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Sampling and Analysis of the Inactive Waste Storage Tank Contents at ORNL

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ABSTRACT

Thirty three inactive waste storage tanks, currently managed by the ORNL Remedial Action Program (RAP), are to be characterized in preparation for final closure/decommissioning to meet environmental, safety, and long-term surveillance objectives. To date, 30 of these tanks have been characterized. The tanks have been inactive for periods of time ranging from about 1 to 30 years, and minimal information was available on the composition of materials within the tanks.

Aqueous liquid and sludge samples from the waste storage tanks were subjected to modified U.S. Environmental Protection Agency (EPA) SW-846 and Contract Laboratory Program methodology to determine Target Compound List and other Appendix VIII organic compounds. Preparation of decontaminated organic extracts in radioactive-zoned facilities permitted final organic analysis in a conventional GC-MS laboratory. Aqueous liquids were analyzed for major volatile organic compounds by direct aqueous-injection gas chromatography in a radioactive-zoned laboratory; trace volatile organics, by remote purge-and-trap followed by thermal desorption and a second purge-and-trap with GC-MS; and semivolatile organics, by solvent extraction and GC-MS. Organic liquids were analyzed for volatile and semivolatile organics and PCBs, while sludges were analyzed only for semivolatile organics.

With few exceptions, low microgram-per-liter (liquids) and milligram-per-kilogram (sludges) concentrations of regulatory organic compounds were found, and the major species were alcohols (e.g., methyl and ethyl alcohols), ketones (e.g., acetone), chlorinated hydrocarbons [e.g., bis(2-ethylhexyl)phthalate] and tributylphosphate. The modified EPA procedures performed reasonably well, although improvements in sample preparation methodology are needed in some areas (particularly for sludges). However, the regulatory analyses accounted for very little of the organic matter suggested by total organic carbon (TOC) measurements. Additional polar species including dibutylphosphate, di(2-ethylhexyl)phosphate, and ethylenediaminetetraacetic acid were tentatively identified after trimethylsilylation of a sample, but the bulk of the TOC remains unidentified. It is speculated that chromatographic "intractables" such as polar, hydrophilic macromolecular matter may be present.

The goal of the inorganic analytical support for the inactive tank-sampling and characterization task is to provide the data necessary to meet both regulatory and engineering treatability requirements. The tanks are located in several areas throughout ORNL and collected radioactive waste from a large variety of programs and facilities over many years. Because of a lack of standard regulatory methods for the analysis of highly radioactive wastes and mixed wastes, the analytical support for this project was complicated by attempts to mimic existing regulatory procedures. With the complexity of the materials analyzed, the radioactivity, and the inappropriate regulatory procedures, this has been and continues to be a difficult and challenging undertaking. To date, the inorganic tank content measurements have included metals (U, Ag, As, Ba, Cd, Cr, Hg, Ni, Pb, Se, and Tl); radionuclides (^{137}Cs, ^{60}Co, ^{90}Sr, ^{3}H, ^{233}U, ^{238}U, ^{252}Cf, ^{238}Pu, ^{239}Pu,

^{244}Cm, ^{241}Am, ^{134}Cs, ^{228}Th, ^{232}Th, ^{232}U, ^{152}Eu, ^{154}Eu, ^{155}Eu, ^{14}C); anions (Cl^-, F^-, NO_3^-, PO_4^{-2}, SO_4^{-2}, CN^-, OH^-, H^+, CO_3^{-2}, and HCO_3^-); and several physical measurements.

Determination of the RCRA status of the tank contents depends upon the hazardous characteristics of the waste and upon a comparison of the waste constituents to the list of RCRA hazardous wastes contained in the Code of Federal Regulations (40 CFR Pts. 261.31, 261.32, and 261.33). Tanks that contained no RCRA characteristically hazardous (or potential RCRA characteristic as determined by the EP Toxicity equivalent of total RCRA metal concentration) or RCRA listed organic constituents were W1, W2, and T30. At this stage of analysis, the remaining tanks should be considered as containing RCRA waste.

1. SAMPLE COLLECTION FROM THE INACTIVE TANKS

1.1 INTRODUCTION

This report presents the results of a 2-year effort to sample and analyze the contents of the 33 inactive radioactive waste storage tanks located at the Oak Ridge National Laboratory (ORNL). To date, 30 of these tanks have been sampled and analyzed; sampling activities are in progress for the remaining three tanks. All these tanks no longer comply with U.S. Environmental Protection Agency (EPA) regulations for storage or treatment of hazardous wastes and, therefore, will require final closure. The sampling and analytical activities described in this report are the first steps necessary for final closure.

This section describes the sample collection activities associated with the 30 tanks. Sections 2 and 3, respectively, describe the methods used to characterize the organic contents in the tanks and the organic analytical results. Section 4 describes the radiochemical and inorganic characterization of the tank contents; Sect. 5 presents a regulatory analysis of the analytical results.

1.2 BACKGROUND

ORNL is located 40 km (25 miles) west of Knoxville, Tennessee, and began operation in 1943. Production of radioactive and/or hazardous chemical wastes has continued since its beginning as a part of normal facility operations. Underground storage tanks have been used to collect, neutralize, store, and transfer the liquid portion of these wastes. Of these tanks, 33 have been placed out of service because of operational difficulties or system improvements to the waste-handling operations. The 33 waste-storage tanks are located throughout ORNL, but most are located within the main plant area (Figs. 1.1 and 1.2).

In general, the wastes from these tanks were pumped out as they were removed from service. But because these tanks were managed by various divisions within ORNL, little information exists on the residual liquid and sludge that remain. These tanks were constructed of steel or concrete, and they vary in size and age (Table 1.1). Of the 30 tanks sampled to date, 27 were found to contain residual liquid, and 17 to contain sludge.

1.2.1 Need for Sampling and Analysis

The primary purpose for sampling the inactive waste tanks is to determine whether these tanks contain hazardous wastes as defined by the EPA Resource Conservation and Recovery Act (RCRA) regulations (40 CFR Pt. 261, Subparts C and D). Closure deadlines would then be in force for any tanks containing such RCRA wastes. Of equal importance, the tank contents need to be characterized sufficiently to select

Table 1.1. Physical data of inactive waste storage tanks

Tank	Capacity (gal)	Volume (gal)		Construction	Service
		Liquid	Sludge		
T-1	15,000	11,047	791	Mild steel	1963–1980
T-2	15,000	11,048	1,205	Mild steel	1963–1980
T-3	25,000	2,063	2,029	Mild steel/ rubber lined	1963–1980
T-4	25,000	9,341	1,328	Mild steel/ rubber lined	1963–1987
T-9	13,000	1,290	481	Mild steel	1963–1980
T-30	824	40	0	Stainless steel	1945–?
TH-1	2,500	278	0	Stainless steel	1948–1970
TH-2	2,400	Not sampled	Not Sampled	Stainless steel	1952–1970
TH-3	3,300	145	0	Stainless steel	1952–1970
TH-4	14,000	16,982	6,315	Concrete	1943–1970
W-1	4,800	1,213	0	Concrete	1943–1960s
W-1a	4,000	25	0	Stainless steel	1951–1986
W-2	4,800	647	0	Concrete	1943–1960s
W-3	42,500	31,847	2,276	Concrete	1943–1960s
W-4	42,500	17,062	3,982	Concrete	1943–1960s
W-5	170,000	10,278	5,131	Concrete	1943–1980
W-6	170,000	77,044	5,131	Concrete	1943–1980
W-7	170,000	7,044	5,131	Concrete	1943–1980
W-8	170,000	28,244	2,573	Concrete	1943–1980
W-9	170,000	12,990	2,573	Concrete	1943–1980
W-10	170,000	70,618	6,425	Concrete	1943–1986
W-11	1,500	897	62	Concrete	1943–1948
W-13	2,000	457	0	Stainless steel	1940–1958
W-14	2,000	259	0	Stainless steel	1940–1958
W-15	2,000	664	0	Stainless steel	1940–1958
W-19	2,250	0	0	Stainless steel	1955–1960s
W-20	2,250	0	0	Stainless steel	1955–1960s
WC-1	2,150	Not sampled	Not sampled	Stainless steel	1950–1968
WC-15	1,000	Not sampled	Not sampled	Stainless steel	1951–1960s
WC-17	1,000	370	Trace	Stainless steel	1951–1960s
7560	1,000	0	0	Stainless steel	1957–1961
7562	12,000	378	Trace	Stainless steel	1957–1987
7860a	4,500	2,774	0	Stainless steel	1981–1985