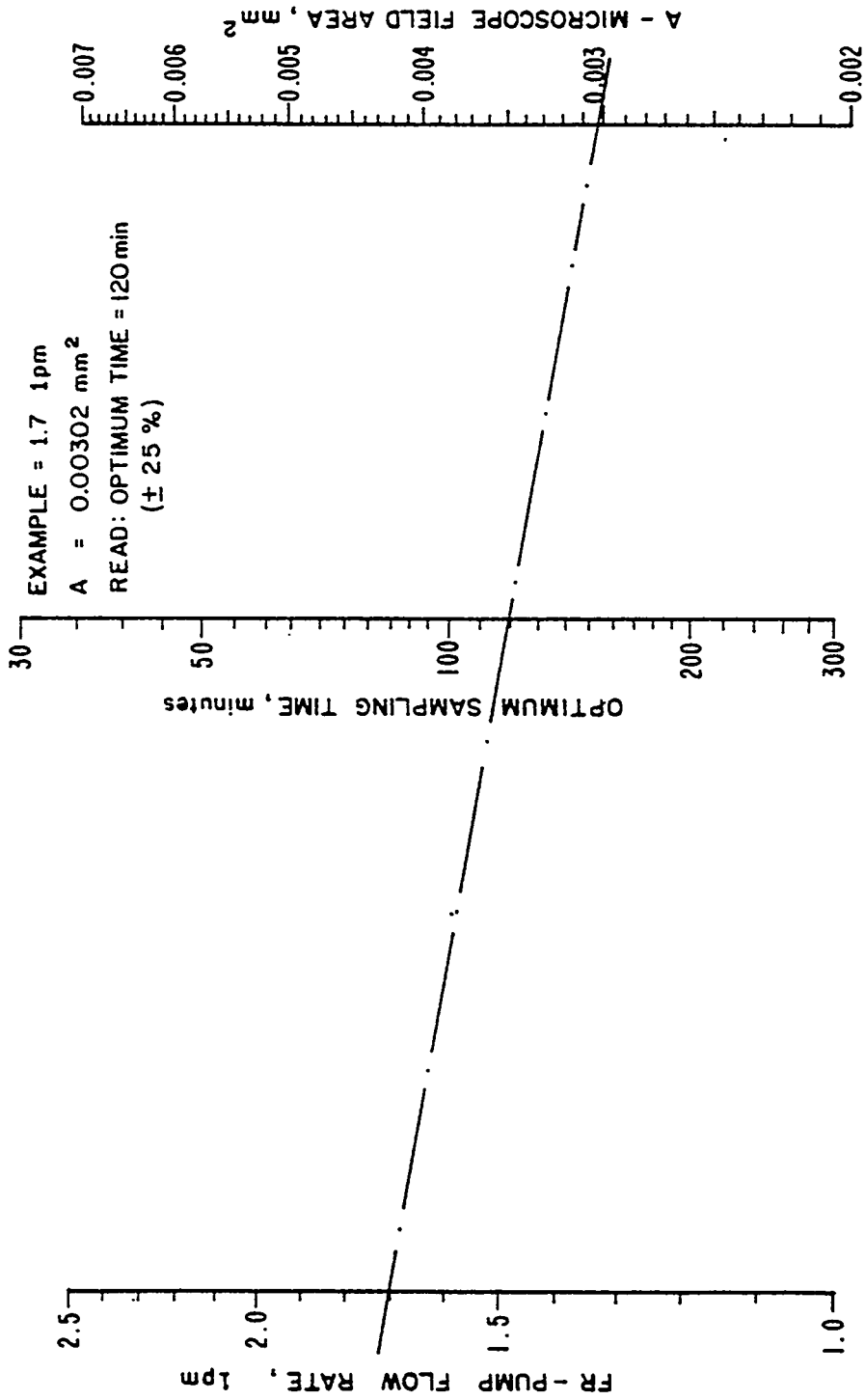

FIGURE 4. Nomogram of optimum sampling times for airborne asbestos fibers in concentrations of 1 to 10 fibers/cm³

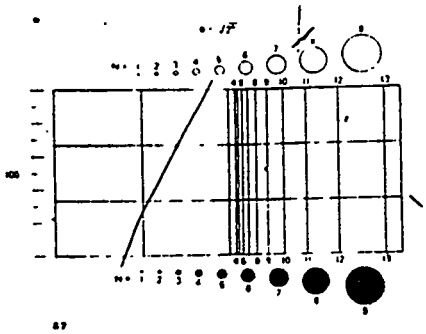

FIGURE 5

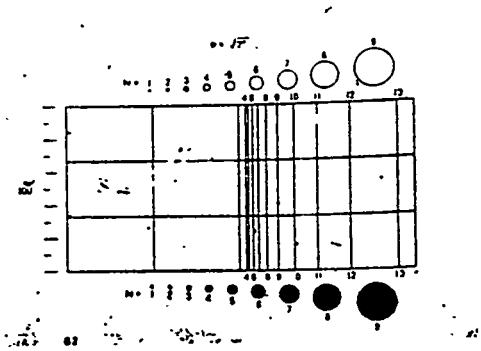

FIGURE 6

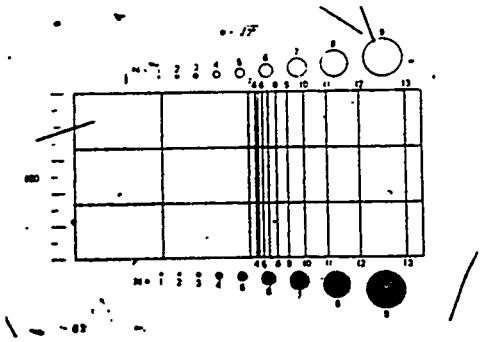

FIGURE 7

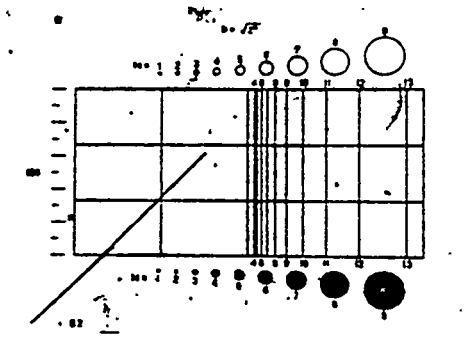

FIGURE 8

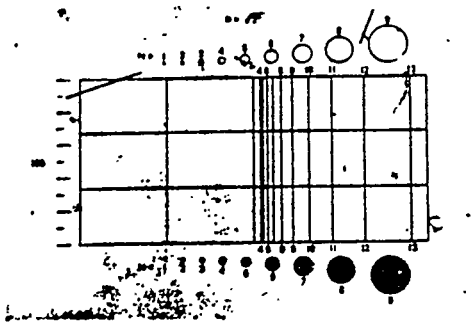

FIGURE 9

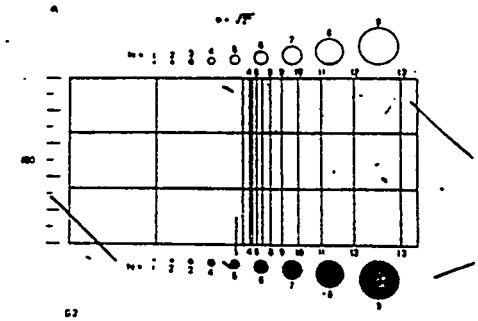

FIGURE 10

LIST OF FIGURES

(5 through 10)

FIGURE 5. DO NOT COUNT. Fiber crosses top and bottom sides.

FIGURE 6. COUNT. One fiber.

FIGURE 7. COUNT. One-half fiber. Fiber crosses left side and one end lies within count area.

FIGURE 8. COUNT. One-half fiber. Fiber crosses bottom side and one end lies within count area.

FIGURE 9. DO NOT COUNT. Fiber crosses two sides.

FIGURE 10. DO NOT COUNT. Fiber crosses two sides (bottom left corner).
COUNT. One-half fiber. Fiber crosses bottom side and one end lies within count area.
COUNT. One fiber (top right corner).

IHA-190 U in air filters, Fluorometric Method

Range 0.05 - 1.0 µg U

Procedure

1. Discuss sample prep.
2. Discuss sample analysis & calib.

Calc

3. Are the calc. checked by anyone for accuracy

Y-123

Use proper format

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE Martin Marietta Energy Systems, Inc. Oak Ridge, Tennessee Paducah, Kentucky	Number IHA-190 Date ~~NIOSH Procedure No.~~ None Supersedes August 27, 1980 Page 1 of 6

Title: **URANIUM IN AIR FILTERS, FLUOROMETRIC METHOD**

Analyte: Uranium	**Method No.:** IHA-190
Matrix: Air	**Range:** 0.05 to 1.0 μg U
Procedure: Filter digestion in acid; TOPO extraction; fluorescence analysis	**Precision:** RSD 5%)fluorometry)

1.0 PRINCIPLE OF THE METHOD

1.1 Air filters (cellulose type) are dissolved with nitric and perchloric acids.

1.2 The uranium is extracted into tri-n-octyl phosphine oxide (TOPO) dissolved in Varsol or hexane.

1.3 An aliquot of the organic phase is fused in a flux of anhydrous sodium fluoride containing 2% lithium fluoride.

1.4 The fluorescence of the pellet is measured using a fluorophotometer and compared to the fluorescence of a uranium standard.

section on sampling, etc.

2.0 RANGE AND SENSITIVITY

This method, as presented, is used for total uranium levels up to 1.0 μg, with a method detection limit (MDL) of 0.05 μg. The range may be extended upward by sample dilution.

3.0 INTERFERENCES

Essentially all interferences from heavy metals are eliminated by the TOPO extraction.

4.0 PRECISION AND ACCURACY

The fluorometric measurement used in this procedure yields and RSD of ±5% at the 0.05 μg U/mL level. The overall precision and accuracy of the procedure have not been evaluated.

5.0 ADVANTAGES AND DISADVANTAGES OF THE METHOD

5.1 The procedure is essentially interference-free.

5.2 The sample preparation is rather lengthy; consequently, care must be taken to avoid contamination.

6.0 APPARATUS

6.1 Fluorophotometer

6.2 Fusion burners, modified Fletcher; or induction furnace

6.3 Platinum fusion dishes, 11/16-in. diam, 1/16-in. lip width, and 1/8-in. deep

6.4 Pelletizer, delivering a 0.3- or 0.6-g pellet

6.5 Infrared lamp, 375 W, and stand

6.6 Laboratory shaker

6.7 Mechanical roller

6.8 Hot plate

6.9 Pipettes, appropriate sizes, semiautomatic.

6.10 Dish holder, aluminum, designed to hold platinum fusion dishes

6.11 Vial, with screw cap, 50 mL

7.0 REAGENTS

7.1 Nitric acid, concentrated, reagent grade.

7.2 Nitric acid, 2 M: Add 62.5 mL of concentrated nitric acid to ~300 mL of distilled water and dilute to 500 mL.

lower temp. ~~borate~~ fusion method

7.3 Sodium fluoride-2% lithium fluoride flux: Put 1350 g (3 lb) of fluorometric grade sodium fluoride and 27 g of lithium fluoride into a clean 5-lb glass reagent jar. Place the jar on the mechanical roller and roll for 48 hours.

7.3.1 Alternate flux, sodium fluoride: The lithium fluoride additive is unnecessary when fusion is completed by induction heat.

7.4 Tri-n-octyl phosphine oxide (TOPO) dissolved in Varsol, 0.05 M (Hexane may be substituted for Varsol): Dissolve 100 g of tri-n-octyl phosphine oxide in 1500 mL of Varsol in a 2000-mL beaker. Filter the solution through fluted filter paper into a 2-gal polyethylene bottle. Add sufficient Varsol to make a total volume of 5 L and mix thoroughly.

7.5 Stock uranium solution: Dissolve 117.9 mg of natural U_3O_8 in 8 M HNO_3 in a 100-mL beaker. Transfer the solution to a 100-mL flask using 2 M HNO_3. Mix thoroughly (1 mL = 1 mg U or 1 g/L).

7.6 Control Standard No. 1: Transfer 10 mL of the stock solution to a 1-L flask and dilute to volume with 2 M HNO_3. Mix thoroughly (1 mL = 10 μg U or 10 mg/L).

7.7 Control Standard No. 2: Transfer 20 mL of the control solution No. 1 to a 1-L flask and dilute to volume with 2 M HNO_3. Mix thoroughly (1 mL = 0.2 μg U or 0.2 mg/L).

7.8 Control standard No. 3: Transfer 50 mL of control solution No. 2 to a 1-L flask and dilute to volume with 2 M HNO_3. Mix thoroughly (1 mL = 0.01 μg U or 0.01 mg/L).

NOTE: Other standard concentrations may be prepared as appropriate from the stock solutions to encompass concentration range of samples.

7.9 Perchloric acid, 70%, reagent grade.

8.0 PROCEDURE

8.1 Sample Preparation

8.1.1 Place the filter in a 150-mL beaker and add 20 mL of concentrated nitric acid. Evaporate to dryness on a hot plate.

8.1.2 Dissolve the residue in 20 mL of concentrated nitric acid and carefully add 2 mL of 70% perchloric acid. Cover with a watch glass and evaporate to dryness in a perchloric hood. (This step is not necessary when using Millipore filters.)

8.1.3 Dissolve the residue in 20 mL of concentrated nitric acid, cover, and heat to dryness.

8.1.4 Dissolve the residue in 10 mL of 2 M nitric acid, cover, and evaporate to a volume of ~2 mL.

8.1.5 Transfer the solution to a 50-mL vial containing 5 mL of TOPO solution. Rinse the beaker several times with small volumes of 2 M nitric acid and add the rinse solution to the vial.

8.1.6 Seal the vial and shake for 2 to 10 minutes on the laboratory shaker.

8.1.7 Remove the vial from the shaker and let the mixture stand for 1 minute, allowing the organic and aqueous layers to separate.

8.1.8 Process a blank and 5 mL of the 0.2- and 0.01-μg U/mL standards along with the samples, starting at Section 8.1.5.

8.2 Fusion using a Modified Fletcher Burner

8.2.1 With a pelletizer, place a 0.3- or 0.6-g pellet of the fluoride flux into each platinum fusion dish to be used.

8.2.2 Place the platinum dishes on a nichrome screen.

8.2.3 In duplicate, pipette 100 or 200 μL of the organic phase from Step 8.1.7 onto each pellet using a semiautomatic pipette. (Use 200 μL for a 0.3-g pellet and 100 μL for a 0.6-g pellet.)

8.2.4 Place the screen under an infrared heat lamp and allow the samples to dry for 30 minutes. The lamp should be ~6 in. above the pellets.

8.2.5 Place the screen over the fusion burner. Fuse for 2 minutes at ~1100°C, then reduce the temperature to 950°C and fuse for 1 minute. (An optical pyrometer will provide temperature estimates.)

8.2.6 Remove the screen from the burner and allow the melts to cool.

8.3 Alternate Fusion Using an Induction Furnace

8.3.1 With the pelletizer, place a 0.3-g pellet of fluoride flux onto each platinum fusion dish to be used.

8.3.2 Place the platinum dishes with the pellets on the aluminum dish holder.

8.3.3 In duplicate, pipette 200 μL of the organic phase from Step 8.1.7 onto each pellet using a semiautomatic pipette.

8.3.4 Place the holder under an infrared heat lamp and allow the samples to dry for 30 minutes. The lamp should be ~6 in. above the pellets.

8.3.5 Remove the holder from under the lamp and place four dishes at a time in the induction furnace coil.

8.3.6 Apply 600 mA current for 60 seconds.

8.3.7 Transfer the dishes back to the holder to cool. (CAUTION: Use forceps.)

8.4 Sample Analysis and Calibration

8.4.1 Place the platinum dishes containing the blank, uranium standards, and fused samples on the turntable of the fluorophotometer.

8.4.2 Move the blank under the ultraviolet light and adjust the zero control until the instrument reads zero.

8.4.3 Move the 0.2-μg/mL standard under the ultraviolet light and adjust the calibration control until the instrument reads the known value of the standard.

8.4.4 Move the 0.02-μg/mL standard under the ultraviolet light. It should read the correct value of the standard if the instrument is properly calibrated. The fluorophotometer is now calibrated for direct readout of uranium concentration of the TOPO from 0.02 through 0.2 μg/mL.

8.4.5 Move the sample pellet under the ultraviolet light of the fluorophotometer and read the uranium concentration in μg/mL.

9.0 CALCULATION

9.1 Uranium in Air Filter

$$\text{Total U in filter, } \mu g = \frac{A}{B} \cdot C,$$

where

A = U on pellet, μg,

B = TOPO extract added to pellet, mL,

C = TOPO volume used in extraction, mL.

$\frac{A}{B}$ may be read directly on a fluorophotometer equipped with direct concentration readout.

9.2 If the fluorophotometer that is used does not have a direct concentration readout capability, meter readings of fluorescence intensity of standards can be used to plot a calibration curve. Intensity readings from samples are then compared to the calibration curve to obtain amounts of uranium in the solution in μg U/mL.

10.0 REFERENCES

10.1 White, J. C.; The Use of Trialkyl Phosphine Oxides as Extractants in the Fluorometric Determination of Uranium; ORNL-2161, November 1, 1956.

10.2 Centanni, F. A., Moss, A. M., and DeSesse, M. A.; "Fluorometric Determination of Uranium"; Anal. Chem., 28, 1651 (1956).

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-190
DATE	August 27, 1980
SUPERSEDES	
PAGE	1 OF 6

URANIUM IN AIR FILTERS, FLUOROMETRIC METHOD

Analyte:	Uranium	Method No.:	IHA-190
Matrix:	Air	Range:	0.05 to 1.0 μg U
Procedure:	Filter digestion in acid; TOPO extraction; fluorescence analysis	Precision:	RSD 5% (fluorometry)

1.0 Principle of the Method

1.1 Air filters (cellulose type) are dissolved with nitric and perchloric acids.

1.2 The uranium is extracted into tri-n-octyl phosphine oxide (TOPO) dissolved in Varsol or hexane.

1.3 An aliquot of the organic phase is fused in a flux of anhydrous sodium fluoride containing 2% lithium fluoride.

1.4 The fluorescence of the pellet is measured using a fluorophotometer and compared to the fluorescence of a uranium standard.

2.0 Range and Sensitivity

2.1 This method, as presented, is used for total uranium levels up to 1.0 μg, with a lower reporting limit of 0.05 μg. The range may be extended upward by sample dilution.

3.0 Interferences

3.1 Essentially all interferences from heavy metals are eliminated by the TOPO extraction.

4.0 Precision and Accuracy

4.1 The fluorometric measurement used in this procedure yields an RSD of ±5% at the 0.05 μg U/ml level. The overall precision and accuracy of the procedure have not been evaluated.

APPROVED BY Y-12	LAB R J McElhaney IH W. S. Everett, Jr.	APPROVED BY ORGDP	LAB T. Kwasnoski IH D. T. Duncan	APPROVED BY UCCND-COORD'R C W Weber
APPROVED BY PGDP	LAB R. E. Simmons IH C. W. Turok	APPROVED BY ORNL	LAB W R Laing IH James A. Eaton	NUMBER IHA-190

5.0 Advantages and Disadvantages of the Method

5.1 The procedure is essentially interference-free.

5.2 The sample preparation is rather lengthy and care must be taken to avoid contamination.

6.0 Apparatus

6.1 Fluorophotometer, modified ORNL Model Q-1165, or equivalent.

6.2 Fusion burners, modified Fletcher; or induction furnace.

6.3 Platinum fusion dishes, 11/16-in. dia, 1/16-in. lip width, and 1/8-in. deep.

6.4 Pelletizer, delivering a 0.3-gram or 0.6-gram pellet.

6.5 Infrared lamp, 375-w, and stand.

6.6 Laboratory shaker.

6.7 Mechanical roller.

6.8 Hot plate.

6.9 Pipets, appropriate sizes, Eppendorf semiautomatic, or equivalent.

6.10 Dish holder, aluminum, designed to hold platinum fusion dishes.

6.11 Vial, screw cap with plastic liner, 2 oz (~50 ml).

7.0 Reagents

7.1 Nitric acid, conc, reagent grade.

7.2 Nitric acid, 2 M: Add 62.5 ml of conc nitric acid to approximately 300 ml of distilled water and dilute to 500 ml.

7.3 Sodium fluoride-2% lithium fluoride flux: Put 1350 grams (3 pounds) of fluorometric grade sodium fluoride and 27 grams of lithium fluoride into a clean 5-pound glass reagent jar. Place the jar on the mechanical roller and roll for 48 hours.

7.3.1 Alternate flux, sodium fluoride: the lithium fluoride additive is unnecessary when fusion is completed by induction heat.

7.4 Tri-n-octyl phosphine oxide (TOPO) dissolved in Varsol, 0.05 M: (Hexane may be substituted for Varsol.) Dissolve 100 grams of tri-n-octyl phosphine oxide in 1500 ml of Varsol in a 2000-ml beaker. Filter the solution through fluted filter paper into a 2-gallon polyethylene bottle. Add sufficient Varsol to make a total volume of 5 liters, and mix thoroughly.

7.5 Stock uranium solution: Dissolve 117.9 mg of natural U_3O_8 in 8 M HNO_3 in a 100-ml beaker. Transfer the solution to a 100-ml flask using 2 M HNO_3. Mix thoroughly. 1 ml = 1 mg U or 1 g/liter.

7.6 Control Standard No. 1: Transfer 10 ml of the stock solution to a 1-liter flask and dilute to volume with 2 M HNO_3. Mix thoroughly. 1 ml = 10 μg U or 10 mg/liter.

7.7 Control Standard No. 2: Transfer 20 ml of control solution No. 1 to a 1-liter flask and dilute to volume with 2 M HNO_3. Mix thoroughly. 1 ml = 0.2 μg U or 0.2 mg/liter.

7.8 Control standard No. 3: Transfer 50 ml of control solution No. 2 to a 1-liter flask and dilute to volume with 2 M HNO_3. Mix thoroughly. 1 ml = 0.01 μg U or 0.01 mg/liter.

7.9 Perchloric acid, 70%, reagent grade.

8.0 Procedure

8.1 Sample Preparation

8.1.1 Place the filter in a 150-ml beaker and add 20 ml of conc nitric acid. Evaporate to dryness on a hot plate.

8.1.2 Dissolve the residue in 20 ml of conc nitric acid and carefully add 2 ml of 70% perchloric acid. Cover with a watchglass and evaporate to dryness in a perchloric hood. (This step is not necessary when using Millipore filters.)

8.1.3 Dissolve the residue in 20 ml of conc nitric acid, cover, and heat to dryness.

8.1.4 Dissolve the residue in 10 ml of 2 M nitric acid, cover, and evaporate to a volume of approximately 2 ml.

8.1.5 Transfer the solution to a 50-ml vial containing 5 ml of TOPO solution. Rinse the beaker several times with small volumes of 2 M nitric acid and add the rinse solution to the vial.

8.1.6 Seal the vial and shake for 2-10 minutes on the laboratory shaker.

8.1.7 Remove the vial from the shaker and let the mixture stand 1 minute, allowing the organic and aqueous layers to separate.

8.1.8 Process a blank and 5 ml of the 0.2- and 0.01-μg U/ml standards along with the samples, starting at Section 8.1.5.

8.2 Fusion using a Modified Fletcher Burner

8.2.1 With a pelletizer, place a 0.3- or 0.6-gram pellet of the fluoride flux into each platinum fusion dish to be used.

8.2.2 Place the platinum dishes on a nichrome screen.

8.2.3 Pipet 100 or 200 microliters of the organic phase from Section 8.1.7 onto each pellet using an Eppendorf pipet. (Use 100 μl for a 0.3-g pellet, and 200 μl for a 0.6-g pellet.)

8.2.4 Place the screen under an infrared heat lamp and allow the samples to dry for 30 minutes. The lamp should be approximately 6 inches above the pellets.

8.2.5 Place the screen over the fusion burner. Fuse for 2 minutes at approximately 1100°C, then reduce the temperature to 950°C and fuse for 1 minute. (An optical pyrometer will provide temperature estimates.)

8.2.6 Remove the screen from the burner and allow the melts to cool.

8.3 Alternate Fusion, using an Induction Furnace

8.3.1 With the pelletizer, place a 0.3-gram pellet of fluoride flux onto each platinum fusion dish to be used.

8.3.2 Place the platinum dishes with the pellets on the aluminum dish holder.

8.3.3 Pipet 200 microliters of the organic phase from Section 8.1.7 onto each pellet using an Eppendorf pipet.

8.3.4 Place the holder under an infrared heat lamp and allow the samples to dry for 30 minutes. The lamp should be approximately 6 inches above the pellets.

8.3.5 Remove the holder from under the lamp and place four dishes at a time in the induction furnace coil.

8.3.6 Apply 600 mA current for 60 seconds.

8.3.7 Transfer the dishes back to the holder to cool. (CAUTION: Use forceps.)

8.4 Sample Analysis and Calibration

8.4.1 Place the platinum dishes containing the blank, uranium standards, and fused samples on the turntable of the fluorophotometer.

8.4.2 Move the blank under the ultraviolet light and adjust the zero control to make the instrument read zero.

8.4.3 Move the 0.2-μg/ml standard under the ultraviolet light and adjust the calibration control until the instrument reads the known value of the standard.

8.4.4 Move the 0.01-μg/ml standard under the ultraviolet light. It should read the correct value of the standard if the instrument is properly calibrated. The fluorophotometer is now calibrated for direct readout of uranium concentration of the TOPO from 0.01 through 0.2 μg/ml.

8.4.5 Move the sample pellet under the ultraviolet light of the fluorophotometer and read the uranium concentration in μg/ml.

9.0 Calculation

9.1 Uranium in Air Filter:

$$\text{Total U in filter, } \mu g = \frac{A}{B} \cdot C \quad ,$$

where:

A = U on pellet, μg,

B = TOPO extract added to pellet, ml, and

C = TOPO volume used in extraction, ml.

$\frac{A}{B}$ may be read directly on a fluorophotometer equipped with direct concentration readout.

9.2 If the fluorophotometer used does not have a direct concentration readout capability, meter readings of fluorescence intensity of standards can be used to plot a calibration curve. Intensity readings from samples are then compared to the calibration curve to obtain amounts of uranium in the solution in μg U/ml.

10.0 References

10.1 White, J. C.; *The Use of Trialkyl Phosphine Oxides as Extractants in the Fluorometric Determination of Uranium*; ORNL-2161, November 1, 1956.

10.2 Centanni, F. A., Moss, A. M., and DeSesse, M. A.; "Fluorometric Determination of Uranium"; Anal. Chem., 28, 1651 (1956).

IHA-130 F, gaseous + H_2O-sol Particulate in Air, SIE meth
(Range 5µg to 1500µg/Sample

Interferences

1. What are known interferences
   a. Presence of acid gases or fumes in the sample collection area – bias low by depleting KCO_3 in filter.
   b. Potential interferences of OH^-, Si^{+3}, Fe^{+3}, & Al^{+3} are eliminated by addition of a pH buffer containing a cation complexing agent prior to measuring the F^- in the sam soln

Precision & Accuracy

2. – 10% or better when >10µg F^- is present
3. – >95% efficient for absorbing atm F in the range of 1 to 20µg/m³ when air was passed thru 2 back-to-back 50mm filters at a flow rate of 0.3 cfm.

Apparatus

4. Look at air sampling system
   a. Discuss system calibration
5. Oven temp check log
   a. How do u know oven temp is accurate?

Reagent

6. Buffer soln prep / Look at glassware used
7. K_2CO_3 prep / Look at balance calib
8. NaF Std stock soln prep
   a. How often do you change buffer soln's?
   b. K_2CO_3 soln?
   c. Na F Std soln?
   d. Do you have paper documentation to support preps
   e. Are prepped solns dated + signed by preparer?

Procedure

9. Discuss filter paper prep.
   a. Why is an untreated filter used at times?
      (to preclude H_2O soluble particulate fluoride)

Collection & Shipping of Samples

10. Discuss

Sample Analysis

11. How much water is used per filter to leach the
12. How long is it allowed to leach?
13. How much sample : buffer soln is used for the mv reading?

Calib & Std

14. Discuss prep & calib curve
15. Who checks the calib calculations?

GDP DRAFT

MARTIN MARIETTA ENERGY SYSTEMS, INC.
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

NUMBER	IHA-130
DATE	
SUPERSEDES	11/27/79
PAGE	1 OF 1

FLUORIDES, PARTICULATE AND GASEOUS IN AIR, SELECTIVE ION ELECTRODE METHOD

NIOSH Method No. 7902

1.0 SCOPE AND APPLICATION

1.1 This method is useful for determining gaseous fluorides such as hydrogen fluoride and both water-soluble and insoluble particulate fluorides in air.

1.2 The working range of the method is 0.1 to 5 mg/~~m~~^{3} M^3 (cap.) for ~~a~~ an 250-L air sample size of.

1.3 The estimated limit of detection is 3 micrograms of fluoride per sample or 0.01 mg/~~m~~^{3} M for ~~a~~ an 250-L air sample size of.

2.0 SUMMARY OF METHOD

2.1 Filtered particulate fluoride is dissolved after fusion with sodium carbonate and the fluoride is measured by a fluoride selective ion electrode.

2.2 If water soluble fluoride is desired, the particulate fluoride is leached with water prior to the fusion step and the leachate is measured for fluoride content.

2.3 Gaseous fluoride is collected on an alkaline treated filter pad. Fluoride is removed from the pad by soaking in a water-buffer solution mixture and the fluoride is then measured by a fluoride selective ion electrode.

3.0 SAMPLE COLLECTION, HANDLING, AND PRESERVATION

3.1 Air is passed through two in-line filter cassettes at a flow rate of 1 to 2 L/min.

3.2 Particulate fluoride is collected on a cellulose acetate membrane filter in the first cassette.

3.3 Gaseous fluoride is collected on an alkaline treated filter pad in the second in-line filter cassette.

4.0 SOURCE OF METHOD

4.1 *NIOSH Manual of Analytical Methods,* Third Edition, Vol. 1, U.S. Department of Health and Human Services, February 1984.

APPROVED BY Y-12	LAB	APPROVED BY ORGDP	LAB	APPROVED BY ENERGY SYSTEMS COORD'R.
	IH		IH	
APPROVED BY PGDP	LAB	APPROVED BY ORNL	LAB	NUMBER
	IH		IH	

UCN-13234
(1235 8-84)

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-130
DATE	Nov. 27, 1979
SUPERSEDES	
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FLUORIDE, GASEOUS AND WATER-SOLUBLE PARTICULATE IN AIR, SELECTIVE ION ELECTRODE METHOD

Analyte: Fluoride, gaseous and water-soluble particulate

Matrix: Air

Procedure: Adsorption on alkaline-treated filter paper; leach with water; and selective ion electrode measurement

Method No.: IHA-130

Range: 5 μg to 1500 μg per sample

Precision: 10% RSD

1.0 Principle of the Method

1.1 A known volume of air is drawn through a sampling train.

1.2 Atmospheric fluoride is collected by absorbing the fluoride on a filter treated with potassium carbonate. Gaseous fluoride may be differentiated from water-soluble particulate fluoride (if desirable) by preceding the treated filter with an untreated filter in the sampling train.

1.3 Fluoride is removed from the filters by leaching them in water. The fluoride is then determined potentiometrically using an ion-selective electrode in conjunction with a standard single junction sleeve-type reference electrode and an expanded millivolt scale electrometer, or a selective ion meter with a direct scale for fluoride.

2.0 Range and Sensitivity

2.1 The lowest amount of fluoride reported is 5 micrograms per sample.

2.2 The upper range is limited only by the capacity of the filter paper used for collecting the gaseous fluoride sample. As much as 1500 micrograms has been collected on two back-to-back 50-mm diameter filters without significant fluoride loss.

3.0 Interferences

3.1 The presence of acid gases or fumes in the sample collection area may bias results low by depleting the potassium carbonate in the filter.

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UCN 13234
(1235 1-79)

3.2 Potential interferences of OH^-, Si^{+4}, Fe^{+3}, and Al^{+3} are eliminated by addition of a pH buffer containing a cation complexing agent prior to measuring the fluoride in the sample solution.

4.0 Precision and Accuracy

4.1 The relative standard deviation of the analysis is estimated to be 10% or better when greater than 10 micrograms of fluoride is present on the filter.

4.2 Field tests conducted at the Paducah Gaseous Diffusion Plant indicated the treated filters were greater than 95% efficient for absorbing atmospheric fluoride in the range of 1 to 20 $\mu g/m^3$ when air was passed through two back-to-back 50-mm filters at a flow rate of 0.3 cfm.

5.0 Advantages and Disadvantages of the Method

5.1 Sampling using filter papers is much more desirable than the use of wet scrubbers and impingers, from the viewpoint of handling and sample preparation. Samples are easily retrieved and new filters can be installed at the same time.

5.2 One moderate disadvantage of the method is that the amount of sample which can be taken is limited by the capacity of the filter paper for absorbing gaseous fluoride. However, as much as 1500 μg of fluoride has been collected on two back-to-back filters.

5.3 Using a conventional sampling train, the precision and accuracy of the method is limited by the reproducibility of the pressure drop across the filter papers. With extended periods of sampling the paper tends to plug somewhat, thus affecting the pressure drop. This drop will affect the flow rate and cause the air volume to be imprecise. Regular adjustment of the flow rate reduces this problem.

6.0 Apparatus

6.1 Air sampling system: the area can be sampled with a combination of a vacuum pump, flow throttle, and air flowmeter, with which flow can be accurately determined at 0.3 cfm or less. To minimize analyte losses in the system, the fluoride filters must be placed at the air entry.

6.2 Electrometer (pH), with expanded mv scale, such as the Orion Model 801 digital pH/mv meter, or equivalent.

6.3 Fluoride ion activity electrode, such as the Orion No. 94-09.

6.4 Reference electrode, single junction, sleeve type, such as Orion No. 90-01, Beckman No. 40454, or Corning No. 476010.

6.5 Magnetic mixer, Teflon-coated stirring bar.

6.6 Membrane filters, 47-mm dia, 0.8-μ pore, Gelman GA-4. These filters have proven to be satisfactory; whereas, similar filters from Millipore have been found to crack during extended periods (several days) of service.

6.7 Filter holders for use with above filters.

6.8 Laboratory oven capable of controlling at 40°C.

6.9 Stainless steel screen wire to support treated filters and fit in oven.

7.0 Reagents

7.1 Buffer solution, pH 5.0-5.5: To approximately 500 ml of distilled water in a 1-liter beaker add 57 ml of glacial acetic acid, 59 g of sodium chloride and 2 g of CDTA (1,2-cyclohexylene dinitrilotetraacetic acid or cyclohexane diaminetetraacetic acid). Stir to dissolve and cool to room temperature. Adjust pH of solution to between 5.0 and 5.5 with 5 N sodium hydroxide (about 150 ml will be required). Transfer to a 1-liter volumetric flask and dilute to volume with distilled water.

7.2 Potassium carbonate, 5% w/v solution. Dissolve 50 g of K_2CO_3 in distilled water and dilute to 1 liter.

7.3 Sodium fluoride standard stock solution: 1 ml = 0.1 mg F. Dissolve 0.2210 g of anhydrous NaF in distilled water and dilute to 1 liter with distilled water. Dilute aliquots of this solution to provide standard solutions as needed.

8.0 Procedure

8.1 Preparation of Filters for Sampling

8.1.1 Pour about 50 ml of 5% K_2CO_3 solution into a disposable weighing dish or other shallow container.

UCN-10766B (12 8-78)

8.1.2 Immerse the membrane filters in the K_2CO_3 solution and allow them to soak about 30 seconds.

8.1.3 Remove each filter with a spatula, allowing the excess solution to drain off, and place the filters on a stainless steel wire screen.

8.1.4 Place the screen in an oven and dry at 40°C. Overheating may discolor the filter paper.

8.1.5 After the filters dry, place two filters in each filter holder. If it is desirable to preclude water-soluble particulate fluoride from the sample, assemble a holder with a single untreated filter to precede the treated filters in the sampling train. Any metal parts of a filter holder exposed to the air sample should be coated with clear acrylic lacquer to prevent losses of fluoride by chemisorption on the metal surfaces.

8.2 Collection and Shipping of Samples

8.2.1 After attachment of the filter holder to the sampling pump, the flow rate is adjusted to an indicated level of 0.3 cfm or less to attain the total sample volume required over a fixed period of time.

8.2.2 After sampling, the filter holders are returned to the laboratory for quantitative fluoride analysis.

8.2.3 No special handling techniques are required after the sample is collected.

8.3 Analysis of Samples

8.3.1 Place the filter paper containing the trapped fluoride into an appropriate beaker and add 25 ml of distilled water. Allow approximately 5 minutes with occasional stirring for the fluoride to solubilize.

8.3.2 Transfer a suitable aliquot into a 100-ml beaker, dilute to 25 ml with distilled water and add 25 ml of buffer solution. Obtain the mv reading by measuring on the selective ion meter as in 9.2.

8.3.3 Determine the amount of fluoride in the sample aliquot from the standard calibration curve prepared in accordance with 9.0.

9.0 Calibration and Standards

9.1 Transfer to 100-ml beakers several 25-ml aliquots of standard sodium fluoride solutions prepared with concentrations sufficient to cover the expected concentration range of the samples. Add 25 ml of buffer solution to each beaker.

9.2 Place each standard on a magnetic stirrer and mix. Immerse the fluoride and reference electrodes in the solution and observe the meter reading while mixing. After the meter reading has stabilized, record the mv reading.

9.3 Prepare a calibration curve by plotting µg F/ml in the standard vs mv reading, using semilogarithmic graph paper. Plot the concentration of fluoride (based on the 25-ml volume of the standards) on the log axis vs the electrode potential developed by the standard on the linear axis, starting with the lowest concentration at the bottom of the scale.

9.4 For calibration of a direct-reading selective ion meter, follow the directions of the manufacturer.

10.0 Calculations

10.1 Fluoride on filter, µg $= \frac{A \times 625}{V}$

where:

A = µg fluoride/ml from calibration curve,

V = sample aliquot, ml, and

625 = 25 ml · 25 ml = dilution factor.

10.2 Fluoride in air, mg/m^3 $= \frac{\text{fluoride on filter, µg}}{1000 \times \text{air volume, m}^3}$.

UCN-10766B (12 8-78)

11.0 References

11.1 Chumbler, D. L., Horntrop, J. O., and Simmons, R. E.; "Treated Filter Paper for Collecting Fluoride from the Atmosphere"; Paducah Plant Development Progress Report, 1973, KYL-646, Part 12.

11.2 Technical Procedures Manual, Technical Services Division, Paducah Gaseous Diffusion Plant, Procedure No. SA-F-2, (1974).

11.3 Manual of Methods for Chemical Analysis of Water and Wastes, U. S. Environmental Protection Agency, p. 65 (1976).

11.4 Standard Methods for the Examination of Water and Wastewater, 14th Edition, p. 391 (1975).

Range - 0.5 to 500 µg Be ; Accuracy ± 10% -

IHA-11S - Be in Air & Smear Samples - Emission Spec Method

Analyst 1- How is photoelectric saturation in the spectrometer photolube detected? (worsening precision

2. Ignition temp of muffle 800°C

3. Maint records on muffle furnace, spectrometer anal balance (0.0005 g) precision

4. Counter-electrode specs - who keeps dec?

GPM Figure N

5. Are u. satisfied w/ reagent grade graphite presently purchased? What about [illegible] graphite powder or equiva

Procedure

Sample Prep

6- When may furnace temp be elevated to 800°C & w (time reduction)

Instr. Calibration

7. Explain how calibration of instrument is done

a. 2 Beks consecutively arced at 30 amps D.C. for 60 sec

b. read @ in turn

c. Same conditions - arc 2 50 µg Be std & read each in turn.

d. Recalibrate if confirmation rdgs are not within limit

Blks = 0 ± 0.3 µg ; stds, 50 ± 4 µg.

Sample Analyses

8. Explain how samples are analyzed.

a. load sam electrodes into auto changer

b. alternately every 10th electrode - blank or std

c. load = # of counter electrodes in the upper changer

d. Adjust ID sam cards in corr order sam, blk, std etc.

e. switch on "Automatic". µg Be punched into cards

Stds

9. Explain how 5000 µg Be/g std is made
   a. weigh 0.1388g BeO & 0.8612g graphite powder (pl vial)
   b. mix 5min in mixer-mill
   c. weigh 0.1g of above mix & 0.9g of graphite powder, mix similarly to obtain the 500 µg Be/g std mix.
10. Explain how 50µg Be calib std is made

References

1. Look at ref books
   a. Automatic Be Analyzer - E.W. Pipes - Maint Tinging Manual Y-12 Plt 14 June '62
   b. Spec Anal of IH sam for Be Using Auto Be Analyzer Doc # Y/P65-223051 Rev A, 10 June '71

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-115
DATE	Nov. 27, 1979
SUPERSEDES	
PAGE	1 OF 5

BERYLLIUM IN AIR AND SMEAR SAMPLES, EMISSION SPECTROGRAPHIC METHOD

Analyte:	Beryllium	Method No.:	IHA-115
Matrix:	Air, smears	Range:	0.5 to 500 μg Be
Procedure:	Optical emission spectroscopy	Precision:	25% at the 95% confidence level
		Accuracy:	~~-10% to +10%~~ ±20%

1.0 Principle of the Method

1.1 This procedure applies to specialized equipment and techniques at the Y-12 Plant.

1.2 Air and smear samples are collected on filter paper (32-mm diameter).

1.3 The filter paper containing the sample is compacted and placed in the crater of a graphite electrode and ashed in a muffle furnace.

1.4 The sample electrode is excited in a direct current arc until the sample is consumed. Light from the arc enters the optical emission spectrometer where the intensity of a beryllium spectral line is measured.

1.5 On the beryllium spectrograph at Y-12, the instrument computes the quantity of beryllium present in the sample electrode from the measured intensity, and prints the results in micrograms Be.

2.0 Sensitivity

2.1 The lower reporting limit is 0.5 microgram.

3.0 Interference

3.1 The exit slit is centered on the 265.06 nm Be line. There are no serious interferences when a spectral bandpass of less than 0.06 nm is used.

4.0 Precision

4.1 In the routine quality control program, precisions of 25% at the

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95% confidence level are normally achieved for Be levels from 10 to 100 μg. At beryllium levels above 100 μg, the precision becomes worse, evidently due to photoelectric "saturation" in the spectrometer phototube.

5.0 Accuracy

5.1 In the routine quality control program, biases range randomly from -10% to +10% of the values in the range from 10 to 100 μg.

6.0 Advantages and Disadvantages of the Method

6.1 The average analyst time per sample is approximately 3.5 minutes.

6.2 The method has a minimum turnaround (results-reporting) time of approximately 15 minutes when an ashing temperature of 800°C is used.

6.3 The spectrograph employed at Y-12 for this measurement is not portable; therefore, all samples must be sent to the Plant Laboratory for analysis.

7.0 Apparatus

7.1 Optical emission spectrometer with a beryllium channel and associated equipment, to convert spectral intensity to micrograms of beryllium by an appropriate linear calibration and subsequently print the result on cards or paper.

7.2 Pellet press for compacting the 32-mm-diameter filter paper sample into a cylinder 4 mm in diameter. (UCC-ND, Y-12 Plant Engineering Drawing E-28585)

7.3 Muffle furnace for igniting samples to 800°C.

7.4 Mixer-mill.

7.5 Block for holding electrodes, lava.

7.6 Scoop for measuring approximately 20 mg of graphite powder.

7.7 Analytical balance, 0.0005-g precision.

7.8 Tool for rolling filter disc for pelletizing.

7.9 Plastic vial, 1/2 x 2 inches (12.7 x 50.8 mm)

7.10 Plastic balls, 3/8-inch diameter. (9.5 mm)

7.11 Graphite tamping tool.

7.12 Electrodes, counter, Y-12 Material Purchase Specification 15-AC-12g, Figure F.

7.13 Electrodes, sample, Y-12 Material Purchase Specification 15-AC-12g, Figure N.

8.0 Reagents

8.1 BeO, reagent grade.

8.2 Graphite powder, 20-mesh, Specpure, Ultra Carbon Co., or equivalent.

9.0 Procedure

9.1 Sample Preparation

9.1.1 Roll the filter paper containing the sample onto the special tool and insert it into the pellet press. An air-actuated plunger compacts the sample into a cylindrical pellet.

9.1.2 Place the pellet into the appropriate electrode in the electrode holder block.

9.1.3 Heat the block of electrodes in the muffle furnace at 600°C for 20 minutes or until sample is thoroughly ashed. (If sample is not sufficiently ashed, the pellets will be ejected from the electrode when the arc is ignited.)

NOTE

A furnace temperature of 800°C may be used to reduce the time required for ashing the samples. However, electrodes must be observed frequently to prevent burning away of the crater rim.

9.1.4 Add a scoop of graphite to the crater of each electrode.

9.1.5 Tamp charge in crater with graphite tamping tool.

9.2 Instrument Calibration

9.2.1 Arc a blank (empty) electrode at 30 amps D.C. for 60 seconds to obtain the zero reading.

UCN-10766B (12 8-78)

9.2.2 Arc a second electrode to confirm the reading.

9.2.3 Using the same conditions, arc a 50-μg Be standard to calibrate the instrument.

9.2.4 Arc a second standard to confirm the reading.

9.2.5 Recalibrate if confirmation readings are not within limits--blanks, 0 ± 0.3 μg; and standards, 50 ± 4 μg.

9.3 Analyzing Samples

9.3.1 Load sample electrodes into the automatic electrode changer. Insert, alternately, a blank or standard every tenth electrode.

9.3.2 Load an equal number of counter electrodes into the carousel of the upper changer.

9.3.3 Place sample identification cards in the card punch in the order in which the samples, blanks, and standards are to be run.

9.3.4 Switch to "Automatic." The electrodes will be sequentially arced and the results in μg Be will be punched onto the cards.

10.0 Standards

10.1 Standard Mix, 5000 μg Be/g

10.1.1 Weigh 0.1388 g BeO and 0.8612 g graphite powder into a plastic vial.

10.1.2 Add a plastic ball to the vial and mix 5 minutes on a mixer-mill.

10.1.3 Weigh 0.1000 g of the above mix and 0.9000 g of graphite powder into a plastic vial with a plastic ball and mix similarly, to obtain the 5000-μg Be/g standard mix.

10.2 Standard Electrode Charging

10.2.1 Weigh 0.010 g of the 5000-μg/g standard mix into an electrode crater to obtain the 50-μg Be calibration standard.

11.0 References

11.1 Pipes, E. W.; *Automatic Beryllium Analyzer*; Maintenance Training Manual MTM-11; Union Carbide Corporation-Nuclear Division, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee, June 14, 1962.

11.2 *Spectrographic Analysis of Industrial Hygiene Samples for Beryllium Using the Automatic Beryllium Analyzer*; Plant Laboratory Instrumental Manual-Spectrographic, Document No. Y/P65-223051 (Revision A); Union Carbide Corporation-Nuclear Division, Oak Ridge, Tennessee, June 10, 1971.

IHA-165 Metals (trace) in Air, AA Spec. (Table 1 & 2)

1. Is this the latest revision to NIOSH P&CAM 173?

Apparatus

2. How often is the personal sampling pump calibrated to maintain accuracy of the volume of air sampled to within ± 5%

3. Do you use borosilicate glassware & clean in 1:1 HNO_3 dist H_2O rinse

4. How do you assure that the thermometer reading is correct? that the manometer is accurate? the stopwatch?

5. What class volumetric glassware do you use? Is it calibrated?

6. Does the air supply have 90 psi minimum pressure when in use? Is it filtered to remove oil & H_2O?

Reagents

7. Is the water double distilled?

8. Is HNO_3 redistilled on site or purchased & tested?

9. Do you use commercially prepared std stock sol'ns or do you prepare on site as per manuf.'s recommend.

Procedure

10. Discuss how equipment is cleaned? Before & after use

11. Discuss collection and shipping of samples

Sample Prep (Blank/10 filter samples)

12. Discuss sample prep procedure.

a. Place filter in a clean 125 ml beaker w/ 6 mL HNO_3, cover w/ watchglass & heat (1-4 hrs) on a hotplate (165°C) until dissolved (slightly yellow soln). Subsequent additions of HNO_3 & heat will produce a clear soln. Rinse watchglass w/ 10% HNO_3 & remove from heat, & place in a steambath (100°C) until dry.

b. What effects the dilution factor?

Sample Analysis

13. Discuss in detail

14. How often is working std soln's made up?

15. Are blank filters carried thru the entire procedure each time samples are analyzed?

16. How do you know to dilute a sample?

17. How often is a mid-range std ~~aspirated~~ to assure the accuracy of the sample det'ns?

18. Are all det'ns based on replicate analysis?

Calib & Stds

19. How long is the Lanthanum soln stable? the Cs soln

20. Std Metal soln's

20. Describe how Ag stds must be stored.

21. Are calib curves prepared using the working stds soln's or std soln's?

22. Are clean membrane filters spiked w/known amts of the elements being det'ned & carried thru the entire proced to insure that the preparation procedure is being prepared followed?

23. When do you use the method of std additions

Calc

24. Who is responsible to check all hand calculat.

K-255

MARTIN MARIETTA ENERGY SYSTEMS, INC.
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

NUMBER	IHA-165
DATE	~~11/3/86~~
SUPERSEDES	8/27/80
PAGE	1 OF 2

METALS (TRACE) IN AIR, AA or ICP method

no blocks of specifics used for the briefsheet

NIOSH method

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to air samples which have been collected on cellulose ester membrane filters.

1.2 This method is an elemental analysis and is not compound specific.

1.3 The analytical range of the method for each element is listed on the referenced procedure.

2.0 SUMMARY

2.1 The filter samples and blanks are digested using the treatment as detailed in the referenced procedures. The metals are determined by using either Atomic Absorption Spectrophotometry (AA) or by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

2.2 The ICP-AES technique permits the simultaneous determination of multiple elements whereas the AA technique determines one element at a time. The technique used is determined by the availability of instrumentation, required detection limit, cost, etc.

2.3 Aliquots of the digested sample can be analyzed separately for many elements when using the atomic absorption technique.

insert station on sampling, sample handling & preservation

3.0

4.0 ~~3.0~~ ~~SAMPLE HANDLING AND PRESENTATION~~ COMMENTS

3.1 A verification should be made to determine that the type of compound in the sample is soluble with the ashing procedure used.

3.2 Some species of Li, Mn, Mo, Sn, W, and Zr will not be completely solubilized by the ICP-AES procedure referenced. Alternate techniques must be used to solubilize these compounds.

3.3 Spectral interferences are the primary interferences encountered in the ICP-AES analysis. These are minimized by judicious wavelength selection, interelement correction factors, and background correction.

APPROVED BY Y-12	LAB	APPROVED BY ORGDP	LAB	APPROVED BY ENERGY SYSTEMS COORD'R.
	IH		IH	
APPROVED BY PGDP	LAB	APPROVED BY ORNL	LAB	NUMBER IHA-165
	IH		IH	

UCN-13234
(1235 8-84)

3.4 Appropriate background correction is required for certain elements determined by AA.

4.0 SOURCE OF METHOD

4.1 NIOSH Manual of Analytical Methods, Third Edition, Vol. 1, U.S. Department of Health, Education, and Welfare, February 1984.

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-165
DATE	August 27, 1980
SUPERSEDES	
PAGE	1 OF 17

METALS (TRACE) IN AIR, ATOMIC ABSORPTION SPECTROPHOTOMETRY

Analyte:	Trace Metals (Tables 1 & 2)	Method No.:	IHA-165 (NIOSH 173)
Matrix:	Air	Range:	Varies with analyte (Table 2)
Procedure:	Filter collection of particulates; atomic absorption spectrophotometry	Precision:	3% RSD (Analytical)

For this analysis, the undersigned committee has approved for inclusion in this manual an existing procedure, exactly as published. Accordingly, the General Procedure for Metals was taken verbatim from the NIOSH Manual of Analytical Methods, Second Edition, Vol. 5, U. S. Department of Health, Education, and Welfare, Method 173, 1979.

The following exceptions to NIOSH 173 should be understood:

A. This procedure employs flame atomization of the analyte metals. However, electrothermal (graphite furnace) atomic absorption spectrophotometry may be substituted for the flame technique. The graphite furnace technique applied in accord with manufacturer's instructions will enhance the sensitivity for most of the metals listed in Table 2 by a factor of 10; some sensitivities will be increased 100-fold or more.

B. Under Section 1.3, line 2:

"...Lead-S314..." should be "...Lead-S341..."

C. Under Section 6.6.4:

A sentence should be added: "A commercially available heated nitrous oxide regulator may be used."

APPROVED BY Y-12	LAB A J McElhaney IH W. S. Everett, Jr.	APPROVED BY ORGDP	LAB T. Kwasnoski IH D. J. Duncan	APPROVED BY UCCND-COORD'R C W Weber
APPROVED BY PGDP	LAB R. E. Simmons IH C. H. Turak	APPROVED BY ORNL	LAB W R Laing IH James A. Ealy	NUMBER IHA-165

Exceptions to NIOSH 173 (continued):

D. Under Section 6.7.1:

The 100-psi cylinder replacement seems unnecessary. Some manufacturers recommend 75 psi.

E. Under 8.1 Cleaning of Equipment:

The use of chromic acid and nitric acid for cleaning glassware to be used for metals procedures requires thorough rinsing. Some laboratories are using commercial detergent-type cleaners in conjunction with, or without, the use of strong acid cleaners.

F. Under Section 8.3.2, line 10:

" . . . footnote 3 . . . " should be " . . . footnote e . . . "

G. Under Section 9.2.1, line 2, and under Section 9.2.2, line 3:

"7.3" should be "7.4."

H. Under Section 9.2.5, lines 11 and 12:

"L" should be "µL."

I. The air sample volume should be calculated in Section 10.1 from sample flow rates corrected to 25°C and 760 mm Hg pressure, using ambient conditions recorded as in Section 8.2.1.

J. Under Table 1, Footnotes d, e, and h:

"g/mL" should be "µg/mL."

K. Under Table 1, Footnote i:

Should be deleted.

L. When using Table 2, the analyst should be reminded of the distinction between "sensitivity" and "detection limit." The definitions for these units and for "working range" are presented in Section 2. Range and Sensitivity.

The following procedure is a photocopied excerpt from: NIOSH Manual of Analytical Methods, Second Edition, Vol. 5, U. S. Department of Health, Education, and Welfare, 1979.

GENERAL PROCEDURE FOR METALS

Measurements Research Branch

Analytical Method

Analyte:	Trace Metals (Tables 1 and 2)	Method No.:	P&CAM 173
Matrix:	Air	Range:	Varies with analyte (Table 2)
Procedure:	Filter collection, acid digestion, AAS	Precision:	3% RSD (Analytical)
Date Issued:	9/17/73		
Date Revised:	5/14/79	Classification:	B (Accepted)

1. Synopsis

1.1 This procedure describes a general method for the collection, dissolution and determination of trace metals in industrial and ambient airborne material. The samples are collected on membrane filters and treated with nitric acid to ash the organic matrix and to dissolve the metals present in the sample. The analysis is subsequently made by atomic absorption spectrophotometry (AAS).

1.2 Samples and standards are aspirated into the appropriate AAS flame. A source of characteristic radiation energy is necessary for each metal. The absorption of this characteristic energy by the atoms of interest in the flame is related to the concentration of the metal in the aspirated sample. The flames and operating conditions for each element are listed in Table 1.

1.3 Metals for which other AAS procedures exist (e.g., Antimony-P&CAM 261 and Lead-S314) should be analyzed using that method.

2. Working Range, Sensitivity, and Detection Limit

The sensitivity, detection limit, and optimum working range for each metal are given in Table 2. The sensitivity is defined as that concentration of a given element which will absorb 1% of the incident radiation (0.0044 absorbance units) when aspirated into the flame. The detection limit is defined as that concentration of a given element which produces a signal equivalent to two times the standard deviation of the blank signal for aqueous solutions. Detection limits and blank values for real samples may be greater than those given in Table 2 since the

blanks resulting from the reagents and the filter material have not been taken into account. The working range for an analytical precision better than 3% is generally defined as those sample concentrations which will absorb greater than 10% of the incident radiation and are in the linear region of the calibration curve. The values for the sensitivity and detection limits are instrument dependent and many vary from instrument to instrument.

3. Interferences

3.1 In atomic absorption spectrophotometry, the occurrence of interferences is less common than in many other analytical determination methods. Interferences can occur, however, and when encountered are corrected for as indicated in the following sections. The known interferences and correction methods for each metal are indicated in Table 1. The methods of standard additions and background monitoring and correction (11.1-11.4) are used to identify the presence of an interference problem. Insofar as possible, the matrix of the samples and standards are matched to minimize the possible interference problems.

3.1.1 Background or non-specific absorption can occur from particles produced in the flame which can scatter the incident radiation causing an apparent absorption signal. Light scattering problems may be encountered when solutions of high salt content are being analyzed. Light scattering problems are most severe when measurements are made at the lower wavelengths (i.e., below about 250 nm). Background absorption may also occur as the result of the formation of various molecular species which can absorb light. The background absorption should be accounted for by the use of background correction techniques (use of D_2 or H_2 continuum or a nearby non-absorbing wavelength)(11.1, 11.6).

3.1.2 Spectral interferences are those interferences which occur as the result of an atom different from that being measured absorbing a portion of the incident radiation. Such interferences are extremely rare in atomic absorption. In some cases, multi-element hollow cathode lamps may cause a spectral interference by having closely adjacent radiation lines from two different elements. In such instances, multi-element hollow cathode lamps should not be used, or the use of more narrow spectral slits or alternate wavelengths may be used to alleviate the problem.

3.1.3 Ionization interferences can occur when easily ionized atoms are being measured. The degree to which such atoms are ionized is dependent upon the atomic concentration and presence of other easily ionized atoms in the sample.

Ionization interferences can be controlled by the addition to the sample of a high concentration of another easily ionized element which will buffer the electron concentration in the flame. Typically, 1000-2000 µg/mL of an alkali metal (K, Na, Cs) salt is added to sample and standard solutions.

3.1.4 Chemical interferences occur in atomic absorption spectrophotometry when species present in the sample cause variations in the degree to which atoms are formed in the flame. Such interferences may be corrected for by controlling the sample and standard matrix, by using the method of standard additions, or by use of a higher temperature flame (11.2, 11.6).

3.1.5 Physical interferences may result if the physical properties of the samples vary significantly. Changes in viscosity and surface tension can affect the sample aspiration rate and thus cause erroneous results. Sample dilution and/or the method of standard additions are used to correct such interferences. High concentrations of silicates in the sample can cause an interference for many of the elements and may cause aspiration problems. No matter what elements are being measured, if large amounts of silicates are extracted from the samples, the samples should be allowed to stand for several hours and centrifuged to remove the silicates.

3.2 This procedure describes a generalized method for sample preparation which is applicable to the majority of samples of interest. There are, however, some relatively rare chemical forms of a few of the elements listed in Table 1 which will not be dissolved by this procedure. If such chemical forms are suspected, results obtained using this procedure should be compared with those obtained using an appropriately altered dissolution procedure. Alternatively, the results may be compared with values obtained utilizing a non-destructive technique which does not require sample dissolution (e.g., x-ray fluorescence, activation analysis).

4. Precision and Accuracy

4.1 The relative standard deviation of the analytical measurement is approximately 3% when measurements are made in the ranges listed in Table 2. The overall relative standard deviation will be somewhat larger than this value due to errors associated with the sample collection and preparation steps.

4.2 Collaborative testing of this method by 16 laboratories, using filters loaded at three concentration levels in a dynamic aerosol generation and sampling system, indicated that the average per-

cent recoveries and standard deviations for representative metals are: Cd, 100.8 ± 9.9; Co, 97.6 ± 13.9; Cr, 96.6 ± 10.8; Ni, 98.6 ± 10.3; and Pb, 98.7 ± 12.2.

5. Advantages and Disadvantages

5.1 The sensitivity is adequate for all metals in air samples provided an adequate volume of air is sampled.

5.2 This method has been ruggedized for Be, Cd, Co, Cr, Cu, Mn, Mo, Ni and Pb and collaboratively tested for Cd, Co, Cr, Ni and Pb.

5.3 A disadvantage of the method is that approximately 2 mL of solution is necessary for each metal determination. Also, the necessary dilution limits the detection of small quantities of analyte or replicate analysis of several elements per sample.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the collection of personal air samples has the following components:

6.1.1 The filter unit, consisting of the filter media (6.2) and appropriate cassette filter holder, either a two- or three-piece filter cassette (Millipore Filter Corporation, Bedford, Massachusetts or equivalent).

6.1.2 A personal sampling pump of sufficient capacity to maintain a face velocity of 2.6 cm/sec (1-2 Lpm using a 37-mm filter). This pump must be calibrated so the volume of air sampled can be measured to an accuracy of ± 5%. The pump must be calibrated with a representative filter unit in the line.

6.1.3 Thermometer.

6.1.4 Manometer.

6.1.5 Stopwatch.

6.1.6 Various clips, tubing, spring connectors and belt for connecting sampling apparatus to worker being sampled.

6.2 Cellulose ester membrane filter, 0.8 μm pore size, 37-mm (Millipore Type AA or equivalent).

6.3 Glassware (borosilicate). Before use, all glassware must be cleaned in 1:1 nitric acid and rinsed several times with distilled water.

6.3.1 125-mL Phillips or Griffin beakers with watchglass covers.

6.3.2 15-mL graduated centrifuge tubes.

6.3.3 10-mL volumetric flasks.

6.3.4 100-mL volumetric flasks.

6.3.5 1-L volumetric flasks.

6.3.6 125-mL polyethylene bottles.

6.3.7 Additional auxiliary glassware such as pipettes and different size volumetric glassware will be required depending on the elements being determined and the dilutions required to have sample concentrations above the detection limit and in the linear response range (i.e., see Table 2). All pipettes and volumetric flasks required in this procedure should be calibrated class A volumetric glassware.

6.4 Hotplate (suitable for operation at 165°C).

6.5 Steambath or 100°C hotplate.

6.6 Equipment for Analysis

6.6.1 Atomic absorption spectrophotometer with burner heads for air-acetylene and nitrous oxide-acetylene flames.

6.6.2 Hollow cathode or electrodeless discharge lamps for each metal and a continuum lamp (D_2 or H_2).

6.6.3 Two-stage regulators for air, acetylene and nitrous oxide.

6.6.4 Heating tape and rheostat for nitrous oxide regulator (second regulator stage and connecting hose to the instrument should be heated to approximately 60°C to prevent freeze up).

6.7 Supplies

6.7.1 Acetylene gas (cylinder) of a grade specified by the manufacturer of the instrument employed. (Replace cylinder when pressure decreases below 100 psi.)

6.7.2 Nitrous oxide gas (cylinder).

6.7.3 Air supply with a minimum pressure of 40 psi filtered to remove oil and water.

7. Reagents

7.1 Purity. ACS analytical reagent grade chemicals or equivalent shall be used in all tests. References to water shall be understood to mean double distilled water or equivalent. Care in selection of reagents and in following the listed precautions is essential if low blank values are to be obtained.

7.2 Concentrated nitric acid (68-71%), redistilled, specific gravity 1.42.

7.3 10% nitric acid.

7.4 Standard stock solutions (1000 µg/mL) for each metal in Table 1, commercially prepared or prepared per instrument manufacturer's recommendations.

7.5 Lanthanum nitrate ($La(NO_3)3 \cdot 6H_2O$).

7.6 Cesium nitrate ($CsNO_3$).

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Before initial use, glassware is cleaned with a saturated solution of sodium dichromate in concentrated sulfuric acid (NOTE: Do not use for chromium analysis) and then rinsed thoroughly with warm tap water, concentrated nitric acid, tap water and deionized water, in that order, and then dried.

8.1.2 All glassware is soaked in a mild detergent solution immediately after use to remove any residual grease or chemicals.

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, it is not necessary to use the chromic acid cleaning solution.

8.2 Collection and Shipping of Samples

8.2.1 Ambient atmospheric particulate matter and industrial dusts and fumes are sampled with cellulose membrane filters. Sample flow rate is monitored with a calibrated rotameter (11.5) or the equivalent. The flow rate, ambient temperature and barometric pressure are recorded at the beginning and the end of the sample collection period.

8.2.2 For personal sampling, 37-mm diameter filters in holders are used. The personal sampling pumps for this application are operated at 1.5 Lpm. In general, a two-hour sample at 1.5 Lpm will provide enough sample to detect the elements sought at air concentrations of 0.2 x TLV.

8.2.3 After sample collection is complete, plug the openings of the cassette and submit the sampling unit to the laboratory. Losses of sample due to overloading (> 2 mg) of the filter must be avoided.

8.2.4 Filter samples should be sealed in individual plastic filter holders for storage and shipment.

8.3 Preparation of Samples

8.3.1 The samples and blanks (minimum of one filter blank for every 10 filter samples) are transferred to clean 125-mL Phillips or Griffin beakers and 6.0 mL HNO_3 is added. Each beaker is covered with a watchglass and heated on a hotplate (165°C) in a fume hood until the sample dissolves and a slightly yellow solution is produced. Approximately four hours of heating will be sufficient for most air samples. However, subsequent additions of HNO_3 may be needed to completely ash and destroy high concentrations of organic material and, under these conditions, longer ashing times will be needed. Once the ashing is complete, as indicated by a clear solution in the beaker, the watchglass is removed and rinsed into the sample beaker with 10% HNO_3. The beakers are then placed on a 100°C steambath and allowed to go to dryness.

8.3.2 Once a sample is dry, rinse the walls of the beaker with 3-5 mL of 10% HNO_3 and reheat for five minutes at 100°C to solubilize the residue. The solution is quantitatively transferred with 10% HNO_3 to a 10-mL volumetric flask. If any elements are being determined which require the ionization buffer, 0.2 mL of 50 mg/mL Cs is added to the volumetric flask (see Table 1, footnote d). If any elements requiring the releasing agent are being determined, 0.2 mL of 50 mg/mL La is added to each volumetric flask (see Table 1, footnote 3). The samples are then diluted to volume with 10% HNO_3.

8.3.3 The 10-mL solution may be analyzed directly for any element of very low concentration in the sample. Aliquots of this solution may then be diluted to an appropriate volume for the other elements of interest present at higher concentrations. (NOTE: Approximately 2 mL of

solution are required for each element being analyzed.) The dilution factor will depend upon the concentration of elements in the sample and the number of elements being determined by this procedure.

8.4 Analysis of Samples

8.4.1 Set the instrument operating conditions as recommended by the manufacturer. The instrument should be set at the radiation intensity maximum for the wavelength listed in Table 1 for the element being determined.

8.4.2 Standard solutions should match the sample matrix as closely as possible and should be run in duplicate. Working standard solutions, prepared fresh daily, are aspirated into the flame and the absorbance recorded. Prepare a calibration graph as described in Section 9.2.3 (NOTE: All combustion products from the AA flame must be removed by direct exhaustion through the use of a good separate flame ventilation system).

8.4.3 Blank filters must be carried through the entire procedure each time samples are analyzed.

8.4.4 Aspirate the appropriately diluted samples directly into the instrument and record the absorbance for comparison with standards. Should the absorbance be above the calibration range, dilute an appropriate aliquot to 10 mL. Aspirate water between each sample. A mid-range standard must be aspirated with sufficient frequency (i.e., once every five samples) to assure the accuracy of the sample determinations. To the extent possible, all determinations are to be based on replicate analysis.

9. Calibration and Standardization

9.1 Ionization and chemical interference suppressants

9.1.1 Lanthanum solution (50 mg/mL). Dissolve 156.32 g of lanthanum nitrate ($La(NO_3)3 \cdot 6H_2O$) in 2% (v/v) HNO_3. Dilute to volume in a 1-L volumetric flask with 2% (v/v) HNO_3. When stored in a polyethylene bottle, this solution is stable for at least one year.

9.1.2 Cesium solution (50 mg/mL). Dissolve 73.40 g of cesium nitrate ($CsNO_3$) in distilled water. Dilute to volume in a 1-L volumetric flask with distilled water. When stored in a polyethylene bottle, this solution is stable for at least one year.

9.2 Standard metal solutions

9.2.1 Dilute standards (100 µg metal/mL). Pipet 10 mL of the stock (1000 µg metal/mL; Section 7.3) into a 100-mL volumetric flask, add 10 mL HNO_3 and dilute to volume with distilled water. Prepare these standards fresh weekly. (NOTE: Silver standards must be stored in amber bottles away from direct light.)

9.2.2 Working standards. Working standards for each metal of interest are prepared by dilution of the dilute standards (9.2.1) or the stock standards (7.3) such that the final acid concentration is the same for the samples and standards (i.e., 10% v/v HNO_3 in most cases). Lanthanum or cesium is added to samples and standards as indicated in Table 1 such that the final concentraton is 1000 µg La or Cs/mL. Concentrations of the working standards should cover the range for the metal of interest (Table 2). Prepare these solutions fresh daily.

9.2.3 The standard solutions are aspirated into the flame and the absorbance (or concentration) recorded. If the instrument used displays transmittance, these values must be converted to absorbance. A calibration curve is prepared by plotting absorbance (units) versus metal concentration. The best fit curve (calculated by linear least square regression analysis) is fitted to the data points. This line or the equation describing the line is used to obtain the metal concentration in the samples being analyzed.

9.2.4 To insure that the preparation procedure is being properly followed, clean membrane filters are spiked with known amounts of the elements being determined by adding appropriate amounts of the previously described standards and carried though the entire procedure. The amount of metal is determined and the percent recovery calculated. These tests will provide recovery and precision data for the procedure as it is carried out in the laboratory for the soluble compounds of the elements being determined.

9.2.5 Analysis by the method of standard additions. In order to check for interferences, samples are initially and periodically analyzed by the method of standard additions and the results compared to those obtained by the conventional analytical determination. For this method, the sample is divided into three 2-mL aliquots. To one of the aliquots an amount of metal approximately equal to that in the sample is added. To another aliquot twice this amount is added. (NOTE: Additions should be made

by micropipetting techniques such that the volume does not exceed 1% of the original aliquot volume, i.e., 10 L and 20 L additions to a 2-mL aliquot.) The solutions are then analyzed and the absorbance readings are plotted against metal added to the original sample. The line obtained from such a plot is extrapolated to 0 absorbance and the intercept on the concentration axis is taken as the amount of metal in the original sample (11.2). If the result of this determination does not agree to within 10% of the values obtained with the procedure described in Section 9.2.3, an interference is indicated and standard addition techniques should be utilized for sample analysis.

10. Calculations

10.1 The corrected volume collected by the filter is calculated by averaging the beginning and ending sample flow rates, converting to cubic meters and multiplying by the sample collection time. The formula for this calculation is:

$$V = \frac{(F_B + F_E)t}{2000}$$

where: V = sample volume (m^3)
F_B = sample flow rate at beginning of sample collection (Lpm)
F_E = sample flow rate at end of sample collection (Lpm)
t = sample collection time (minutes)

10.2 After any necessary correction for the blank has been made, metal concentrations are calculated by multiplying the micrograms of metal per mL in the sample aliquot by the aliquot volume and dividing by the fraction which the aliquot represents of the total sample and the volume of air collected by the filter:

$$\mu g \text{ metal}/m^3 = \frac{(C \times V_A) - B}{v \times F}$$

where: C = concentration (µg metal/mL) in the aliquot
V_A = volume of aliquot (mL)
B = total µg of metal in the blank
F = fraction of total sample in the aliquot used for measurement (dimensionless)
v = volume of air sampled (m^3)

11. References

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R. Delon Hull
Inorganic Methods Development Section

Table 1. Instrument Parameters

Element	Type of Flame o = oxiziding r = reducing	Analytical Wavelength (nm)	Interferences[b]	Remedy[b]	References
Ag	Air-C_2H_2(o)	328.1	IO_3^-,WO_4^{-2},Mn_4^{-3}	c	(5)
Al[a]	N_2O-C_2H_2(r)	309.3	Ionization,SO_4^{-2}, V,Fe,HCl,H SO	c,d,e	(4,6)
As	Air-C_2H_2(o)	193.7	Background absorption	g	(6)
Ba	N_2O-C_2H_2(r)	553.6	Ionization,large conc. of Ca	d,f	(1,4)
Be[a]	N_2O-C_2H_2(r)	234.9	Al,Si,Mn	e,c,g	(4)
Bi	Air-C_2H_2(o)	223.1		g	
Ca	Air-C_2H_2(r) N_2O-C_2H_2(r)	422.7	Ionization and chemical	d,e	(1,4)
Cd	Air-C_2H_2(o)	228.8		e,g	
Co[a]	Air-C_2H_2(o)	240.7		e,g	
Cr[a]	Air-C_2H_2(r)	357.9	Fe,Ni	e,c	(4)
Cu	Air-C_2H_2(o)	324.8			
Fe	Air-C_2H_2(o)	248.3	High Ni conc.,Si	c,g	(1,4)
In	Air-C_2H_2(o)	303.9	Al,Mg,Cu,Zn,$H_xPO_4^{x-3}$	c	(10)
K	Air-C_2H_2(o)	766.5	Ionization	d	(1,4)
Li	Air-C_2H_2(o)	670.8	Ionization	d	(11)
Mg	Air-C_2H_2(o) N_2O-C_2H_2(o)	285.2	Chemical ionization	e d	(1,4)
Mn	Air-C_2H_2(o)	279.5			
Mo	N_2O-C_2H_2(r)	313.5	Ca and other ions	e,h	(6)
Na	Air-C_2H_2(o)	589.6	Ionization	e	(1,4)
Ni	Air-C_2H_2(o)	232.0		e,g	
Pb	Air-C_2H_2(o)	217.0 283.3	Ca,High conc. $SO_4^{=}$	e,c,g	(7)
Pd	Air-C_2H_2(o)	247.6	Al,Co,Ni,Pt,Rh, Ru	e	(6)
Rb	Air-C_2H_2(o)	780.0	Ionization	d	(1,8)
Si	N_2O-C_2H_2(r)	251.6	Avoided by not using multi-element lamp containing Fe		
Sr	Air-C_2H_2(r) N_2O-C_2H_2(r)	460.7	Ionization and chemical	d,e	(1,8)
Te	Air-C_2H_2(o)	241.3		g	(6)
Tl	Air-C_2H_2(o)	276.8			
V[a]	N_2O-C_2H_2(r)	318.4			
Zn	Air-C_2H_2(o)	213.9		g	

a. Some compounds of these elements will not be dissolved by the procedure described here. When determining these elements one should verify that the types of compounds suspected in the sample will dissolve using this procedure (see Section 3.2).

b. High concentrations of silicates in the sample can cause an interference for many of the elements in this table and may cause aspiration problems. No matter what elements are being measured, if large amounts of silicates are extracted from the samples, the samples should be allowed to stand for several hours and centrifuged or filtered to remove the silicates.

c. Samples are periodically analyzed by the method of additions to check for chemical interferences. If interferences are encountered, determinations must be made by the standard additions method or, if the interferent is identified, it may be added to the standards.

d. Ionization interferences are controlled by bringing all solutions to 1000 g/mL Cs (samples and standards).

e. 1000 g/mL solution of La as a releasing agent is added to all samples and standards.

f. In the presence of very large Ca concentrations (greater than 0.1%) a molecular absorption from $Ca(OH_2)$ may be observed. This interference may be overcome by using background correction when analyzing for Ba.

g. Use D_2 or H_2 continuum for background correction.

h. Add 1000 g/mL Al to both standards and samples.

i. Use alternate Sb line (231.2 nm).

Table 2. Sensitivity Data

Element	Sensitivity[a] µg/mL	Solution Detection Limits[a] µg/mL	Range[a,b] µg/mL	Range[a,b] µg/m³ [c,d]	Minimum[e,f] TLV µg/m³
Ag	0.06	0.002	0.5-4.0	21-170	10 (metal and soluble compounds)
Al	1.0	0.02	5-50	210-2100	NL
As	0.8	0.2	10-50	420-2100	50 (arsenic trioxide production)
					500 (arsenic and compounds as As)
Ba	0.4	0.008	1-25	42-1050	500 (soluble compounds)
Be	0.025	0.001	0.1-2.0	4.2-84	2
Bi	0.5	0.025	1-30	42-1250	NL
Ca	0.08	0.005	0.1-5.0	4.2-210	2,000 (CaO)
Cd	0.025	0.001	0.1-2.0	4.2-84	50 (metal dust, soluble salts, cadmium oxide fume)
Co	0.15	0.01	0.5-5.0	21-210	50 (metal fume and dusts)
Cr	0.1	0.003	0.5-5.0	21-210	500 (soluble chromic, chromous salts)
					100 (chromic acid and chromate, as CrO_3)
					100 (chromite ore processing, as CrO_3)
Cu	0.09	0.002	0.5-5.0	21-210	1,000 (dusts and mists)
					200 (fume)
Fe	0.12	0.005	0.5-5.0	21-210	5,000 (iron oxide fume, as iron oxide)
					1,000 (soluble compounds)
In	0.7	0.02	5-50	210-2100	100 (metal and compounds)
K	0.04	0.002	0.1-2.0	4.2-84	2,000 (as KOH)
Li	0.035	0.0003	0.1-2.0	4.2-84	25 (as lithium hydride)

Element	Sensitivity[a] µg/mL	Solution Detection Limits[a] µg/mL	Range[a,b] µg/mL	Range[a,b] µg/m³ c,d	Minimum[e,f] TLV µg/m³
Mg	0.007	0.0001	0.05-0.50	2.1-21	10,000 (as magnesium oxide fume)
Mn	0.055	0.002	0.5-3.0	21-125	5,000 (metal and compounds)
Mo	0.5	0.02	15-40	625-1650	5,000 (soluble,as Mo) 10,000 (insoluble,as Mo)
Na	0.015	0.0002	0.05-1.0	2.1-42	2,000 (as NaOH)
Ni	0.15	0.005	0.5-5.0	21-210	100 (metal and soluble compounds)
Pb	0.5	0.01	1-20	42-840	150 (inorganic compounds, fumes and dusts)
Pd	0.25	0.02	4-15	170-625	NL
Rb	0.1	0.002	0.5-5.0	21-210	NL
Si	1.8	0.02	50-150	2100-6300	10,000
Sr	0.12	0.002	0.5-5.0	21-210	NL
Te	0.5	0.03	5-25	210-1050	100
Tl	0.5	0.01	5-20	210-840	100 (soluble compounds
V	1.7	0.04	10-150	420-6300	500 (V_2O_5 dust) 50 (V_2O_5 fume)
Zn	0.018	0.001	0.1-1.0	4.2-42	5,000 (ZnO fume)

a. Data from "Analytical Methods for Atomic Absorption Spectrophotometry," Perkin-Elmer Corp., Norwalk, Connecticut, 1976.

b. Data from "Analytical Methods for Flame Spectroscopy," Varian Techtron, Australia, 1972.

c. The atmospheric concentrations were calculated assuming a collection volume of 0.24 m^3 (2 Lpm for two hours) and an analyte volume of 10 mL for the entire sample.

d. For elements whose TLV is less than the lower limits of the range, a larger sampling volume will be required.

e. Threshold limit values of airborne contaminants and physical agents with intended changes adopted by ACGIH for 1976. All values listed are expressed as elemental concentrations except as noted.

f. NL signifies No Limit expressed for this element or its compounds.

IHA-150 Hg in Air, Flameless AA Method

Range 0.05-1.0 total µg (extendable to 10µg)
Precision ~5% RSD

Interferences
1. What are the interferences in this procedure? (Hg at 253.7nm wavelength 50:100 dilution)
Precision & Accuracy
2. What is the average recovery 97%.
Apparatus
3. How do you calibrate the flowmeter to assure that it will deliver gas at 1l/min?
4. Is there a procedure set up which documents the temp of your H_2O bath to assure that the temp is being maintained at 95±2°C?
Reagents
5. Have u ever had to distill UR HNO_3 B4 use because it was >0.05µg as a blank?
6. What's the longest amt of time that u've used UR working Hg soln B4 making up a new one?
Procedure
7. How do you clean UR glassware? (1:1 HNO_3 for 30min H_2O rinse)
8. How long do u actually take to get a sample? at what flowrate? (Typical 6hrs at 0.2L/min)
9. How long does it take to get the sample to the lab for anal?
10. Is there any chance that if samples are not delivered promptly that the analyte diffuses out of the tube?
Sample Prep
11. Discuss how this is done
a. 2 samples per tube in 250ml bottles (glass or plastic?)
b. add to @ 50mL H_2O, 5mL H_2SO_4, 2.5mL HNO_3, 15mL $KMnO_4$ soln + 8mL $K_2S_2O_8$ soln

c. 2 hrs in 95°C H_2O bath

d. cool at 6 ml NaCl-hydroxylamine sulfate soln to reduce permanganate.

e. dilute to volume in 100 ml volumetric flask

Analysis of Sample

12. Discuss sample analysis.

Calib & Stds

13. Discuss how this is actually performed.

Calculations

14. Who checks the results of calculations?

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-150
DATE	Nov. 27, 1979
SUPERSEDES	
PAGE	1 OF 6

MERCURY IN AIR, FLAMELESS AA METHOD

Analyte:	Mercury	Method No.:	IHA-150
Matrix:	Air	Range:	0.05 - 1.0 total μg
Procedure:	Adsorption on treated charcoal, acid desorption, digestion; measured by flameless atomic absorption	Precision:	~5% RSD (estimated, not evaluated)
		Bias:	-3%

1.0 Principle of the Method

1.1 Air is drawn through a sampling tube containing activated charcoal impregnated with iodine and potassium iodide. The flow rate and sampling time are chosen to provide a representative workplace air sample.

1.2 The charcoal is digested in an acid-permanganate-persulfate solution at 95°C for 2 hours. Elemental mercury is then liberated by reduction with $SnSO_4$, and measured by flameless atomic absorption.

1.3 All forms of mercury--elemental, inorganic, organic--are determined by this method.

2.0 Range and Sensitivity

2.1 The normal working range is up to 1.0 μg of mercury. The lowest concentration reported is 0.05 μg.

2.2 Provision is made for extending the range to 10 μg.

3.0 Interferences

3.1 Organic compounds interfere by absorption at the 253.7 nm wavelength. This interference is minimized by the digestion step.

4.0 Precision and Accuracy

4.1 No precision studies have been made; however, specific amounts of mercury vapor were loaded on sampling tubes and analyzed by this method with the following results:

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APPROVED BY PGDP	LAB R. E. Simmons IH C. W. Turok	APPROVED BY ORNL	LAB W R Laing IH J. A. Ealy	NUMBER IHA-150

UCN-13234
(1/35 1-79)

µg Hg added	µg Hg found	Recovery, %
50	50.9	101.8
40	35.8	89.5
30	26.9	89.7
5	4.7	94.0
4	4.0	100.0
3	3.2	106.7

The average recovery was 97%.

5.0 Apparatus

5.1 Atomic absorption spectrophotometer, with an absorption cell at least 10-cm long x 2-cm I.D. with quartz endwindows.

5.2 Mercury hollow cathode lamp.

5.3 Strip-chart recorder.

5.4 Reagent bottles, 250-ml.

5.5 Gas supply: air, N_2, or argon.

5.6 Flowmeter, to deliver gas at 1 liter per minute.

5.7 Aerating tube: fitted with a straight cylindrical flat-end glass frit of coarse porosity.

5.8 Drying tube: a 15-cm x 19-mm O.D. tube packed with magnesium perchlorate desiccant. The apparatus is assembled as shown in Figure 1.

5.9 Water bath, capable of maintaining 95 ± 2°C.

5.10 Charcoal tubes: glass tube with both ends flame-sealed, 7 cm long with 6-mm O.D. and 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C and impregnated with 0.3% I_2 and 0.6% KI prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section.

These tubes, as described, are commercially available.

6.0 Reagents

All reagents are reagent grade and water is double-distilled or deionized.

6.1 Sulfuric acid, conc.

6.2 Sulfuric acid, 0.5 N: Add 14.0 ml of conc sulfuric acid to about 900 ml of water and dilute to 1 liter.

6.3 Nitric acid, conc: Reagent grade of low mercury content. TRANSISTAR grade (Mallinckrodt) is suitable. If this grade is not used, and a reagent blank of >0.05 μg is obtained, it will be necessary to distill the nitric acid.

6.4 Stannous sulfate suspension: Add 25 g of stannous sulfate to 250 ml of 0.5 N sulfuric acid. This mixture should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

6.5 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in water and dilute to 100 ml. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

6.6 Potassium permanganate, 5% solution (W/V): Dissolve 5 g of potassium permanganate in 100 ml of water.

6.7 Potassium persulfate, 5% solution (W/V): Dissolve 5 g of potassium persulfate in 100 ml of water.

6.8 Stock mercury solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of water, add 10 ml of conc nitric acid, and dilute to 100 ml. 1 ml = 1 mg Hg.

6.9 Working mercury solution: Add 1 ml of the stock mercury solution to 1.5 ml of conc nitric acid and dilute to 1000 ml with water. 1 ml = 1 μg Hg. This solution is stable for several months.

7.0 Procedure

7.1 Cleaning of Equipment: Acid-clean all glassware by soaking in 1:1 HNO_3 for 30 minutes and rinsing with water.

7.2 Collection and shipping of samples

7.2.1 Open both ends of the sample tube and connect to a sampling pump. Collect a sample at a given flow rate for a given time period. A flow rate of 0.2 L/min for 6 hrs is typical.

7.2.2 At the end of the sampling period, remove the tube from the pump, cap both ends, and transport to the laboratory.

UCN-10766B (12 8-78)

7.3 Sample Preparation

7.3.1 Remove the end caps and add the two sections of charcoal to separate 250-ml bottles.

7.3.2 Add to each bottle in succession: 50 ml of water, 5 ml of H_2SO_4, 2.5 ml of HNO_3, 15 ml of $KMnO_4$ solution (6.6), and 8 ml of $K_2S_2O_8$ solution (6.7).

7.3.3 Place the bottles in a water bath at 95°C for 2 hours.

7.3.4 Cool and add 6 ml of sodium chloride-hydroxylamine sulfate solution (6.5) to each bottle to reduce the excess permanganate.

7.3.5 Transfer the contents of each bottle to a 100-ml volumetric flask and dilute to volume.

7.4 Analysis of Sample

7.4.1 Transfer 10 ml of each sample to a 250-ml bottle and dilute to ∿100 ml with water.

7.4.2 Add 5 ml of the stannous sulfate suspension to a bottle and immediately attach the bottle to the aeration assembly (Figure 1).

7.4.3 Set the bypass valves to allow the gas (@ 1 liter/min) to sweep the elemental mercury from the bottle to the absorption cell. The absorbance will reach maximum within 30 seconds.

7.4.4 As soon as the absorbance begins to decrease, open the bypass valves and continue the aeration until the recorder returns to baseline.

7.4.5 Repeat 7.4.2 through 7.4.4 for each 10→100 dilution. If the level of mercury is too high in the 10→100 dilution, repeat 7.4.1 through 7.4.4 with a smaller aliquot (diluted to 100 ml) until the mercury level is within the range of the standards. If the 10→100 dilution is too low, repeat 7.4.1 through 7.4.4 with the remaining 90 ml of sample, diluted to ∿100 ml (See Note 1).

Note 1

After adding the 5 ml of stannous sulfate suspension to a 90→100 dilution, the bottle must be stoppered and a delay of 10 minutes observed before attaching the bottle to the aeration assembly. This delay is necessary to overcome the effects of interferences which are encountered only in the 90→100 dilution.

Note 2

If a dual-channel spectrophotometer is available, the entire 100-ml sample from 7.3.5 may be processed. (Observe the delay discussed in Note 1.) The scale expansion controls of each channel can be adjusted to record low levels on one channel and high levels on the other channel, thus eliminating the need to make multiple dilutions.

8.0 Calibration and Standards

8.1 Transfer 0, 100, 300, 500, and 1000-µl aliquots of the working mercury solution (6.9) to a series of 250-ml bottles. Note: Reagent blank values should not exceed 0.05 µg.

8.2 Dilute to 100 ml with water and treat as samples beginning with the H_2SO_4 addition in 7.3.2 and ending with 7.3.4.

8.3 Analyze the standards beginning with 7.4.2.

8.4 Plot peak heights versus µg mercury as a calibration curve.

9.0 Calculations

9.1 The total µg mercury found in each charcoal section is found using the following formula:

$$\text{Hg, } \mu g = (A-B) \times \frac{100}{V}$$

where A = Hg found from the calibration curve, µg,

B = Hg found in the reagent blank, µg, and

V = volume of aliquot taken in 7.4, ml.

9.2 The Hg content of each charcoal section is reported separately to allow evaluation of the efficiency of the sampling.

10.0 Reference

10.1 Procedure No. IHA-450, this manual.

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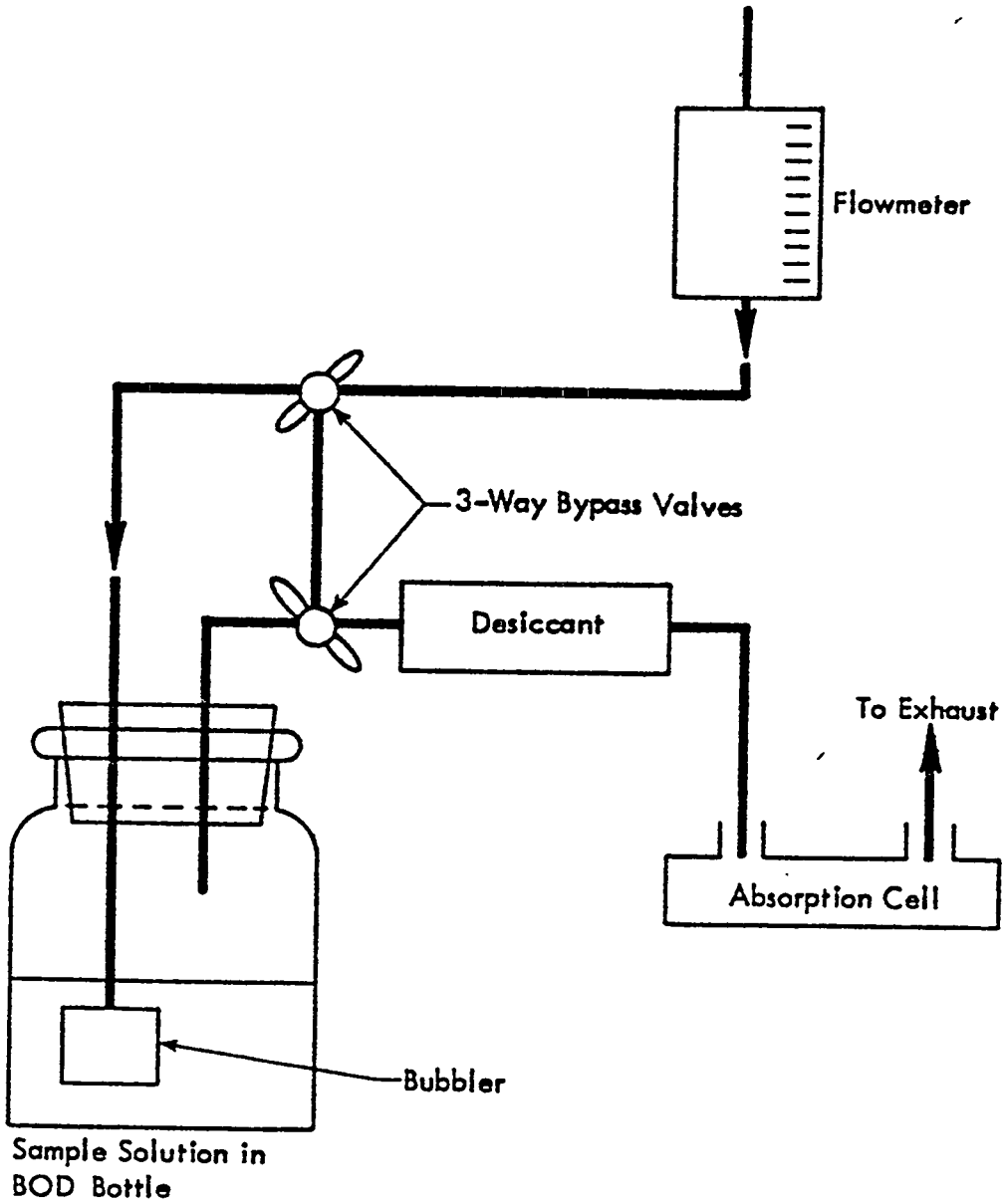

Figure 1. APPARATUS FOR FLAMELESS MERCURY DETERMINATION.

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-250
DATE	May 28, 1980
SUPERSEDES	
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ORGANIC SOLVENTS IN AIR, GAS CHROMATOGRAPHIC METHOD

Analyte:	Organic solvents (See Table 1)	Method No.:	IHA-250 (NIOSH 127) 1501, 1602, 1003,
Matrix:	Air	Range:	See Table 1, specific compound
Procedure:	Adsorption on charcoal; desorption with carbon disulfide; GC with flame ionization detection	Precision:	10.5% RSD
		Accuracy:	10%

For this analysis, the undersigned committee has approved for inclusion in this manual an existing procedure, exactly as published. Accordingly, the following pages are taken verbatim from the NIOSH Manual of Analytical Methods, Second Edition, Vol. 1, U. S. Department of Health, Education, and Welfare, Method 127, 1977.

The following exceptions to NIOSH 127 should be understood:

A. Peak heights may be used instead of peak areas for calibration and determination of these organic solvents.

B. The list of organic solvents in Table 1 may be expanded generally to include any which can be sampled by charcoal adsorption, desorbed by carbon disulfide, and detected in a gas chromatograph with a flame ionization detector.

C. Within the practice of UCC-ND, the following organics have also been determined by this method. They are listed with several parameters relevant to analysis:

Organic Solvent	Detection Limit (mg/sample)	Sample Volume (liters)* Minimum	Maximum	GC Column Temp. (°C)	Molecular Weight
Acetonitrile	0.10	5	15	180	41.05
Tetrahydrofuran	0.50	5	27	185	72.10
1,1,2-Trichloro-1,1,2-trifluoroethane (Refrigerant-113)	1.1	1	80	150	187.39

*See Table 1, Footnotes, of NIOSH 127.

APPROVED BY Y-12	LAB R J McElhaney IH W. S. Everett Jr	APPROVED BY ORGDP	LAB T. Kwasnoski IH D. J. Dunce	APPROVED BY UCCND-COORD'R C W Weber
APPROVED BY PGDP	LAB R. E. Simmons IH C. H. Turok	APPROVED BY ORNL	LAB W R Laing IH J. A. Ealy	NUMBER IHA-250

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The following procedure is a photocopied excerpt from: NIOSH Manual of Analytical Methods, Second Edition, Vol. 1, U. S. Department of Health, Education, and Welfare, 1977.

ORGANIC SOLVENTS IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Organic Solvents (See Table 1)	**Method No.:**	P&CAM 127
Matrix:	Air	**Range:**	For the specific compound, refer to Table 1
Procedure:	Adsorption on charcoal desorption with carbon disulfide, GC		
Date Issued:	9/15/72	**Precision:**	10.5% RSD
Date Revised:	2/15/77	**Classification:**	See Table 1

1. **Principle of the Method**

   1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

   1.2 The charcoal in the tube is transferred to a small, graduated test tube and desorbed with carbon disulfide.

   1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

   1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. **Range and Sensitivity**

   The lower limit in mg/sample for the specific compound at 16 × 1 attenuation on a gas chromatograph fitted with a 10:1 splitter is shown in Table 1. This value can be lowered by reducing the attenuation or by eliminating the 10:1 splitter.

3. **Interferences**

   3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.

   3.2 When two or more solvents are known or suspected to be present in the air, such information (including their suspected identities), should be transmitted with the sample, since with differences in polarity, one may displace another from the charcoal.

   3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Hence, retention time data on a single column, or even on a number of columns, cannot be considered as proof of chemical identity. For this reason it is important that a sample of the bulk solvent(s) be submitted at the same time so that identity(ies) can be established by other means.

3.4 If the possibility of interference exists, separation conditions (column packing, temperatures, etc.) must be changed to circumvent the problem.

4. **Precision and Accuracy**

4.1 The mean relative standard deviation of the analytical method is 8% (11.4).

4.2 The mean relative standard deviation of the analytical method plus field sampling using an approved personal sampling pump is 10% (11.4). Part of the error associated with the method is related to uncertainties in the sample volume collected. If a more powerful vacuum pump with associated gas-volume integrating equipment is used, sampling precision can be improved.

4.3 The accuracy of the overall sampling and analytical method is 10% (NIOSH-unpublished data) when the personal sampling pump is calibrated with a charcoal tube in the line.

5. **Advantages and Disadvantages of the Method**

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more solvents suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists. During sample storage, the more volatile compounds will migrate throughout the tube until equilibrium is reached (33% of the sample on the backup section).

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. **Apparatus**

6.1 An approved and calibrated personal sampling pump for personal samples. For an area sample, any vacuum pump whose flow can be determined accurately at 1 liter per minute or less.

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 lpm.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (20 ft × ⅛ in) with 10% FFAP stationary phase on 80/100 mesh, acid-washed DMCS Chromosorb W solid support. Other columns capable of performing the required separations may be used.

6.5 A mechanical or electronic integrator or a recorder and some method for determining peak area.

6.6 Microcentrifuge tubes, 2.5 ml, graduated.

6.7 Hamilton syringes: 10 μl, and convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. **Reagents**

7.1 Spectroquality carbon disulfide (Matheson Coleman and Bell).

7.2 Sample of the specific compound under study, preferably chromatoquality grade.

7.3 Bureau of Mines Grade A helium.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. **Procedure**

8.1 **Cleaning of Equipment:** All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 **Calibration of Personal Pumps.** Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 **Collection and Shipping of Samples**

8.3.1 Immediately before sampling, the ends of the tube should be broken to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The small section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be vertical during sampling to reduce channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 The flow, time, and/or volume must be measured as accurately as possible. The sample should be taken at a flow rate of 1 lpm or less to attain the total sample volume required. The minimum and maximum sample volumes that should be collected for each solvent are shown in Table 1. The minimum volume quoted must be collected if the desired sensitivity is to be achieved.

8.3.6 The temperature and pressure of the atmosphere being sampled should be measured and recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly before they are shipped to minimize tube breakage during shipping.

8.3.10 Samples of the suspected solvent(s) should be submitted to the laboratory for qualitative characterization. These liquid bulk samples should not be transported in the same container as the samples or blank tube. If possible, a bulk air sample (at least 50 l air drawn through tube) should be shipped for qualitative identification purposes.

8.4 **Analysis of Samples**

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a small stoppered test tube. The separating section of foam is removed and discarded; the second section is transferred to another test tube. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, one-half ml of carbon disulfide is pipetted into each test tube. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 85 cc/min. (70 psig) helium carrier gas flow.
2. 65 cc/min. (24 psig) hydrogen gas flow to detector.
3. 500 cc/min. (50 psig) air flow to detector.
4. 200°C injector temperature.
5. 200°C manifold temperature (detector).
6. Isothermal oven or column temperature — refer to Table 1 for specific compounds.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blowback or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10 μl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume.. The needle is removed from the solvent, and the plunger is pulled back about 0.2 μl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-μl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back a short distance to minimize evaporation of the sample from the tip of the needle. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 **Determination of Desorption Efficiency**

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process for a given compound, provided the same batch of charcoal is used. NIOSH has found that the desorption efficiencies for the compounds in Table 1 are between 81% and 100% and vary with each batch of charcoal.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 5-cm, 4-mm I.D. glass tube, flame-sealed at one end (similar to commercially available culture tubes). This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the compound is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. The amount injected is usually equivalent to that present in a 10-liter sample at a concentration equal to the federal standard.

At least five tubes are prepared in this manner and allowed to stand for at least overnight to assure complete absorption of the specific compound onto the charcoal. These five tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of CS_2 with the same syringe used in the preparation of the sample. These are analyzed with the samples.

The desorption efficiency equals the difference between the average peak area of the samples and the peak area of the blank divided by the average peak area of the standards, or

$$\text{desorption efficiency} = \frac{\text{Area sample} - \text{Area blank}}{\text{Area standard}}$$

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml CS_2 because samples are desorbed in this amount of CS_2. To minimize error due to the volatility of carbon disulfide, one can inject 20 times the weight into 10 ml of CS_2. For example, to prepare a 0.3 mg/0.5 ml standard, one would inject 6.0 mg into exactly 10 ml of CS_2 in a glass-stoppered flask. The density of the specific compound is used to convert 6.0 mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area.

NOTE: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 The weight, in mg, corresponding to each peak area is read from the standard curve for the particular compound. No volume corrections are needed, because the standard curve is based on mg/0.5 ml CS_2 and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{Correct mg} = mg_a - mg_b$$

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where:

mg_s = mg found in front section of sample tube

mg_b = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 The corrected amounts present in the front and backup sections of the same sample tube are added to determine the total measured amount in the sample.

10.4 This total weight is divided by the determined desorption efficiency to obtain the corrected mg per sample.

10.5 The concentration of the analyte in the air sampled can be expressed in mg per m^3.

$$mg/m^3 = \frac{\text{Corrected mg (Section 10.4)} \times 1000\ (\text{liters}/m^3)}{\text{Air volume sampled (liters)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$ppm = mg/m^3 \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L. D., D. G. Taylor, P. A. Mauer, and R. E. Kupel, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere", Am Ind Hyg Assoc J 31:225, 1970.

11.2 Young, D. M. and A. D. Crowell, Physical Adsorption of Gases, pp. 137-146, Butterworths, London, 1962.

11.3 Federal Register, 37:202:22139-22142, October 18, 1972.

11.4 NIOSH Contract HSM-99-72-98, Scott Research Laboratories, Inc., "Collaborative Testing of Activated Charcoal Sampling Tubes for Seven Organic Solvents", pp. 4-22, 4-27, 1973.

TABLE 1

Parameters Associated With P&CAB Analytical Method No. 127

Organic Solvent	Method Classification	Detection limit (mg/sample)	Sample Volume (liters) Minimum(a)	Sample Volume (liters) Maximum(b)	GC Column Temp.(°C)	Molecular Weight
Acetone	D	–	0.5	7.7	60	58.1
Benzene	A	0.01	0.5	55	90	78.1
Carbon tetrachloride	A	0.20	10	60	60	154.0
Chloroform	A	0.10	0.5	13	80	119
Dichloromethane	D	0.05	0.5	3.8	85	84.9
p-Dioxane	A	0.05	1	18	100	88.1
Ethylene dichloride	D	0.05	1	12	90	99.0
Methyl ethyl ketone	B	0.01	0.5	13	80	72.1
Styrene	D	0.10	1.5	34	150	104
Tetrachloroethylene	B	0.06	1	25	130	166
1,1,2-trichloroethane	B	0.05	10	97	150	133
1,1,1-trichloroethane (methyl chloroform)	B	0.05	0.5	13	150	133
Trichloroethylene	A	0.05	1	17	90	131
Toluene	B	0.01	0.5	22	120	92.1
Xylene	A	0.02	0.5	31	100	106

(a) Minimum volume, in liters, required to measure 0.1 times the OSHA standard

(b) These are breakthrough volumes calculated with data derived from a potential plot (11.2) for activated coconut charcoal. Concentrations of vapor in air at 5 times the OSHA standard (11.3) or 500 ppm, whichever is lower, 25°C, and 760 torr were assumed. These values will be as much as 50% lower for atmospheres of high humidity. The effects of multiple contaminants have not been investigated, but it is suspected that less volatile compounds may displace more volatile compounds (See 3.1 and 3.2)

UMBER
IHA-250

URANIUM IN URINE, FLUOROMETRIC METHOD

Analyte: Uranium
Matrix: Urine
Procedure: Fluorometric after fluoride pellet fusion

Method No.: IHA-490
Range: 0.005 to 10.0 μg/mL
Precision: 15% RSD at 0.01 μg/mL
7.5% RSD at 0.05 μg/mL

1.0 PRINCIPLE OF THE METHOD

1.1 A small aliquot of urine is placed in a small, flat platinum dish and evaporated to dryness by an infrared lamp.

1.2 A flux pellet is placed in the dish and fused by controlled heat. The dish is then cooled.

1.3 The yellow-green uranium fluorescence induced by ultraviolet illumination is measured using a fluorophotometer and compared to the fluorescence of known uranium standards.

2.0 RANGE AND SENSITIVITY

2.1 The normal operating range of the method is 0.005 to 1.0 μg/mL. The range may be extended to 10 μg/mL by using higher concentration calibration standards.

2.2 The lowest concentration reported (LCR) is 0.005 μg/mL.

3.0 SAMPLE COLLECTION, HANDLING, AND PRESERVATION

3.1 Collecting and Shipping Sample

3.1.1 Each participant in this urine program is scheduled to void a sample on an assigned date, which is always preceded by two scheduled days off. This minimizes the effect of any recent soluble uranium exposure.

3.1.2 The sample should be voided prior to entering the work area and prior to changing into work clothing to reduce the possibility of sample contamination.

3.1.3 The times of present voiding and last previous voiding are recorded on the sample label along with the name, employee number, date, and department number--all provided by the employee.

3.1.4 The sample should be refrigerated immediately and should arrive at the laboratory within 24 hours.

4.0 INTERFERENCE

No interfering substances are encountered in urine at concentrations normally experienced.

5.0 PRECISION AND ACCURACY

5.1 The precision (limit-of-error) at the 95% confidence level is ±30% [15% relative standard deviation (RSD)] at 0.01 μg/mL and ±15% (7.5% RSD) at 0.05 μg/mL.

5.2 The accuracy of the method depends on how well the matrix of the calibration standards matches that of the sample being analyzed. No significant bias has been identified.

6.0 ADVANTAGES AND DISADVANTAGES OF THE METHOD

6.1 Advantages over previous methods include simplicity, speed, and sensitivity.

6.2 One disadvantage is that, without chemical separation of the uranium, the accuracy of the measurement depends on the amount of dissolved solids in the sample and on how well this matches the calibration standard.

7.0 APPARATUS

7.1 Fluorophotometer

7.2 Furnace, induction; or burner, modified Fletcher

7.3 Dishes, platinum fusion, 1/2 in. diam, 1/16 in. lip, 1/8 in. deep

7.4 Fusion dish holder

7.5 Pelletizer, delivering 0.3 or 0.6-pellet of flux

7.6 Infrared lamp and stand, 375 W

7.7 Pipette, 100 or 200 μL, semiautomatic

8.0 REAGENTS

8.1 Sodium fluoride - 2% lithium fluoride flux: Put 1359 g (3 lb) of fluorometric grade sodium fluoride and 27 g of lithium fluoride into a clean 5-lb glass reagent jar. Place the jar on a mechanical roller and roll for 48 hours.

8.1.1 Alternate flux, sodium fluoride: The lithium fluoride additive is unnecessary when induction heating is used for the fusion.

8.2 Stock uranium solution: Dissolve 117.9 mg of natural U_3O_8 in 8 M HNO_3 in a 100-mL beaker. Transfer the solution to a 100-mL volumetric flask using 2 M HNO_3 to transfer. Dilute to volume with 2 M HNO_3 and mix thoroughly (1 mL = 1 mg U).

8.3 Calibration Standards

Dilute suitable aliquots of the stock uranium solution (Step 8.2) with acidified, blanked, and blended urine to give at least two appropriate standards within the operating range of 0.005 to 10 μg/mL. The standards, usually a high and a low, should bracket the working range needed.

9.0 PROCEDURE

9.1 Cleaning Fusion Dishes

9.1.1 Adequate cleaning of the platinum fusion dishes is critical to the prevention of cross-contamination. Thoroughly mix two tablespoons of boric acid with 150 mL of water in a Pyrex dish. Carefully add 100 mL of concentrated sulfuric acid and boil the platinum dishes gently in this solution for 2 hours. Drain and rinse the dishes with distilled water.

9.1.2 Cover the dishes with 1:1 HNO_3 and slowly add 30% hydrogen peroxide until mild effervescence occurs. Soak overnight.

9.1.3 Dishes can be tested for cleanliness in the fluorophotometer. Dishes that resist cleaning by the method described in Steps 9.1.1 and 9.1.2 can be cleaned by fusing potassium pyrosulfate pellets in them and then soaking them overnight in 1:1 HNO_3.

9.2 Pelletizing and Fusion

9.2.1 Place the required number of platinum fusion dishes in the dish holder or on a nichrome screen.

9.2.2 Swirl each sample bottle to mix the sample and to suspend all solids. Process a blank and the calibration standards with each set of samples.

9.2.3 Quickly insert the semiautomatic pipette in the sample bottle and withdraw an appropriate aliquot of solution (usually 100 μL for a 0.3-g pellet or 200 μL for a 0.6-g pellet); discharge the contents of the pipette into a platinum dish. Run each sample in duplicate.

9.2.4 Place the dish holder or screen and the platinum dishes under the infrared lamp and evaporate all samples to dryness. Then remove the holder or screen from under the lamp.

9.2.5 With the pelletizer, place a 0.3- or 0.6-g pellet of the fluoride flux into each platinum fusion dish.

9.2.6 Fusion using a modified Fletcher Burner

9.2.6.1 Place the screen over the fusión burner; fuse for 2 minutes at ~1100°C, then reduce to 950°C and fuse for 1 minute. (An optical pyrometer will provide temperature estimates.)

9.2.6.2 Remove the screen containing the dishes from the burner and allow to cool.

9.2.7 Alternate fusion using an Induction Furnace

9.2.7.1 Place four dishes at a time in the induction furnace coil.

9.2.7.2 Apply 600 mA current for 60 seconds.

9.2.7.3 Transfer the dishes back to the holder to cool. (CAUTION: Use Forceps.)

9.3 Fluorescence Measurement

9.3.1 Place the platinum dishes containing the blank, uranium standards, and sample melts on the fluorophotometer's turntable.

9.3.2 Move the blank under the ultraviolet light and adjust the zero control knob until the instrument reads zero.

9.3.3 Move the high standard melt under the ultraviolet light and adjust the calibration control until the instrument reads the known value of the standard.

9.3.4 Move the low uranium standard melt under the ultraviolet light. It should read the known value of the standard if the instrument is properly calibrated. The fluorophotometer is now calibrated for direct readout of uranium in the working range, which could extend from 0.005 to 10 μg/mL. Readout may be in appropriate units other than μg/mL.

9.3.5 Move the sample pellets under the ultraviolet light of the fluorophotometer and read the uranium content of the aliquots. Record the readings.

10.0 <u>CALCULATIONS</u>

10.1 If the readings are in μg/mL, no further calculations are necessary.

10.2 If the readings are in μg or ng, use the following formulas:

$$U,\ \mu g/mL = \frac{\mu g\ U}{A}$$

$$U,\ \mu g/mL = \frac{ng\ U}{A \cdot 1000}$$

where

A = volume of sample (see 9.2.3) pipetted onto the pellet, mL.

10.3 If the μg U/day for an employee is to be reported, use the following formula:

$$U,\ \mu g/day = U\ \mu g/mL \times \frac{V}{T} \times 24$$

where

V = volume excreted, mL,

T = time interval, hour,

24 = hour/day.

11.0 REFERENCE

Centanni, F. A., Moss, A. M., and DeSesse, M. A.; "Fluorometric Determination of Uranium;" Anal. Chem., 28, p. 1651 (1956).

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-490
DATE	June 15, 1983
SUPERSEDES	Nov. 27, 1979
PAGE	1 OF 5

URANIUM IN URINE, FLUOROMETRIC METHOD

Analyte:	Uranium	Method No.:	IHA-490
Matrix:	Urine	Range:	0.005 to 10.0 µg/mL
Procedure:	Fluorometric after fluoride pellet fusion	Precision:	15% RSD at 0.01 µg/mL 7.5% RSD at 0.05 µg/mL

1.0 Principle of the Method

1.1 A small aliquot of urine is placed in a small flat platinum dish and evaporated to dryness by an infrared lamp.

1.2 A flux pellet is placed in the dish and fused by controlled heat. The dish is then cooled.

1.3 The yellow-green uranium fluorescence induced by ultraviolet illumination is measured using a fluorophotometer and compared to the fluorescence of known uranium standards.

2.0 Range and Sensitivity

2.1 The normal operating range of the method is 0.005 to 1.0 µg/mL. The range may be extended to 10 µg/mL by using higher concentration calibration standards.

2.2 The limit of detection is 0.005 µg/mL.

3.0 Interference

3.1 No interferring substances are encountered in urine at concentrations normally experienced.

4.0 Precision and Accuracy

4.1 The precision (limit of error) at the 95% confidence level is ±30% (15% relative standard deviation, RSD) at 0.01 µg/mL and ±15% (7.5% RSD) at 0.05 µg/mL.

APPROVED BY Y-12	LAB R J McElhaney IH D. L. Bean	APPROVED BY ORGDP	LAB D. H. Frazier IH D. J. Duncan	APPROVED BY UCCND-COORD'R C W Weber
APPROVED BY PGDP	LAB R. E. Simmons IH C. H. Turak	APPROVED BY ORNL	LAB N. M. Ferguson IH James A. Early	NUMBER IHA-490

UCN-13234
(1235 1-79)

4.2 The accuracy of the method depends on how well the matrix of the calibration standards matches that of the sample being analyzed. No significant bias has been identified.

5.0 Advantages and Disadvantages of the Method

5.1 Advantages over previous methods include simplicity, speed, and sensitivity.

5.2 One disadvantage is that, without chemical separation of the uranium, the accuracy of the measurement depends on the amount of dissolved solids in the sample, and on how well this matches the calibration standard.

6.0 Apparatus

6.1 Fluorophotometer, modified Oak Ridge National Laboratory Model Q-1165, or equivalent.

6.2 Furnace, induction; or burner, modified Fletcher.

6.3 Dishes, platinum fusion, 1/2-inch diameter, 1/16-inch lip, 1/8-inch deep.

6.4 Fusion dish holder.

6.5 Pelletizer, delivering 0.3 or 0.6-g pellet of flux.

6.6 Infrared lamp and stand, 375-w.

6.7 Pipet, 100-or 200-µL, semiautomatic.

7.0 Reagents

7.1 Sodium fluoride - 2% lithium fluoride flux: Put 1359 g (3 pounds) of fluorometric grade sodium fluoride and 27 grams of lithium fluoride into a clean 5-pound glass reagent jar. Place the jar on the mechanical roller and roll for 48 hours.

7.1.1 Alternate flux, sodium fluoride: the lithium fluoride additive is unnecessary when induction heating is used for the fusion.

7.2 Stock uranium solution: Dissolve 117.9 mg of natural U_3O_8 in 8 M HNO_3 in a 100-mL beaker. Transfer the solution to a 100-mL volumetric flask using 2 M HNO_3 to transfer. Dilute to volume with 2 M HNO_3 and mix thoroughly. (1 mL = 1 mg U.)

7.3 Calibration Standards:

7.3.1 Dilute suitable aliquots of the stock uranium solution (7.2) with acidified, blanked, and blended urine to give at least two appropriate standards within the operating range of 0.005 to 10 µg/mL. The standards--usually a high and a low--should bracket the working range needed.

8.0 Procedure

8.1 Cleaning Fusion Dishes

8.1.1 Adequate cleaning of the platinum fusion dishes is critical to the prevention of cross-contamination. Thoroughly mix 2 tablespoons of boric acid with 150 mL of water in a Pyrex dish. Carefully add 100 mL of conc sulfuric acid and boil the platinum dishes gently in this solution for 2 hours. Drain and rinse the dishes with distilled water.

8.1.2 Cover the dishes with 1:1 HNO_3 and slowly add 30% hydrogen peroxide until mild effervescence occurs. Soak overnight.

8.1.3 Dishes can be tested for cleanliness in the fluorophotometer. Dishes that resist cleaning by the method described in 8.1.1 and 8.1.2 can be cleaned by fusing potassium pyrosulfate pellets in them and then soaking them in 1:1 HNO_3 overnight.

8.2 Pelletizing and Fusion

8.2.1 Place the required number of platinum fusion dishes in the dish holder or on a nichrome screen.

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8.2.2 Swirl each sample bottle to mix the sample and to suspend all solids. Process a blank and the calibration standards with each set of samples.

8.2.3 Quickly insert the semiautomatic pipet into the sample bottle and withdraw an appropriate aliquot of solution (usually 100 µL for a 0.3-g pellet or 200 µL for a 0.6-g pellet); discharge the contents of the pipet into a platinum dish.

8.2.4 Place the dish holder or screen and the platinum dishes under the infrared lamp and evaporate all samples to dryness. Then remove the holder or screen from under the lamp.

8.2.5 With the pelletizer, place a 0.3- or 0.6-g pellet of the fluoride flux into each platinum fusion dish.

8.2.6 Fusion using a modified Fletcher Burner.

8.2.6.1 Place the screen over the fusion burner; fuse fo, 2 minutes at approximately 1100°C, then reduce to 950°C and fuse for 1 minute. (An optical pyrometer will provide temperature estimates.)

8.2.6.2 Remove the screen containing the dishes from the burner and allow to cool.

8.2.7 Alternate fusion, using an Induction Furnace:

8.2.7.1 Place four dishes at a time in the induction furnace coil.

8.2.7.2 Apply 600 ma current for 60 seconds.

8.2.7.3 Transfer the dishes back to the holder to cool. (CAUTION: Use forceps.)

8.3 Fluorescence Measurement

8.3.1 Place the platinum dishes containing the blank, uranium standards, and sample melts on the turn-table of the fluorophotometer.

8.3.2 Move the blank under the ultraviolet light and adjust the zero control knob to make the instrument read zero.

8.3.3 Move the high uranium standard melt under the ultraviolet light and adjust the calibration control until the instrument reads the known value of the standard.

8.3.4 Move the low uranium standard melt under the ultraviolet light. It should read the known value of the standard if the instrument is properly calibrated. The fluorophotometer is now calibrated for direct readout of uranium in the working range, which could extend from 0.005 to 10 µg/mL. Readout may be in appropriate units other than µg/mL.

8.3.5 Move the sample pellets under the ultraviolet light of the fluorophotometer and read the uranium content of the aliquots. Record the readings.

9.0 Calculations

9.1 If the readings are in µg/mL, no further calculations are necessary.

9.2 If the readings are in µg or ng, use the following formulas:

$$U,\ \mu g/mL = \frac{\mu g\ U}{A}$$

$$U,\ \mu g/mL = \frac{ng\ U}{A \cdot 1000}$$

where: A = volume of sample (see 8.2.3) pipetted onto the pellet, mL.

9.3 If the µg U/day for an employee is to be reported, use the following formula:

$$U,\ \mu g/day = U\ \mu g/mL \times \frac{V}{T} \times 24$$

where: V = volume excreted, mL
T = time interval, hr
24 = hr/day

10.0 Reference

10.1 Centanni, F. A., Moss, A. M., and DeSesse, M. A.; "Fluorometric Determination of Uranium"; Anal. Chem., 28, p. 1651 (1956).

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INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-420
DATE	Nov. 27, 1979
SUPERSEDES	
PAGE	1 OF 4

FLUORIDE IN URINE, SELECTIVE ION ELECTRODE METHOD

Analyte:	Fluoride	Method No.:	IHA-420
Matrix:	Urine	Range:	Lower Limit Urine 0.19 mg/L
Procedure:	Selective Ion Electrode	Precision:	25% RSD at 0.8 mg/L
		Bias:	-5% at 0.8 mg/L

1.0 Principle of the Method

1.1 Urine samples are diluted with an equal volume of a pH-activity coefficient buffer solution.

1.2 A fluoride sensitive selective ion electrode and a reference electrode are inserted into the buffered sample. The observed potential difference between the electrodes can then be related to the fluoride concentration in the sample by calibration curves prepared with the same buffer and electrodes.

2.0 Range and Sensitivity

The range and sensitivity of this method have not been established at this time. The electrode recommended range is 0.19-1900 mg/liter urine.

3.0 Interferences

Hydroxide is the only positive interference in the measurement and is eliminated by use of the pH buffer. Negative interferences, which may result from complexing of fluoride by cations such as calcium, are minimized by the complexing agent in the buffer mixture. The buffer also yields a solution of high ionic strength in which the activity coefficient of fluoride is relatively constant.

4.0 Precision and Accuracy

4.1 The 95% confidence limits are ±50% of the value (25% RSD) at the 0.8 mg/L level.

4.2 The recovery on synthetic (spiked urine) samples is 95% of the added value at the 0.8 mg/L level.

APPROVED BY Y-12	LAB A. J. McElhaney IH W. S. Everett, Jr.	APPROVED BY ORGDP	LAB T. Kuronoshi IH D. G. Duncan	APPROVED BY UCCND-COORD'R C. W. Weber
APPROVED BY PGDP	LAB R. E. Simmons IH C. H. Turak	APPROVED BY ORNL	LAB W. R. Laing IH J. A. Ely	NUMBER IHA-420

UCN-13234
(1235 1-79)

5.0 Advantages and Disadvantages of the Method

5.1 Advantages over previous methods include simplicity, accuracy, speed, selectivity, and elimination of ashing, distillation, or diffusion steps.

5.2 Interfering ions are complexed by the buffer mixture.

5.3 No significant disadvantages are known.

6.0 Apparatus

6.1 Fluoride sensitive selective ion electrode, Model 94-09, Orion Research Corporation (Cambridge, Massachusetts), or equivalent.

6.2 Reference electrode, calomel or silver/silver chloride, sleeve junction preferable but not necessary.

6.3 pH/Millivolt meter, capable of measuring ±0.5 millivolt.

6.4 Magnetic stirrer, equipped with small stirring bars which can spin freely in the sample beakers.

6.5 Glass beakers (50-ml) and sample collection bottles (200-ml capacity).

6.6 Laboratory glassware.

7.0 Reagents

All chemicals used should be ACS Reagent grade, or equivalent. After being prepared in clean glassware, all fluoride-containing solutions should be stored in plastic beakers and bottles.

7.1 Double distilled water.

7.2 1,2-Cyclohexylenedinitrilotetraacetic acid (CDTA).

7.3 Glacial acetic acid.

7.4 Sodium chloride, crystals.

7.5 Sodium hydroxide solution, 5 M: Dissolve 20 g of sodium hydroxide pellets in 70 ml of distilled water and dilute to 100 ml.

7.6 Total Ionic Strength Adjustment Buffer (TISAB): Place 500 ml of double distilled water in a 1-liter beaker. Add 57 ml of glacial acetic acid, 58 g of sodium chloride, and 2.0 g of CDTA. Stir to dissolve. Place beaker in a water bath (for cooling). Slowly add 5 M sodium hydroxide until the pH is between 5.0 and 5.5. Cool to room temperature and pour into a 1-liter volumetric flask; add double distilled water to the mark.

7.7 Sodium fluoride, for preparation of standards.

7.8 Standard fluoride solutions. All solutions should be stored in plastic bottles. The 0.1 M fluoride standard is reported to be stable for at least two months. All other dilutions should be prepared fresh weekly.

7.8.1 Fluoride standard solution, 1900 mg/L: Dissolve 4.200 g of sodium fluoride in water and dilute to 1000 ml. This solution can also be purchased from Orion Research, Inc., Cambridge, Massachusetts.

7.8.2 Fluoride standard solution, 190 mg/L: Dilute 10 ml of 7.8.1 to 100 ml with water.

7.8.3 Fluoride standard solution, 19 mg/L: Dilute 10 ml of 7.8.2 to 100 ml with water.

7.8.4 Fluoride standard solution, 1.9 mg/L: Dilute 10 ml of 7.8.3 to 100 ml with water.

7.8.5 Fluoride standard solution, 0.19 mg/L: Dilute 10 ml of 7.8.4 to 100 ml with water.

8.0 Procedure

8.1 Cleaning of equipment

8.1.1 All plastic and glassware must be washed free of any fluoride before use.

8.2 Storage of Samples

8.2.1 Samples that cannot be analyzed within 48 hours should be refrigerated. (Do not freeze.)

8.3 Analysis of Urine Samples

8.3.1 Transfer 20 ml of well-mixed urine sample and 20 ml of TISAB buffer solution into a 50-ml beaker, and add a magnetic stirring bar.

8.3.2 Immerse the electrodes in the solution. Adjust stirring speed and positions of the stirrer and electrodes to avoid splashing and hitting the electrodes.

8.3.3 After the EMF (voltage) reading stabilizes (that is, EMF drift is less than 0.5 millivolt per minute) record the EMF to the nearest millivolt.

For most samples, the EMF will stabilize in a minute or two if the fluoride concentration is 2 μg/ml or more. Stabilization may take longer at lower concentrations.

8.3.4 Rinse the electrodes with double distilled water and wipe dry with a clean tissue before proceeding with the next aliquot.

9.0 Calibration and Standards

9.1 Use the standard fluoride solutions prepared in 7.8 and treat them in the same way as the samples, Section 8.3. Start with the most dilute standard solution (0.19 mg/L) and proceed to 190 mg/L.

9.2 Prepare a calibration curve by plotting the concentration vs EMF data on semi-log paper with the fluoride concentration on the log axis.

9.3 Calibrations should be repeated or confirmed at least twice daily.

10.0 Calculations

10.1 The concentration of fluoride is obtained by converting the millivolt reading directly into concentration, using the calibration curve.

10.2 The concentration is reported as mg F per liter of urine.

11.0 References

11.1 *Instruction Manual for Fluoride Electrode Model 94-09*, Orion Research Incorporated, Cambridge, Massachusetts.

11.2 Sun, Mu-Wan; *Fluoride Ion Activity Electrode for Determination of Urinary Fluoride*; Amer. Ind. Hyg. Assoc. J., 30, 133, 1969.

11.3 NIOSH Manual of Analytical Methods, Second Edition, Vol. 1, U. S. Department of Health, Education, and Welfare, Method 114, 1977.

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-450
DATE	Nov. 27, 1979
SUPERSEDES	
PAGE	1 OF 6

MERCURY IN URINE AND BLOOD, FLAMELESS AA METHOD

Analyte:	Mercury	Method No.:	IHA-450
Matrix:	Urine, Blood	Range:	0.010-0.200 μg/ml urine 0.025-0.500 μg/ml blood
Procedure:	Oxidative digestion; mercury reduction and liberation; flameless atomic absorption	Precision:	∿ 6% RSD urine

1.0 Principle of the Method

1.1 Whole blood and urine samples are digested with HNO_3, H_2SO_4, and potassium permanganate at room temperature, and lastly with potassium persulfate at 95°C for 2 hours.

1.2 After reduction of excess permanganate, elemental mercury is liberated by reduction with $SnSO_4$ solution and measured by flameless atomic absorption at 253.7 nm.

2.0 Range and Sensitivity

2.1 The actual range and sensitivity of the procedure have not been established. However, the lowest concentrations reported are 0.010 μg/ml for urine using a 5-ml aliquot, and 0.025 μg/ml for blood using a 2-ml aliquot, with the practical upper limit at 20 times these values.

2.2 The working range may be extended by decreasing the sample size.

3.0 Interferences

3.1 Organic vapors absorb at the 253.7-nm Hg line and must be absent.

4.0 Precision and Accuracy

4.1 Samples of NBS SRM 2672, Freeze-Dried Urine Certified for Mercury, were analyzed according to this procedure with the following results:

APPROVED BY Y 12	LAB A. J. McElhaney IH W. S. Everett Jr.	APPROVED BY ORGDP	LAB T. Kwasnoski IH D. T. Duncan	APPROVED BY UCCND-COORD'R C W Weber
APPROVED BY PGDP	LAB R. E. Simmons IH C. W. Turak	APPROVED BY ORNL	LAB W. R. Laing IH J. A. Eaton	NUMBER IHA-450

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Level	Found, µg/ml	Certified, µg/ml
Low	0.0453 ± 0.0024	0.0498 ± 0.0042
Elevated	0.291 ± 0.018	0.294 ± 0.024

The values (Found) are the means obtained in the measurement of seven samples while the uncertainties represent the 95 percent confidence limits.

4.2 No similar statistics are available for blood. No certified mercury-in-blood standards are available.

5.0 Apparatus

5.1 Atomic absorption spectrophotometer, with an absorption cell at least 10-cm long x 2-cm I.D. with quartz end-windows.

5.2 Mercury hollow cathode lamp.

5.3 Strip-chart recorder.

5.4 Reagent bottles, 250-ml.

5.5 Gas supply: air, N_2, or argon.

5.6 Flowmeter, to deliver gas at 1 liter per minute.

5.7 Aerating tubing: a straight cylindrical flat-end glass frit of coarse porosity.

5.8 Drying tube: a 15-cm x 19-mm O.D. tube packed with magnesium perchlorate desiccant. The apparatus is assembled as shown in Figure 1.

5.9 Heparinized vacutainers, mercury-free, 3-ml, equipped with sterilized stainless steel needles.

5.10 Water bath, capable of maintaining 95°C.

6.0 Reagents

All reagents are reagent-grade and water is double-distilled or deionized.

6.1 Sulfuric acid, conc.

6.2 Sulfuric acid, 0.5 N: Add 14.0 ml of conc sulfuric acid to about 900 ml of water and dilute to 1.0 liter.

6.3 Nitric acid, conc: Reagent grade of low mercury content. Transistor-grade Mallinckrodt appears to be suitable. If this grade is not used, and a reagent blank of $\geq$ 0.05 μg is obtained, it will be necessary to distill the nitric acid.

6.4 Stannous sulfate suspension: Add 25 g of stannous sulfate to 250 ml of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

6.5 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100.0 ml. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

6.6 Potassium permanganate: 5% solution, w/v: Dissolve 5 g of potassium permanganate in 100 ml of distilled water.

6.7 Potassium persulfate: 5% solution, w/v: Dissolve 5 g of potassium persulfate in 100 ml of distilled water.

6.8 Stock mercury solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of distilled water. Add 10 ml conc nitric acid and adjust the volume to 100.0 ml (1 ml = 1 mg Hg).

6.9 Working mercury solution: Make successive dilutions of the stock mercury solution to obtain a working standard solution of 1 ml = 0.1 μg. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

7.0 Procedure

7.1 Cleaning of Equipment. Acid-clean all glassware by soaking in 1:1 HNO_3 for 30 minutes and rinsing with deionized water.

7.2 Collection and Shipping of Samples

7.2.1 Urine samples are collected in Hg-free plastic bottles and preserved by the addition of 0.1 g potassium persulfate per 100 ml of urine. Urine preserved in this manner is stable at room temperature for two weeks.

7.2.2 Blood samples are collected in Hg-free heparinized vacutainers equipped with sterilized stainless steel needles. Refrigerated samples are stable for two weeks. (Do not freeze.)

7.3 Sample Preparation

7.3.1 Pipet 5 ml of urine or 2 ml of blood into a 250-ml reagent bottle, dilute to 100 ml with deionized water and mix.

7.3.2 Add 5 ml of conc H_2SO_4 and 2.5 ml of conc HNO_3 to each bottle and mix.

7.3.3 Add 15 ml of $KMnO_4$ solution (6.6) to each bottle, mix, and allow to stand for 15 minutes.

7.3.4 Add 8 ml of $K_2S_2O_8$ solution (6.7) to each bottle, mix, and heat in a water bath at 95°C for 2 hours.

7.3.5 Cool and add 6 ml of sodium chloride-hydroxylamine sulfate solution (6.5) to each bottle to reduce the excess permanganate.

7.4 Analysis of Sample

7.4.1 Add 5 ml of the stannous sulfate suspension (6.4) and immediately attach the bottle to the aeration assembly (See Figure 1).

7.4.2 Set the bypass valves to allow the gas (@ 1 liter/min) to sweep the elemental mercury from the bottle to the absorption cell. The absorbance will increase and reach maximum within 30 seconds.

7.4.3 As soon as the absorbance begins to decrease, open the bypass valves and continue aeration until the recording returns to baseline.

7.4.4 Repeat Steps 7.4.1 through 7.4.3 for each sample.

8.0 Calibration and Standards

8.1 Transfer 0 (Blank), 1.0, 2.0, 5.0, and 10.0-ml aliquots of the 0.1-μg/ml working mercury solution (6.9) to a series of 250-ml reagent bottles. Note: Reagent blank values should not exceed 0.05 μg.

8.2 Dilute to 100 ml with deionized water, mix, and treat as samples, beginning with 7.3.2.

8.3 Plot peak heights vs. μg mercury as a calibration curve.

9.0 Calculations

9.1 Hg in sample, μg/ml = $\frac{A - B}{V}$.

Where A = Hg (μg) found in sample (calibration curve),

B = Reagent blank, μg, and

V = Volume of sample, ml.

10.0 Reference

10.1 *NIOSH Manual of Analytical Methods*, 2nd edition, Vol. 1, April 1977; P & CAM 165 and 167.

UCN-10766B (12 8-78)

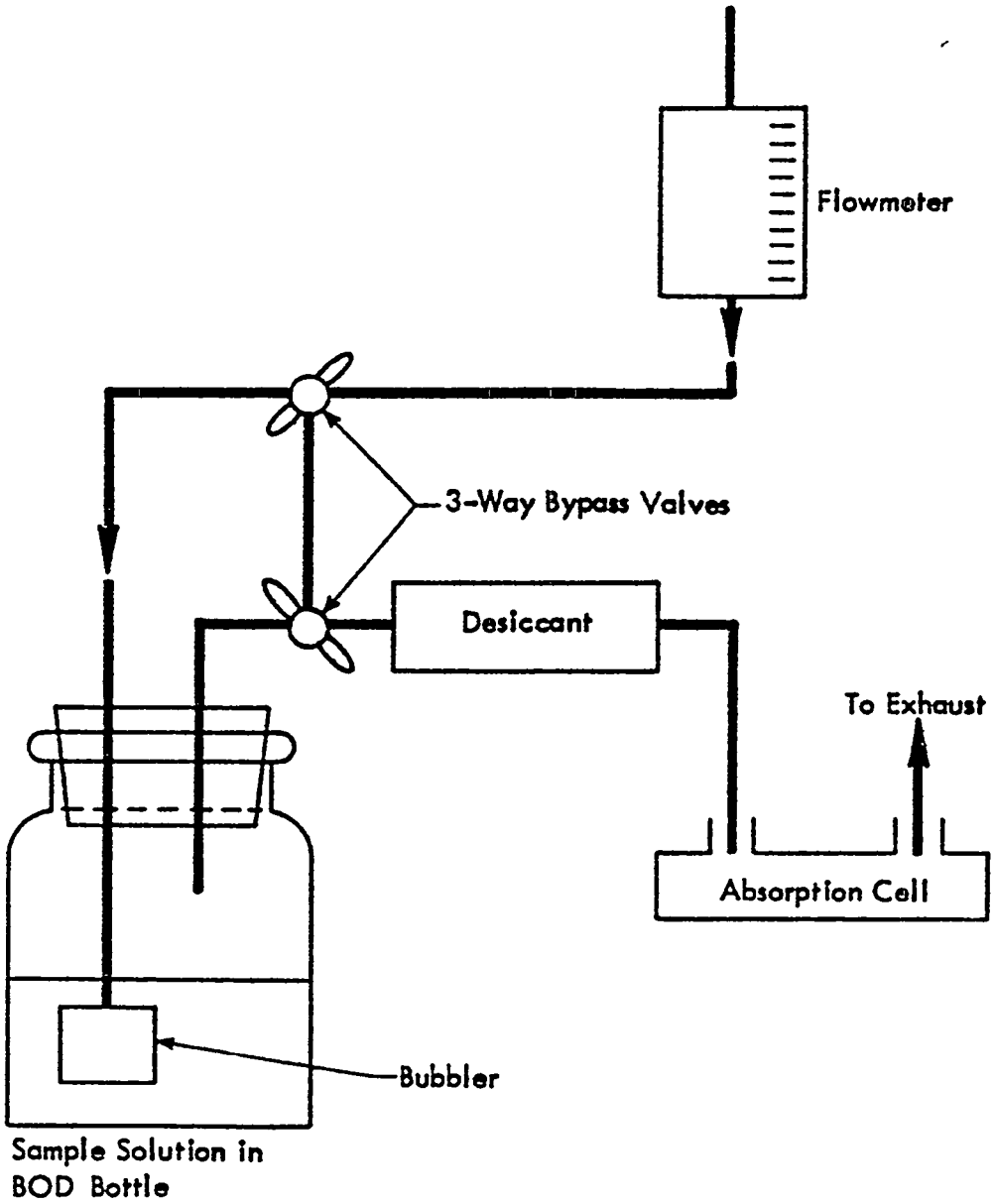

Figure 1. APPARATUS FOR FLAMELESS MERCURY DETERMINATION.

K-255

MARTIN MARIETTA ENERGY SYSTEMS, INC.
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

Please draft 1-Sec

INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

NUMBER	IHA-460
DATE	~~10/30/86~~
SUPERSEDES	
PAGE	1 OF 5

METALS (SELECTED, HEAVY) IN WHOLE BLOOD, FURNACE ATOMIC ABSORPTION METHOD

→ Insert block of specifics for full procedures, just as in old procedures

1.0 SCOPE AND APPLICATION

1.1 This method is suitable over the entire range of lead, cadmium, chromium, and nickel blood levels encountered in industrial workers.

1.2 The concentration range of the method is shown in the following table:

	Lower Limit mg/100 g	Upper Limit mg/100 g
Lead	0.010	0.100
Cadmium	0.002	0.020
Chromium	0.005	0.050
Nickel	0.010	0.200

The upper limit may be extended by simple dilution.

2.0 SUMMARY

2.1 Whole, venous blood is diluted with water and analyzed by atomic absorption spectroscopy using graphite furnace atomization.

2.2 Background correction is necessary to correct for nonatomic absorption, and the method of standard additions is necessary to correct for matrix interferences.

3.0 SAMPLE HANDLING AND ~~PRESENTATION~~ Preservation

3.1 The venous blood sample should be collected using a 3-cc heparinized Vacutainer or a 20-cc Vacutainer container 1 ml of heparin.

3.2 The samples should be mixed gently and refrigerated until ready for analysis.

4.0 SOURCE OF METHOD

4.1 Ely, J. A., Bolton, N. E. McElhaney, R. J., and Morrow, R. W.; "Determination of Lead in Whole Blood by Graphite Furnace Atomic Absorption Spectrophotometery," American Industrial Hygiene Association Journal; Vol. 35, No. 9, p. 556 (1974).

APPROVED BY Y-12	LAB	APPROVED BY ORGDP	LAB	APPROVED BY ENERGY SYSTEMS COORD'R.
	IH		IH	
APPROVED BY PGDP	LAB	APPROVED BY ORNL	LAB	NUMBER IHA-460
	IH		IH	

UCN-13234
(1235 8-84)

4.2 Analytical Methods for Furnace Atomic Absorption Spectroscopy, Perkin-Elmer Corporation, Norwalk, Connecticut 06856 (1980).

5.0 COMMENTS · add 200 µg/ml of Fisher Std containing Ba to the Std for a matrix match. Main interferent

5.1 The principal interferences arise from the inability to completely ash the sample in the furnace prior to atomization of the metal. The background correction removes the "smoke" contribution to absorbance during atomization; and calibration by the method of standard additions eliminates interferences due to variable matrices.

5.2 The method is simple, fast, and inexpensive.

5.3 The method determines the total metal present and provides no information about its form in the blood media.

6.0 APPARATUS

6.1 Atomic absorption spectrophotometer, with automatic background compensation and a graphite furnace atomizer.

6.2 Vacutainer collection tube: 3-cc heparinized or 20-cc nonheparinized tubes.

6.3 Microliter pipets: various sizes for standards preparation and sample injection.

7.0 REAGENTS

7.1 Nitric acid, ACS.

7.2 Lead stock solution, 1000 mg/L: Dissolve 1.559 g of reagent grade $Pb(NO_3)_2$ in deionized water; add 10 ml of HNO_3, and dilute to 1000 ml. Commercially prepared standards are available; e.g., Fisher Scientific Co.

7.3 Cadmium stock solution, 1000 mg/L: Dissolve 1.000 g of cadmium in a minimum volume of 1:1 HNO_3 and dilute to 1000 ml. Commercially prepared standards are available; e.g., Fisher Scientific Co.

7.4 Chromium stock solution, 1000 mg/L: Dissolve 2.8290 g of reagent grade $K_2Cr_2O_7$ in deionized water and dilute to 1000 ml. Commercially prepared standards are available, e.g., Fisher Scientific Co.

7.5 Nickel stock solution, 1000 mg/L: Dissolve 1.000 g of nickel in 1:1 HNO_3 and dilute to 1000 ml. Commercially prepared standards are available; e.g., Fisher Scientific Co.

7.6 Standard solutions are prepared using one of the following methods:

7.6.1 Standard working solutions: Make successive dilutions of the stock solutions to obtain an appropriate working solution for each element.

7.6.2 Combined standard solution: Combine the stock solution in a 1-L volumetric flask according to the following schedule:

	ml of Stock	mg/L in Standard
Pb	10.0	10
Cd	2.0	2
Cr	5.0	5
Ni	20.0	20

7.7 Heparin (ammonium salt), for 20-cc Vacutainers.

7.8 Triton X-100: Dilute with deionized water to give a 0.01% solution.

8.0 PROCEDURE

8.1 Collect venous blood using a 3-cc heparinized Vacutainer or a 20-cc Vacutainer containing 1 ml of heparin, and mix gently. Refrigerate until ready for anlaysis.

8.2 Weigh 1.0 g of the sample into a 10-ml volumetric flask, dilute to volume with the Triton X-1000 solution, and mix.

8.3 Inject a 10-to-50-µl aliquot into the graphite furnace; operate the spectrophotometer and furnace according to the manufacturer's recommendations for the given element.

8.4 Record the peak height or area from the instrument readout or accessary recorder.

9.0 CALIBRATION AND STANDARDS

9.1 Calibration is accomplished by the method of standard additions. A typical sample is chosen as the standard and is spiked with appropriate levels of the element(s) of interest from the standard solutions.

9.2 On a plot of total metal signals (peak heights or areas) versus spike levels, a parallel line is drawn through "zero," thus constructing a calibration curve. This is used to determine the metal content in each sample.

9.3 Calibration may also be accomplished using the conventional method of standard additions, in which each sample analyzed is spiked with appropriate levels of the element(s) of interest from the standard solutions.

10.0 CALCULATION

10.1 Blood metal levels are usually reported in units of mg/100 g. The general formula for converting mg/L (in the measured solution) to mg/100 g (in the blood sample) is:

$$\text{mg/100 g} = \text{mg/L} \times \frac{\text{diluted-sample volume (ml)}}{\text{blood sample weight (g)}} \times \frac{100}{1000\ \text{ml/L}}$$

10.2 Therefore, when 1 g of blood is diluted to 10 ml, the formula becomes:

Metal, mg/100 g (in the blood sample) = Metal, mg/L (in the measured solution)

11.0 PRECISION AND ACCURACY

11.1 Repeated measurements of chromium, nickel, and lead in spiked blood samples, using the method of standard additions, showed an average relative standard deviation of about 8%, 6%, and 6%, respectively. Precision for cadmium has not been determined but is expected to be about the same as for lead.

11.2 An informal comparison was made between the lead measurements by this method and those by an isotopic-dilution spark-source mass spectrometric method. Results were within the observed experimental errors of the methods and indicate no significant bias for lead.

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INDUSTRIAL HYGIENE ANALYSIS PROCEDURE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE, TENNESSEE - PADUCAH, KENTUCKY

NUMBER	IHA-460
DATE	March 16, 1981
SUPERSEDES	
PAGE	1 OF 4

METALS (SELECTED, HEAVY) IN WHOLE BLOOD, FURNACE ATOMIC ABSORPTION METHOD

Analyte:	Lead, cadmium, nickel	Method No.:	IHA-460
Matrix:	Whole blood	Range:	See Section 2.2
Procedure:	Graphite furnace atomic absorption spectrophotometry	Precision:	6% RSD Pb
		Accuracy:	No bias for Pb; others not evaluated

1.0 Principle of the Method

1.1 Whole, venous blood is diluted with water and analyzed by atomic absorption spectroscopy using graphite furnace atomization.

1.2 Background correction is necessary to correct for nonatomic absorption and the method of standard additions is necessary to correct for matrix interferences.

2.0 Range and Sensitivity

2.1 The method is suitable over the entire range of lead, cadmium, and nickel blood levels encountered in industrial workers.

2.2 The concentration range of the method is shown in the following table:

	Lower Limit mg/100 g	Upper Limit mg/100 g
lead	0.010	0.100
cadmium	0.002	0.020
nickel	0.020	0.200

The upper limit may be extended by simple dilution.

3.0 Interferences

3.1 The principal interferences are due to the inability to completely ash the sample in the furnace prior to atomization of the metal. The background correction removes the "smoke" contribution to

APPROVED BY Y-12	LAB R. J. McElhaney IH D. L. Bean	APPROVED BY ORGDP	LAB T. Kwasnoski IH D. T. Duncan	APPROVED BY UCCND-COORD'R C W Weber
APPROVED BY PGDP	LAB R. E. Simmons IH C. W. Turak	APPROVED BY ORNL	LAB W R Laing IH James A. Early	NUMBER IHA-460

absorbance during atomization; and calibration by the method of standard additions eliminates interferences due to variable matrices.

4.0 Precision and Accuracy

4.1 Repeated measurements of lead in spiked blood samples, using the method of standard additions, showed an average relative standard deviation of about 6%. Precisions for cadmium and nickel have not been determined but are expected to be about the same as for lead.

4.2 An informal comparison was made between the lead measurements by this method and those by an isotopic-dilution spark-source mass spectrometric method. Results were within the observed experimental errors of the methods and indicate no significant bias for lead.

5.0 Advantages and Disadvantages of the Method

5.1 The method is simple, fast, and inexpensive.

5.2 The method determines the total metal present and provides no information about its form in the blood media.

6.0 Apparatus

6.1 Atomic absorption spectrophotometer, with automatic background compensation and a graphite furnace atomizer.

6.2 Vacutainer collection tube: 3-cc heparinized or 20-cc nonheparinized tubes.

6.3 Microliter pipets: various sizes for standards preparation and sample injection.

7.0 Reagents

7.1 Nitric acid, ACS.

7.2 Lead stock solution, 1000 μg/ml: Dissolve 1.599 g of reagent grade $Pb(NO_3)_2$ in deionized water, add 10 ml of HNO_3, and dilute to 1000 ml. Commercially prepared standards are available; e.g., Fisher Scientific Co.

7.3 Cadmium stock solution, 1000 μg/ml: Dissolve 1.000 g of cadmium in a minimum volume of 1:1 HNO_3 and dilute to 1000 ml. Commercially prepared standards are available; e.g., Fisher Scientific Co.

7.4 Nickel stock solution, 1000 µg/ml: Dissolve 1.000 g of nickel in 1:1 HNO_3 and dilute to 1000 ml. Commercially prepared standards are available; e.g., Fisher Scientific Co.

7.5 Standard solutions are prepared using one of the following methods:

7.5.1 Standard working solutions: Make successive dilutions of the stock solutions to obtain an appropriate working solution for each element.

7.5.2 Combined standard solution: Combine the stock solutions in a 1-L volumetric flask according to the following schedule:

	ml of Stock	µg/ml in Standard
Pb	10.0	10
Cd	2.0	2
Ni	20.0	20

7.6 Heparin (ammonium salt), for 20-cc Vacutainers.

8.0 Procedure

8.1 Collect venous blood using a 3-cc heparinized Vacutainer or a 20-cc Vacutainer containing 1 ml of heparin, and mix gently. Refrigerate until ready for analysis.

8.2 Weigh 1.0 g of the sample into a 10-ml volumetric flask, dilute to volume with deionized water, and mix.

8.3 Inject a 10-to-50-µl aliquot into the graphite furnace; operate the spectrophotometer and furnace according to the manufacturer's recommendations for the given element.

8.4 Record the peak height or area from the instrument readout or accessory recorder.

9.0 Calibration and Standards

9.1 Calibration is accomplished by the method of standard additions. A typical sample is chosen as the standard and is spiked with appropriate levels of the element(s) of interest from the standard solutions.

9.2 On a plot of total metal signals (peak heights or areas) versus spike levels, a parallel line is drawn through "zero," thus constructing a calibration curve. This is used to determine the metal content in each sample.

9.3 Calibration may also be accomplished using the conventional method of standard additions, in which each sample analyzed is spiked with appropriate levels of the element(s) of interest from the standard solutions.

10.0 Calculation

10.1 Blood metal levels are usually reported in units of mg/100 g. The general formula for converting µg/ml (in the measured solution) to mg/100 g (in the blood sample) is:

$$\text{mg/100 g} = \mu\text{g/ml} \times \frac{\text{diluted-sample volume (ml)}}{\text{blood sample weight (g)}} \times \frac{100}{1000\ \mu\text{g/mg}}$$

10.2 Therefore, when 1 g of blood is diluted to 10 ml, the formula becomes:

Metal, mg/100 g (in the blood sample) = Metal, µg/ml (in the measured solution)

11.0 Reference

11.1 Ealy, J. A., Bolton, N. E., McElhaney, R. J., and Morrow, R. W.; "Determination of Lead in Whole Blood by Graphite Furnace Atomic Absorption Spectrophotometry"; American Industrial Hygiene Association Journal; Vol. 35, No. 9, p. 556 (1974).

Doris Frazier's list

ATTACHMENT 2

AIR

not using but using method 7400

PARAMETER	IHA PROCEDURE #/DATE	
IH Asbestos Y-12 using 7400 A-rules	IHA-110 (11/79)	NIOSH 7400 now (all plants) have this.
Uranium	IHA-190 (8/80)	new draft (out for 5-pt review)
Joe S. Fluoride NA	IHA-130 (11/79)	new draft (" " " " ")
Y-12 Beryllium Y-12 enhanced draft	IHA-115 (11/79)	
MF Lead	IHA-165 (8/80)	new draft (" " " " ")
Mercury Feldman dissolution	IHA-150 (11/79)	permanganate dissolution → didn't
IH Organics NA at Y-12	IHA-250 (5/80)	

URINE

Uranium 99.95 depleted U Fluor 490 ear IHA-483	IHA-490 (6/83)	new draft (in pack now being signed for going to Reprod'n)
Joe S – Fluoride Y-12 NA	IHA-420 (11/79)	
Y-12 yes → Mercury no program for this at ORNL	IHA-450 (11/79)	

BLOOD

MF ergusson Lead prep. modification IHA-460 no included in new draft procedure Y-12 NA	IHA-460 (3/81)	new draft (out for 5-pt. review

SEP 29 1987

9-25-87

Doris Frazier -

As per our conversation this A.M., I have enclosed the latest drafts of all those procedures for which I've received drafts. Of the eleven procedures you've listed (Attachit 2), all but five are covered by new drafts which have been received at all plants. Unfortunately, I can not say for sure that they all saved copies of what they received and returned to me, and I have received the reviews from several plants. So they are responsible for either the version now in the manual or the revised draft. (Technically, they are often very similar.)

For five IHA procedures, I've received no new drafts yet, so the manual prevails. And for NIOSH-7400 (revised), you have a copy of that, as do all plants.

I'm also enclosing the Table of Contents page and several items included in a packet being prepared for signature and issuance to our IHA manual. The Introduction (IHA-001) should be studied, to understan how our manual is undergoing a new face-lift. And IHA-031 and IHA-040, which cover Quality Control; the new "External" program and the internal programs — may be useful to you in your audit.

Good luck in the surveillances. Call if I can help further.

Charlie Weber
(4-9914)

INTRODUCTION

This manual of analytical procedures is a compilation of methods used within Martin Marietta Energy Systems, Inc. (MMES) in support of the industrial hygiene programs of the five plants. The emphasis is on chemical analysis procedures conducted in the laboratory on samples collected by, or under the direction of, the Industrial Hygiene Departments.

Industrial hygiene programs within the chemicals industry have received increased attention in recent years. Enhanced awareness of toxic substances by industrial management, employees, government, and the public has brought forth a number of new federal regulations. Some of these are under the charge of the Environmental Protection Agency; those most concerned with the industrial workplace are promulgated and administered by the Occupational Safety and Health Administration (OSHA), often at the recommendation of the National Institute for Occupational Safety and Health (NIOSH).

The protection of employees from exposure to toxic chemicals has been a traditional concern of MMES and has been regularly scrutinized by management, by Martin Marietta Corporation, and by the Department of Energy and its predecessors. Accordingly, the methodology for monitoring the working environments has been quite well established for a variety of recognized hazards. Nevertheless, the five plants of MMES, all dealing closely with a variety of chemicals, have reviewed their industrial hygiene programs with increased frequency and have generally increased the scope of workplace monitoring. The laboratories have therefore been challenged to keep pace, to try to anticipate new plant programs which may need area sampling, to modernize their methodology, and often to gear for increased workloads.

As the Table of Contents for this manual reveals, the samples associated with industrial hygiene are generally derived from the working air environments, collected by special traps, absorbers, or filters. Additionally, some toxics may be monitored by analyses of urine, feces, or blood samples. The chemical types include both inorganics and organics. Some of the toxics are also radioactive; a few of the analytical procedures therefore are radiochemical methods; and while the radiochemical procedures are principally applied to samples and programs administered by the Health Physics functions of MMES, the analytical results are also of interest to industrial hygienists, as confirmation of potential chemical toxicological problems. A category of miscellaneous sample analysis has also been included in the manual, to cover such industrial hygiene interests as insulating materials, drinking water quality, and certain chemicals which can contaminate work surfaces.

The resources employed in generating industrial hygiene analytical procedures for use in the laboratory are many. The laboratory procedures manuals of the five plants have documented a host of techniques, some developed within MMES, and some adopted from analytical journals. A relatively recent resource which has become useful to the industrial hygiene programs is the:

NIOSH Manual of Analytical Methods: Third Edition, Volumes 1-2 (February 5, 1984): U. S. Department of Health, Education, and Welfare, National Institute for Occupational Safety and Health.

The NIOSH Manual, Third Edition, represents a significant improvement over the earlier editions. In addition to technical revisions, chapters are included on quality assurance, and air sampling. The NIOSH Manual Coordinator has issued a supplement to the manual and may issue others. Until the Third Edition is complete, procedures in the Second Edition (1977-1981) are acceptable. Because federal budgetary limitations may delay the NIOSH program, the manual coordinator has also recommended as a resource the following:

OSHA Analytical Methods Manual: Organic and Inorganic; 1985; OSHA Analytical Laboratory, Salt Lake City, Utah, U. S. Department of Labor, Occupational Safety and Health Administration.

The above NIOSH and OSHA methods are expected to bring about an enhanced level of uniformity and quality in the analytical support of industrial hygiene programs in the United States. Whenever the analytical needs in the MMES laboratories are appropriately met by the methods available in these resources, they are being used. Because these manuals are generally available, all laboratories and other users of the MMES manual are encouraged to avail themselves of the government methods.

As procedures are selected or updated to be placed in the MMES manual, those which originate in the NIOSH or OSHA manuals will not be included in their full detailed form; that would be considered as a redundant effort. Instead, they will be presented as abbreviated summary sheets including key aspects of analysis and sampling; they will also include clear traceability to the government procedures.

The procedures in the manual are reviewed and approved by the Energy Systems Five-Plant Committee on Industrial Hygiene Analysis Procedures. The present committee members are:

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The updating of this manual is an ongoing effort in which all five plants are involved. To facilitate this effort, a subcommittee was organized, including two members from each of the analytical laboratories. The present members of the subcommittee are:

L. W. McMahon, Chairman, and C. R. Kirkpatrick,
Analytical Chemistry Department, ORGDP

B. R. Clark and M. P. Maskarinec,
Analytical Chemistry Division, ORNL

R. E. Simmons and J. K. Prickett,
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QUALITY CONTROL, EXTERNAL PROGRAM - ENERGY SYSTEMS

1.0 SCOPE AND APPLICATION

1.1 Appropriate quality controls on each parameter are employed by each of the laboratories to ensure that the reported analytical data are valid and meet the needs of the Industrial Hygiene organization at each plant in its monitoring program.

1.2 As part of the Quality Assurance program at each plant, the analytical services employed to support the Industrial Hygiene functions must ensure reliable data, available in a timely and cost-effective manner, to demonstrate that pollutants to which employees are exposed at each plant are adequately monitored and are in compliance with the limitations established by the U. S. Occupational Safety and Health Administration (OSHA) and the U. S. Department of Energy (DOE).

2.0 SUMMARY OF PROGRAM

2.1 In addition to the appropriate internal controls (IHA-040) and calibration techniques applied by each laboratory to ensure correct results, external quality control programs are employed that permit the comparison of analytical performance of each laboratory with that of other laboratories and allow each Industrial Hygiene department to participate directly in the monitoring of analytical quality.

2.2 An effective external quality control program in use at all Energy System's plants was initiated and is administered by the Industrial Hygiene departments, with the encouragement and support of the Energy System's ESA staff. This program is designed to be broader in analyte scope and more directly effective than the PAT external program described in IHA-030; however, it is not a substitute for the PAT program. Through the planning and actions of a Control Sample Subcommittee organized to relate to the Energy System's Industrial Hygiene Committee, this external program has been installed at all Energy System's plants.

2.3 The program uses blind control samples that are sent to the laboratories along with real monitoring samples, with analytical results reported back to the originators, which are the Industrial Hygiene departments.

2.4 The samples are of several types and are prepared by laboratory personnel at the four plants that are qualified in such work and who are administratively separated from the laboratories responsible for sample analysis.

3.0 DESCRIPTION OF PROGRAM

3.1 The initiating Control Sample Subcommittee consisted of:

D. T. Duncan, Chairman, ORGDP IH Department
J. A. Ealy, Y-12 Plant IH Department
B. A. Jerome, ORNL IH Department
C. W. Weber, Energy Systems Environmental Analysis Coordinator

Because of distance, the Paducah Gaseous Diffusion Plant's Industrial Hygiene Department declined to participate directly in the subcommittee meetings but have concurred and participated in its recommendations.

3.2 Subcommittee Recommendations

3.2.1 It is preferred that all sites be consistent in their participation in the external control program.

3.2.2 Control samples should be submitted "blind" through the IH departments, preferably along with real samples.

3.2.3 A minimum of two control samples should be submitted for each batch of four or more samples.

3.2.4 Every third batch of three samples (or less) should have two control samples submitted with it.

3.2.5 When the frequency of sampling for an analyte is less than quarterly, each Industrial Hygiene department should consider submitting a pair of control samples at least quarterly.

3.2.6 For an analyte not frequently monitored and for which no control is included in this program, control samples should be submitted for a contaminant determined using the same analytical procedure, if feasible.

3.2.7 Control samples should be spiked with contaminants in the same general concentration range as those provided in the PAT (NIOSH-administered) external quality control program.

3.2.8 When planning for sample supplies to the program, estimates of costs should be obtained from both commercial laboratories and from in-house (Energy Systems) laboratories for the preparation of control samples containing analytes of specific interest at our plants and in sufficient quantities to support the external quality control program for a period of about three years.

3.2.9 The program is intended primarily for intraplant use, but all plants will be encouraged to submit control sample results to a common site for potential statistical review for the general benefit of all plants.

3.2.10 The program will be reviewed periodically to identify desired revisions in parameters of interest, to consider possible redistribution of control samples among the plants, and to consider revisions in the subcommittee recommendations.

3.2.11 The membership and chairmanship of the Control Sample Subcommittee may be changed to accommodate the schedules of its members and the interests of the Energy Systems Industrial Hygiene Committee.

4.0 CONTROL SAMPLE REQUIREMENTS

4.1 Following a general expression of interests in certain analytes at the four plants, the Control Sample Subcommittee prepared a list of relatively routine analytes and canvassed the Industrial Hygiene departments to identify probable control sample quantities to be used over a three-year period. The anticipated quantities needed by each plant are presented in Table 1. Additional quantities (10%) were also included to allow preliminary evaluation of sample-to-sample uniformity.

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Table 1. Energy Systems Industrial Hygiene External Quality Control Sample Preparation

	Analyte	Approx. target values	Quantity needed X-10	Y-12	K-25	PAD	Totals (+ 10%)
Group I	Acetonitrile	1.0 mg	-	100	-	-	110
	Methyl Chloroform	1.0 mg	15	75	-	10	110
	Perchloroethylene	1.0 mg	150	150	30	2	367
	Mixture: Benzene	0.1 mg	70	10	30	6	128
	Mixture: Toluene	1.0 mg					
	Mixture: Xylene	1.0 mg					
	Methyl Ethyl Ketone	1.5 mg	150	25	15	4	214
Group II	Cadmium	10.0 μg	150	10	10	-	187
	Nickel	50.0 μg	50	-	60	50	176
	Iron	150.0 μg	-	-	30	50	88
	Chromium	20.0 μg	30	-	30	10	77
	Lithium (Whatman 41)	1.0 μg	-	100	-	-	110
	Boron	5.0 μg	-	100	-	-	110
Group III	Mercury (Hg Charcoal Tubes)	1.2 μg	-	150	-	-	165
	Lead	20.0 μg	260	25	40	4	362

Group I prepared by ORNL - B. R. Clark, Analytical Chemistry Division, 4500S, MS D-160

Group II prepared by ORGDP - W. D. Hedge, Analytical Chemistry Department, K-1004-C, MS 440

Group III prepared by PGDP - G. T. Cook, Analytical Laboratory Department, C-710

4.2 Technical Specifications

4.2.1 The external control samples, to be submitted along with real samples by the Industrial Hygiene departments, are intended to be the same in appearance and to be treated as real samples in the Analytical Laboratory.

4.2.2 The target values (Table 1) for contained analytes on the sampling media are approximate levels. The emphasis is on replication of a value for precision among the samples and analytical confirmation of the target values.

4.2.3 The control sample media taken from supplies of singular lot numbers for media blank uniformity were provided by the Industrial Hygiene departments.

4.2.4 All organic samples were prepared on charcoal tubes, injected at one end by a syringe, controlled by a precise repetitive pipettor.

4.2.5 Charcoal tube samples were flame-sealed at both ends for reliable long-term storage. Before sending to an analytical laboratory, the sealed ends are broken off and covered by plastic caps to simulate a real sample.

4.2.6 Metals (except mercury) were prepared by precise solution injection onto 37-mm cellulose acetate membrane filters, unless otherwise specified (Table 1), to match the media used in the monitoring practice. Filters are individually packaged in plastic petri dishes (supplied by the Industrial Hygiene departments).

4.2.7 Mercury samples were prepared by taking precise syringe volumes of mercury solution. The fixed doses were delivered to commercial charcoal tubes that had been pretreated for retention of mercury. These charcoal tubes were also carefully flame-sealed for longer term storage.

4.2.8 All samples were individually labeled to indicate the analyte of interest.

5.0 CONTROL SAMPLE PREPARATION

5.1 The subcommittee obtained estimates of costs for conducting the sample preparation work from several laboratories, including commercial laboratories and the laboratories within the Energy System's plants. After consideration of the comparative costs, delivery schedule, and expected quality of the samples, it was decided to have the work conducted by Energy System's laboratories. The technology for the work had been demonstrated previously at ORNL, and the uniformity of test samples had been confirmed by analyses at all plants.

5.2 A prime consideration in the selection of laboratories to prepare control samples is the need for those laboratories to be physically and administratively separated from the laboratories analyzing the samples. That objective was met, as indicated by the groups of samples in Table 1, and the laboratories were selected to conduct the preparation work.

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5.3 Because of the pressures of heavy work schedules at the time, the Y-12 Plant Laboratory selected not to participate in the sample preparation, but assisted in the confirmatory analysis of control samples.

5.4 The groupings of sample preparation (shown in Table 1) were designed to accommodate the laboratories' work capacities and convenient delivery schedules.

6.0 DATA EVALUATION

6.1 This program was initiated by the Industrial Hygiene departments to permit them a timely evaluation of the quality of the data furnished by the analytical laboratories. In this context, both the laboratories and the Industrial Hygiene customers are interested in the quality of the data.

6.2 The Industrial Hygiene departments carry the initial burden of evaluating the analytical data received in this program, since they are responsible for submitting the control samples and knowing the identify of the samples.

6.3 Each Industrial Hygiene department will maintain records of the analytical values for each analyte measured in the QC samples. Chronological tables or graphs are also recommended to permit detection of a bias, a trend (drift) in values, or excessive imprecision.

6.4 The precision and accuracy of the results should be consistent with realistic evaluation of the analytical methods used in the laboratory, recognizing that routine practice rarely provides the same quality of results as generated by the expert technologist during development of the laboratory procedure.

6.5 Periodic feedback of the analytical results versus known values is a mandatory feature of a good QC program. Prompt feedback is necessary when results are out-of-control or threatening to become out-of-control. It is also important for the laboratories to learn when acceptable quality has been restored. This communication responsibility must rest with the customers, the Industrial Hygiene departments.

6.6 As analytical data become available with experience in this program at all the Energy System's plants, it is a key objective of the Control Sample Subcommittee to submit the results to periodic statistical review. This can be accomplished by collecting results from all plants periodically at one site and treating the data in a computerized statistical program. The statistical group will issue an evaluation report which may help the users of the QC samples recognize whether the samples are deteriorating in storage, whether the analytical laboratories are providing consistent and acceptable services, or whether some sample types should be submitted at a decreased or increased frequency at some plants.

6.7 The Control Sample Subcommittee will meet either periodically or at the discretion of the chairman to oversee the total body of analytical data available and to judge whether programmatic revisions should be made.