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ANALYTICAL CHARACTERIZATION OF HIGH-LEVEL MIXED WASTES USING MULTIPLE SAMPLE PREPARATION TREATMENTS

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ABSTRACT

The Analytical Chemistry Laboratory at the Pacific Northwest Laboratory in Richland, Washington, is actively involved in performing analytical characterization of high-level mixed waste from Hanford's single shell and double shell tank characterization programs. A full suite of analyses is typically performed on homogenized tank core samples. These analytical techniques include inductively-coupled plasma-atomic emission spectroscopy, total organic carbon methods and radiochemistry methods, as well as many others, all requiring some type of remote sample-preparation treatment to solubilize the tank sludge material for analysis. Most of these analytical methods typically use a single sample-preparation treatment, inherently providing elemental information only. To better understand and interpret tank chemistry and assist in identifying chemical compounds, selected analytical methods are performed using multiple sample-preparation treatments. The sample preparation treatments used at Pacific Northwest Laboratory for this work with high-level mixed waste include caustic fusion, acid digestion, and water leach. The type of information available by comparing results from different sample-prep treatments includes evidence for the presence of refractory compounds, acid-soluble compounds, or water-soluble compounds. Problems unique to the analysis of Hanford tank wastes are discussed. Selected results from the Hanford single shell ferrocyanide tank, 241-C-109, are presented, and the resulting conclusions are discussed.

I. INTRODUCTION

The analytical characterization of U. S. Department of Energy (DOE) high-level mixed wastes (HLMW) requires specialized laboratory facilities, robust analytical procedures with supporting research and development, staff with a strong experience base and a well-structured organization. The Pacific Northwest Laboratory (PNL) in Richland, WA, and in particular, PNL's Analytical Chemistry Laboratory (ACL), is actively developing these attributes and is extensively involved in the analysis of HLMW from Hanford single-shell (SST) and double-shell tanks (DST).

In the analysis of HLMW from Hanford's SST and DST programs, a full suite of analyses is typically performed, and several analytical techniques involve multiple sample-preparation treatments, such as fusion, acid digestion, or water leaching. Comparing analytical results from multiple sample-preparation treatments provides significant information on tank chemistry and chemical species, information otherwise not easily obtainable. This information allows distinguishing between compounds that are water-soluble, acid-soluble, or refractory. The analytical techniques selected for discussion include inductively-coupled plasma-atomic emission spectroscopy (ICP-AES), total organic carbon (TOC), total alpha, total beta, and gamma energy analysis (GEA). Analytical problems specific to the analysis of Hanford tank waste, in the areas of analytical techniques, as well as sample-prep treatments, are discussed. Example data from the Hanford SST

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ferrocyanide tank 241-C-109 [1,2] and the comparison of sample-prep treatment results are discussed.

II. BACKGROUND

The Hanford site near Richland, Washington, is operated by the DOE. Environmental restoration and environmental management programs on the site involve more than 500 square miles. This national site includes 178 underground waste-storage tanks that contain HLMW of liquid, sludge and salt cake, ranging from 50K gallons to one million gallons of waste volume. These combined wastes, from a wide variety of fuel reprocessing and supporting process activities, were stored in single-shell carbon-steel tanks and double-shell carbon-steel tanks as early as the 1940s. The radioactive and chemical mixtures stored in these tanks present special and unique challenges in providing analytical data to support the Hanford efforts to characterize, retrieve, and dispose of these complex mixtures.

PNL's Analytical Chemistry Laboratory is a primary resource to a wide spectrum of Hanford site programs, providing analytical chemistry services, at established QA/QC standards, and is developing new technologies to meet site needs. The laboratories and equipment are located in the 300 area of the Hanford site and occupy approximately 30,000 ft². A full range of radiochemical, inorganic, and organic analytical capabilities are available, including routine analyses and R&D activities, methods development, full-shielded facilities support, analytical applications transition to industry, and the ability to prepare data packages to U.S. Environmental Protection Agency (EPA) CLP standards. High-level radiochemistry facilities consisting of hot cells and remote handling manipulators are used to handle the highly radioactive samples. Staff carry out homogenizations, sub-sampling, sample-preparation treatments, and dilutions, as well as chemical and physical testing in these hot cells. The ACL is organized specifically to support the analytical characterization of Hanford SST and DST wastes.

III. SAMPLING AND SAMPLE PREPARATION TREATMENTS

The tank waste characterization process involves a complex sampling, sub-sampling, sample preparation treatment, and analysis scheme. The process begins with extrusion of tank core material and rheology tests followed by physical mixing and homogeneity tests. After homogeneity testing and analysis is completed and homogeneity is established, full sampling begins and

sample-preparation treatments are initiated in the Shielded Analytical Laboratory. Sample splits are performed and distributed to all laboratories, and rigorous QA/QC procedures are followed as analytical operations are carried out. Typically, the tank core samples are analyzed as three or four axial core segments along the length of the full core, as core composites, consisting of a representative mixture of the core segments, and the drainable liquid.

Table 1 provides a general summary of each of the four basic sample preparation treatments routinely performed on the HLMW tank core material analyzed in the ACL. These include caustic fusion, acid digestion, water leach, and the residual solids following water leach. Although other specific sample prep treatments are also used, these four general treatments, used for several analytical techniques in the ACL, will be discussed here.

The acid digestion treatment brings most of the acid-soluble compounds into solution with minimal dilution, and is ideal for most metals analysis, though full solubilization is a constant concern. Difficultly soluble refractory compounds and metals may still be unaffected by the acid digestion procedure; therefore, the fusion procedure is also used. This KNO₃-KOH caustic fusion procedure, in a nickel crucible, has been selected as being most successful for most of the tested tank waste, though a Na₂O₂ fusion procedure, in a zirconium crucible, is sometimes also performed. However, a fusion procedure results in high dilution and high concentrations of salts, impacting ICP-AES analyses as well as causing corrosion of and high concentrations from the crucible material. The water leach procedure provides the additional comparative information on water-soluble compounds, while the residual solids procedure, used for GEA, provides data on water-insoluble compounds.

Several sample prep treatment problems are unique to the type of Hanford tank HLMW analyzed in the ACL. For example, this fusion procedure, used for the analysis of the toxic metals such as Cd, Pb, As, Se, Cr, Ba, Hg and Ag, results in high salt content and high dilutions, causing severe problems in accurately measuring these metals. For the acid digestion treatment, as well as the fusion procedure, the selection of the final acid is a concern. Hydrochloric acid must be used for measuring Rh, while nitric acid is used for measuring Ag. Though HCl is the preferable choice for most analyses, the waste issue of handling and treating laboratory-generated chloride waste is a continual problem. The widely variable nature of the Hanford

Table 1: General Sample-Prep Treatments for HLMW

Treatment	General Summary
Caustic Fusion	A representative weighed 0.2 to 0.5-g sample is added to a tared Ni crucible, water is added, the pH is brought to 7.0, and the sample is dried under a heat lamp. A ten-fold amount of KNO_3 -KOH flux is added to the reweighed sample. The fusion is carried out at 500°C for 30 min. The melt is leached with water, 6 M HCl is added, and the solution is diluted and is ready for analysis.
Acid Digestion	A representative weighed 1-g sample is digested in HNO_3 and H_2O_2 in a series of refluxes at 90° - 95°C . The digestate then undergoes a final reflux with either HNO_3 or HCl, depending upon the analyte set of interest. After filtering and dilution, the solution is ready for analysis.
Water Leach	A representative weighed 1-g sample is mixed with 100 ml water, and the mixture is agitated by ultrasonic bath for 1 h at ambient temperature. The mixture is filtered through a 0.45-micron filter, diluted, and is ready for analysis.
Residual Solids	The residual solids remaining from the above water leach procedure are used for analysis.

tank waste, from tank to tank, causes a great need for continuing methods development to support the ACL analytical operations.

IV. SELECTED ANALYTICAL METHODS

As shown in Table 2, several analytical techniques are performed in the ACL using multiple sample-preparation treatments. These analytical techniques include ICP-AES, TOC, cyanide, and the radiochemistry procedures of total alpha, total beta, GEA, and carbon-14. While each of these procedures inherently provides only elemental information, the use of multiple sample-prep treatments allows potential additional chemical information resulting from the comparison of test results.

For example, the presence or absence of insoluble metal-aluminosilicates can be inferred from such data. Layering or separation of insoluble compounds, such as cesium nickel ferrocyanide, can be determined. Comparing results can provide evidence that measured carbon exists as either water-soluble compounds or insoluble carbon compounds. This information can also further support, for instance, gas chromatography tests to identify the existing carbon compounds. Of the suite of analytical methods, ICP-AES, TOC, total alpha, total beta, and GEA will be discussed here, along with some of their problems unique to the analysis of Hanford tank HLMW.

A. ICP-AES

The analysis of metals by ICP-AES, using a single sample preparation method such as fusion or acid digestion, provides elemental information only. In the present application using multiple sample-prep treatments on tank core samples, comparing results provides qualitative or semi-quantitative information on the chemical nature of the metal compounds present. Comparative results from the fusion and acid-digestion treatments help identify the presence of acid-soluble metal compounds versus acid-insoluble refractory metal compounds. For example, metals measured at near-equal concentrations in both the fusion and acid digestion treatments provide good evidence that the compounds in the original matrix are not refractory, but are totally acid-soluble. If the fusion result is greater than the acid result by at least 20%, then some refractory metal compound may be suspected as being present. Neither single sample-prep treatment alone provides that information.

While ICP-AES is a standard technique in industry, unique problems occur in applying it to Hanford tank HLMW. For example, the use of the fusion treatment for solid/sludge material results in high total dissolved solids. This can cause ICP-AES nebulizer problems and/or highly diluted samples. The required inter-element corrections are generally a much more severe problem with HLMW containing such problem analytes as U, Pu, Ce, Nb, and Ca. Generally for every tank

Table 2: Analyses Performed on Multiple Sample-Prep Treatments

Analytical Method	Sample-Prep Treatments	Purpose
ICP-AES (metals)	Caustic fusion Acid digestion Water leach	Refractory compounds Acid-only soluble Water-only soluble
TOC/TIC/TC	Direct Water leach	Hot-acid soluble Water-only soluble
Total Alpha/Total Beta	Fusion Water leach	Refractory Water-only soluble
Gamma Energy Analysis	Fusion Water leach Residual solids	Refractory Water-only soluble Water-only insoluble
Cyanide	Direct Water-leach	Acid-soluble Water-only soluble
Carbon-14	Direct Water leach	Hot-acid soluble Water-only soluble

sample, all channels need to be scanned for spectral interferences. These spectral interferences can range from 5% to 50% of the analyte signal. Approximately 10% of the elemental lines are different from the EPA-recommended wavelengths due to the presence of interfering lines from U, Pu, or one of the other rare earth elements.

B. TOC

Total organic carbon instrumental methods in industry are usually applied to trace analysis of drinking water, marine water samples, or other industrial-process water waste streams. The application of existing TOC methods to the very complex matrix of Hanford tank solid and sludge wastes, containing up to several percent carbon, is a challenging prospect.

Pacific Northwest Laboratory currently has three very different methods for measuring TOC in the described HLMW, covering the full range of sample type or matrix received. These methods include 1) silver-catalyzed hot persulfate wet oxidation with coulometric detection, 2) UV-catalyzed persulfate with nondispersive infrared (NDIR) detection, and 3) high-temperature total combustion with coulometric detection. Each of the three methods has distinct chemistry, as well as advantages and disadvantages. The experience at PNL has shown that no single TOC

method is ideal for Hanford tank sludge material. It has been found to be most useful, at PNL, to have this variety of TOC methods available for use on HLMW. A comparison of the methods and a discussion of the associated problems are more fully described elsewhere [3].

The silver-catalyzed hot persulfate method, with oxidation occurring at 92-95°C, is in routine use on HLMW sludge and slurry samples at PNL. This method has been found to be the most conveniently implemented method for shielded cell, remote operation. Most of the tank sludge sample material tested to date has been found to be nearly entirely dissolved by this hot sulfuric acid/persulfate treatment. This method has been shown to provide good results for most non-volatile compounds, as established in a recently completed study at PNL [3]. Two weaknesses with the hot persulfate method are that 1) certain difficultly oxidizable compounds, and 2) volatile compounds, give low recoveries. However, in this application, volatile compounds generally are not expected to be present. The water leach samples are measured by the UV-catalyzed persulfate method, at ambient temperature. This method has been shown to give good, reliable results, since only water-soluble compounds, with no solids or particulates present, are measured. The furnace method at PNL involves combustion in oxygen at 600°C for TOC and 1000°C

for total carbon (TC), on separately weighed samples. While this method has been used periodically in the past on HLMW, there have been mixed results. Compounds that are difficultly oxidizable in the hot persulfate method appear to generally give better recovery by this method. But most tank sludge samples have been shown to cause severe matrix problems, chemical attack of the quartz apparatus, partial decomposition of inorganic compounds at 600°C resulting in high TOC values, and chemical interferences with the coulometric detector, resulting from combustion of these high-salt matrices.

The comparison of TOC results from either the hot persulfate or furnace method with the UV-catalyzed method provides evidence for the measured carbon being present as either water-soluble or water-insoluble compounds. Continuing methods development is still needed to further improve TOC method reliability from tank to tank.

C. Radiochemistry Procedures

The radiochemistry procedures of total alpha, total beta, and GEA performed on the multiple sample-preparation treatments of fusion, acid digestion, and residual solids from the water leach process can also provide significant information on the chemical nature of the radioisotope compounds present.

The total alpha activity was obtained by drying a small aliquot of the prepared sample, following the sample prep treatment, on a counting plate and then measuring it by scintillation detector. The total beta was determined similarly by drying a small portion of the prepared sample and measuring by beta proportional counter. The GEA on solutions is determined by counting a small aliquot of prepared solution within a calibrated-geometry vial. The GEA on the residual solids is performed directly on the solids within the counting vial. Comparing results by these radiochemistry techniques using different sample prep methods can provide evidence of the radionuclides existing in either an insoluble or water-soluble compound. Examples of this are addressed in the Discussion section.

V. DISCUSSION

The majority of the analytical techniques in place in the ACL for analyzing HLMW inherently provide elemental information only from single sample-prep treatments. Therefore, conclusions regarding the presence of compounds and the understanding of tank

chemistry must be deduced primarily from elemental information. But additional information is available from these very same analytical techniques simply by comparing results from multiple sample-prep treatments. This additional chemical information contributes significantly to the knowledge of tank chemistry and the full understanding of the chemical environment in the storage tanks.

Careful examination of the Hanford Tank 241-C-109 analytical data can provide good examples of the value of multiple sample-prep treatments. Tank 241-C-109 is known as a ferrocyanide tank and was analyzed by the ACL and has been reported previously [1,2]. Table 3 shows selected results from Tank 241-C-109, cores 47, 48, and 49. The data shown highlight results which show a significant difference between various sample-prep treatments. Based on this data, some conclusions regarding the chemical nature of the tank material can be drawn, as follows.

Fusion dissolution methods appear necessary to obtain good dissolution of Al and Si. The presence of high Al and Si in Core 47, compared to the acid results, suggests evidence of acid-insoluble alumina and silica. But a lack of correspondingly high fusion data for heavier metals suggests the lack of any refractory metal-aluminosilicate compounds. For Core 48, acid digestion results compare fairly well with fusion results for Al, implying little evidence for the presence of refractory alumina. The fusion treatment appears necessary for dissolution of most of the Si, implying the presence of a refractory compound of Si. For Core 49, fusion is necessary for complete dissolution of Al and Si, but not for the heavier metals. Therefore, as for Core 47, Al and Si probably exist as alumina and silica, not as refractory metal-aluminosilicates.

An examination of the radiochemistry data, particularly for ^{137}Cs , total alpha and total beta, also provides a good comparison. Most of these results show water leach values two orders of magnitude lower than fusion values. For example, the fusion ^{137}Cs data ranges from 560 to 1030 uCi/g, whereas the water leach data ranges from only 5 to 9 uCi/g. This comparison provides good evidence for the presence of a water-insoluble ^{137}Cs compound. This conclusion is supported by tank history, with the very insoluble compound, cesium nickel ferrocyanide, thought to be present. The high ^{137}Cs levels also correspond to high cyanide levels throughout the cores. Likewise, the total alpha and total beta results both show about two orders of magnitude higher fusion results compared to water leach results, implying the presence of water-insoluble

Table 3: Tank 241-C-109 Results Highlighting Differences Between Sample-Prep Treatments

Analyte	Units	Core 47		Core 48		Core 49	
		Fusion or Direct	W/L or Acid	Fusion or Direct	W/L or Acid	Fusion or Direct	W/L or Acid
¹³⁷ Cs by GEA	μCi/g	870 ^a	9 ^c	1030 ^a	9 ^c	560 ^a	5 ^c
Total Alpha	μCi/g	0.99 ^a	0.0048 ^c	0.065 ^a	0.0001 ^c	0.129 ^a	0.0006 ^c
Total Beta	μCi/g	2750 ^a	17 ^c	1300 ^a	9 ^c	2300 ^a	9 ^c
Al by ICP-AES	μg/g	116,800 ^a	72,900 ^d	8,600 ^a	6,400 ^d	126,600 ^a	83,700 ^d
Si by ICP-AES	μg/g	15,800 ^a	1,900 ^d	2,200 ^a	1,300 ^d	2,300 ^a	1,400 ^d
TOC	μg/g	3200 ^b	2300 ^c	3000 ^b	3100 ^c	2500 ^b	2300 ^c

^aby fusion, ^bby direct analysis, ^cby water leach, ^dby acid digestion

compounds containing alpha and beta radionuclides.

In contrast, the TOC data show nearly equivalent results for direct versus water leach for Cores 48 and 49, implying that the TOC in these two cores is water soluble. Core 47 shows somewhat different results, with the direct treatment data being about 1/3 higher than the water leach data. This implies that for Core 47, approximately 1/3 of the present TOC exists as a water-insoluble organic compound.

VI. CONCLUSIONS

The analysis of tank sludge HLMW from the Hanford SST and DST characterization programs provides many unique challenges to the analytical laboratory. Based on experience gained in the ACL during the analyses of many tank core samples, several conclusions can be summarized, as follows:

1. Each of the described analytical techniques have been used successfully, meeting established QA/QC standards, on SST and DST core material. Most of the analytical methods require continuing methods development for this complex and challenging HLMW.
2. Each of the described remote sample preparation methods of caustic fusion, acid digestion, and water leach have been implemented for HLMW, also often requiring continuing methods development.

3. While each of the described analytical methods inherently provides elemental information, the use of a comparative process, comparing results from fusion, acid digestion, and/or water leach sample preparation methods, has been shown to provide useful information on the chemical nature of the compounds present.

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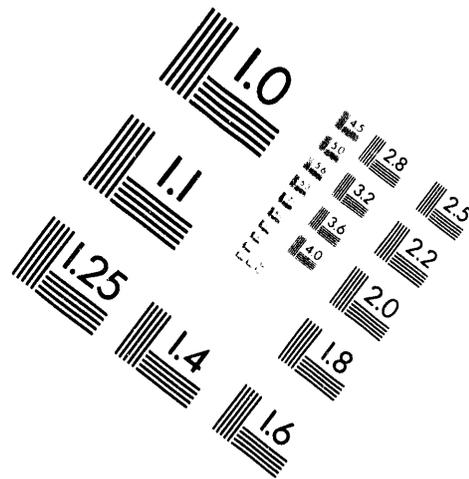
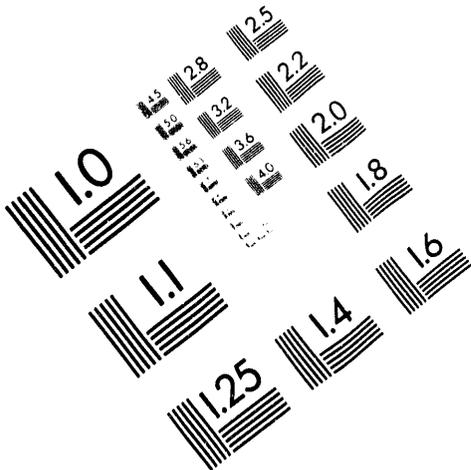
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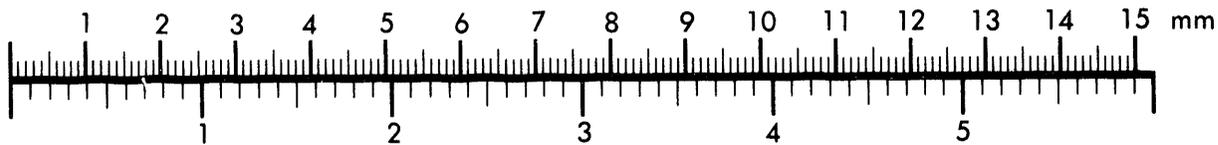
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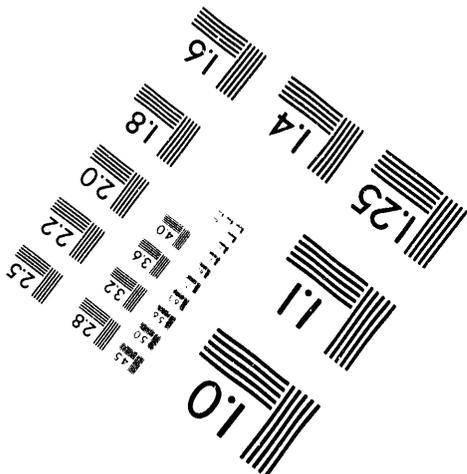
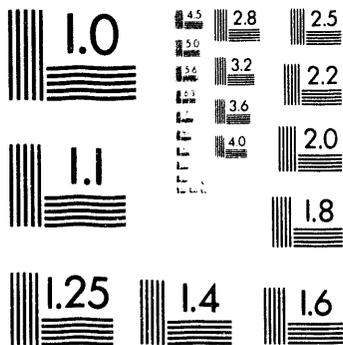
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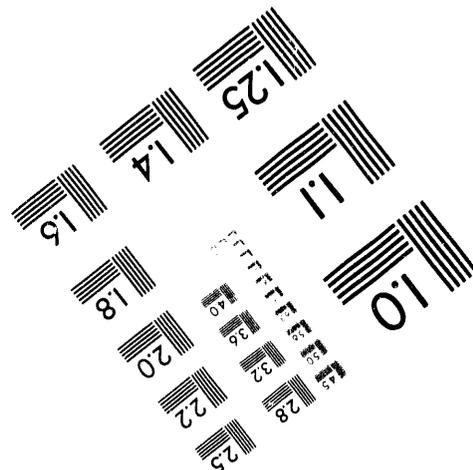
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