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Waste Tank Organic Safety Program

Advanced Organic Analysis and Analytical Methods Development: FY 1995 Progress Report

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Abstract

This report describes the work performed during FY 1995 by Pacific Northwest Laboratory in developing and optimizing analysis techniques for identifying organics present in Hanford waste tanks. The main focus was to provide a means for rapidly obtaining the most useful information concerning the organics present in tank waste, with minimal sample handling and with minimal waste generation. One major focus has been to optimize analytical methods for organic speciation. Select methods, such as atmospheric pressure chemical ionization mass spectrometry and matrix-assisted laser desorption/ionization mass spectrometry, were developed to increase the speciation capabilities, while minimizing sample handling. A capillary electrophoresis method was developed to improve separation capabilities while minimizing additional waste generation. In addition, considerable emphasis has been placed on developing a rapid screening tool, based on Raman and infrared spectroscopy, for determining organic functional group content when complete organic speciation is not required. This capability would allow for a cost-effective means to screen the waste tanks to identify tanks that require more specialized and complete organic speciation to determine tank safety.

Summary

During FY 1995, the Organic Analytical Methods Development task improved on existing analytical methods used to analyze organic compounds in tank waste and further developed new methods that have the potential for improving organic analysis capabilities. The new analytical methods being developed must meet at least one, preferably more, of the following criteria to be considered an improvement over existing techniques and to justify the need for further development:

- minimize sample handling
- provide rapid analysis time
- minimize waste generation
- enhance precision
- identify unknown degradation products
- analyze polymerized and long-chain organic species
- address specific problems of simulant or real-waste analysis.

Atmospheric pressure chemical ionization mass spectrometry is being developed for coupling to separations techniques, such as high-performance liquid chromatography or ion chromatography, for determining unknown degradation products. Ion chromatography, developed under the Flammable Gas Safety Project (Campbell et al. 1995), has proven to be very effective for quantitative analysis of low molecular weight acids in tank waste. Coupling atmospheric pressure chemical ionization mass spectrometry to ion chromatography would provide molecular-weight information from separated components and thus help determine the identity of unknown organic components.

Matrix-assisted laser desorption ionization/time-of-flight mass spectrometry is another analytical technique that should provide information on the presence or absence of organic compounds that are not presently analyzed. This technique has the potential for molecular-weight determination of non-volatile organics such as polymers, long-chain organic acids, and metal-chelate complexes. Current analytical techniques employed do not provide this information. The matrix-assisted laser desorption ionization/time-of-flight mass spectrometry technique would be an ideal quick screening tool for determining the presence of higher molecular weight organics that could potentially be a safety concern in tank-waste samples.

During analytical support efforts, interferences from matrix components and difficulty in extracting dibutyl phosphate (DBP) under conditions sufficient for gas chromatography/mass spectrometry (GC/MS) analysis originally proposed became impractical. Efforts to improve analytical capability for analyzing DBP were directed toward ion-pair chromatography with refractive-index detection and capillary isotachopheresis. Preliminary results are very encouraging with both standard solutions and simulant waste preparations.

During the middle of FY 1995, a redirection of efforts took place at the request of Westinghouse Hanford Company (WHC). More emphasis was placed on functional-group analysis capabilities with reductions in development in other areas of organics analysis. In some cases, functional-group information, instead of complete organic speciation, may be sufficient to determine tank safety from an organics standpoint. Preliminary compound work toward developing a rapid screening tool for organic functional-group content has been initiated. This screening tool is based on Raman and/or infrared spectroscopy as a way of determining C-H content in waste samples.

Organic chemical species analyses were performed by WHC on samples obtained from waste tanks 241-C-102, 241-C-103, and 241-BY-108 to support the resolution of a safety concern regarding the entrainment of organics in waste solids. The Test Plan and sample analyses were a

joint effort of staff from Pacific Northwest Laboratory (PNL) and WHC. The analyses, originally scheduled to be completed by PNL, were transferred to WHC due to temporary closure of the hot cell facilities at PNL. Results from analyses completed to date are summarized here since oversight of analysis was included under this work scope.

Reference

Campbell, J. A., S. A. Clauss, K. E. Grant, V. Hoopes, B. D. Lerner, G. M. Mong, J. Rau, R. Steele, and K. L. Wahl. 1995. *Flammable Gas Safety Program Analytical Methods Development: FY 1995 Progress Report*. Pacific Northwest Laboratory, Richland, Washington.

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Glossary

DBP	dibutyl phosphate
DSC	differential scanning calorimetry
ED3A	ethylenediaminetriacetic acid
EDTA	ethylenediaminetetraacetic acid
FY	fiscal year
GC/MS	gas chromatography/mass spectrometry
GEA	gamma energy analysis
HEDTA	N-(2-hydroxyethyl)ethylenediaminetriacetic acid
ICP	inductively coupled plasma
IR	infrared
MBP	monobutyl phosphate
MS	mass spectrometry
<i>m/z</i>	mass-to-charge ratio
NPH	normal paraffin hydrocarbon
NTA	nitrilotriacetic acid
PNL	Pacific Northwest Laboratory
TBP	tributyl phosphate
TGA	thermogravimetric analysis
TIC	total inorganic carbon
TOC	total organic carbon
UV	ultraviolet
WHC	Westinghouse Hanford Company

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1.0 Introduction

The Analytical Methods Development task was started during FY 1994 as part of the Organic Tanks Safety Project under the direction of Westinghouse Hanford Company (WHC). The work under this task was performed by Pacific Northwest Laboratory^(a) (PNL) for WHC to develop and improve analysis techniques that could be used to quantitatively identify organic species present in tank-waste samples. The beginning of FY 1995 was a continuation of development efforts initiated during FY 1994. During the second half of FY 1995, redirection of the task was initiated by WHC towards more functional group determinations. The task was changed to stress the reduced efforts in new development work and more emphasis on actual waste analysis.

Previous efforts have focused on developing new analytical techniques that may be applicable to tank-waste organic analysis. Originally, emphasis was placed on organic speciation to identify what compounds were actually in the tank waste. Therefore, most of the initial development focused on ways to determine specific organic components in complex inorganic matrices typical of tank waste. Total organic carbon (TOC) accountability is a way of determining the effectiveness of organic speciation efforts. Initial (1993) attempts at analyzing organics in tank waste produced only about 20% TOC accountability. Improvements in the sample preparation and analytical methods resulted in an improvement in TOC accountability to approximately 80 to 90% (Campbell et al. 1994a). Information gained from organic analyses of tank waste (Campbell et al. 1994a) has been used to develop tank-waste simulants used for other research projects related to organic-tanks safety. For example, these simulants were used to study waste-aging processes (Camaioni et al. 1994 and 1995) and organic concentration mechanism (Gerber 1994).

Additional tank samples need to be analyzed to determine the ruggedness of the analytical methods being used for waste analysis. Although efforts to date have been extremely successful in determining organics present in tank samples analyzed, minor adjustments of analytical methods will most likely be required to account for inevitable changes in the sample matrix. Therefore, continuous efforts to improve the robustness of organic-analysis techniques are warranted.

Methods currently used to analyze tank-waste samples for organics include derivatization gas chromatography/mass spectrometry (GC/MS), high-performance liquid chromatography, and liquid chromatography/mass spectrometry (Campbell et al. 1994a and 1994b). While these analysis techniques provide valuable information about the organic components in the waste samples, they are, in general, time-consuming, generate a substantial amount of secondary laboratory waste, and can introduce interferences or artifacts due to the derivatization based side reactions associated with GC/MS procedures. To address these limitations, methods development during FY 1994 focused on identifying and testing alternative analytical methods that may provide the desired results of organic analysis more effectively. The techniques tested during FY 1994 were electrospray ionization mass spectrometry, capillary electrophoresis, supercritical fluid extraction, and Raman spectroscopy (Campbell et al. 1994c). Preliminary results for all of these techniques showed promise for improving organic analysis.

Due to limitations in methods development funding and redirection of emphasis to functional group determinations during FY 1995, electrospray ionization mass spectrometry and supercritical fluid extraction development efforts have been minimal. Work with electrospray ionization mass spectrometry was replaced by atmospheric pressure chemical ionization mass spectrometry, which should apply more directly to the

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analysis of compounds of concern, such as low molecular weight acids. While atmospheric pressure chemical ionization mass spectrometry is not as gentle an MS interface technique as electrospray ionization mass spectrometry, which is important for analyzing large non-volatile molecules or non-covalent complexes such as metal-chelate complexes, atmospheric pressure chemical ionization mass spectrometry is ideally suited for small-molecule analysis and should be more tolerant of matrix components.

Ion chromatography, developed recently under the Flammable Gas Safety Program (Campbell et al. 1995a), has proven very effective for low molecular weight acids analysis. Combining the ion chromatography separation with atmospheric pressure chemical ionization mass spectrometry should allow for easy speciation determination of degradation products observed, but not readily identified, by ion chromatography alone. The atmospheric pressure chemical ionization mass spectrometry technique should provide molecular-weight information on the separated components from ion chromatography with no additional sample preparation required.

In addition to atmospheric pressure chemical ionization mass spectrometry, another new MS technique, matrix-assisted laser desorption/ionization has recently been pursued for determination of large non-volatile molecules, such as surfactants and metal-chelate complexes. The potential advantages of the matrix-assisted laser desorption/ionization technique are quick analysis time, small-volume sample sizes, and minimal sample handling, while providing molecular-weight information. Both atmospheric pressure chemical ionization mass spectrometry and matrix-assisted laser desorption/ionization will be described in more detail along with preliminary results obtained by applying these techniques to organic compounds of interest.

Two separations methods are being pursued to improve capabilities for analyzing and quantitating dibutyl phosphate (DBP) in the presence of large concentrations of nitrate and nitrite. They are ion-pair chromatography with refractive-index detection and capillary isotachophoresis with ultraviolet detection. Capillary isotachophoresis is a form of electrophoresis where separations are performed based on differences in mobility of charged analytes in an electric field. Dibutyl phosphate is a fuel rich organic compound of concern that is present in many waste tanks. It is a safety concern due to its high-enthalpy in waste mixtures. Preliminary results from efforts to find a robust analysis technique for DBP are promising.

Development of a functional-group screening tool based on Raman and infrared spectrometry began near the end of FY 1995. This was complemented by differential scanning calorimetry (DSC) and TOC analyses to obtain a good estimate of the enthalpy of organics present in waste. The goal is to have rapid, cost-effective screening tools to get approximate organic energetics information. When necessary to resolve a safety issue or interpret conflicting data from other characterization efforts, the more expensive complete organic speciation will be performed to gain more detailed information on the organic content of the tanks. This screening-tool development is scheduled to continue during FY 1996 and a report on this development will be prepared in FY 1996. Preliminary results from the early stages of development of this screening tool are encouraging.

Another major effort of this task during FY 1995 was completing a Test Plan for the analysis of waste samples from Tanks 241-C-102, 241-C-103, and 241-BY-108 in support of resolving a safety concern regarding the entrainment of organic solvents and other chemicals in waste solids. The Test Plan was a joint effort of staff from PNL and WHC; analyses were scheduled to be a joint effort as well. Analyses and results obtained to date have been obtained by WHC, with the direction and assistance of PNL. Unknown circumstances at WHC 222-S laboratory prevented samples from being transferred to PNL. Preliminary results and details of the Test Plan have been published {Campbell et al. (1995b)}.

This report will discuss the state of development of organic analysis methods and provide preliminary results from the organic functional group screening development. Specifically, preliminary results from the development of atmospheric pressure chemical ionization mass spectrometry and matrix-assisted laser desorption/ionization/MS for tank waste applications and the use of ion-pair chromatography and capillary isotachopheresis for DBP analysis will be presented. In addition, the analytical procedures used for organic analysis of simulant waste samples to support the waste aging organic safety task (Camaioni et al. 1995) will be discussed.

2.0 Analyses for Determination of Degradation Products and Non-Volatile Organics

Previous organic speciation efforts have focused on the volatile and semi-volatile organics that comprise the majority of the TOC found in the waste tanks. There is, however, a need to be able to verify the existence, or absence, of larger, non-volatile organics, such as long chain organics and surfactants that could be the products of polymerization in the tank waste. Such materials are expected to have high enthalpies and may be invisible to standard persulfate TOC measurements. Recent discoveries with the Waste Aging Studies (Camaioni et al. 1994 and 1995) indicate that a potential may exist for creating larger organic compounds that are not readily identified by the current organic analysis techniques, such as GC/MS, being used on tank-waste samples. Gas chromatography analysis can only be applied to volatile or semi-volatile organics that have been derivatized to enhance volatility. Separations techniques such as liquid chromatography are required to identify non-volatile or thermally labile organic components. Mass spectrometric detection is required to speciate unknown components.

Special interfaces are required to couple liquid chromatography to mass spectrometry (Voyksner 1994). One such interface is atmospheric pressure chemical ionization which transfers organic components from the liquid phase eluent of the liquid chromatograph to the gas phase and into the mass spectrometer with minimal analyte fragmentation or thermal degradation. Once in the gas phase, this interface provides a chemical ionization mechanism to fragment uncharged analyte molecules. Matrix-assisted laser desorption/ionization is another mass spectrometric technique for the analysis of larger non-volatile compounds, such as polymers, without solubilizing them before analysis. This technique is not directly suited to interfacing with liquid chromatography separations. These two mass spectrometry techniques are complementary because of their different ionization mechanisms. The combination of these two mass spectrometric techniques would be very valuable for determining unknown degradation products and for determining semi-volatile and non-volatile components in tank waste samples without the need for sample derivatization. Only minimal screening of these techniques for applicability to tank waste analyses have been completed. These preliminary results are reported here.

2.1 Atmospheric Pressure Chemical Ionization Mass Spectrometry for Identifying Aging Degradation Products

An atmospheric pressure chemical ionization mass spectrometry interface for the JEOL high-resolution MS was acquired and preliminary results for the analysis of low molecular weight organic acids were obtained. This interface is an efficient way for coupling high-performance liquid chromatography to MS to help identify unknown degradation products observed during analysis of waste samples. This interface technique is well suited for typical high-performance liquid chromatography flow rates (e.g., 1 mL/min). A schematic of an atmospheric pressure chemical ionization mass spectrometry source is shown in Figure 2.1. Pneumatic nebulization is used to vaporize the solute and sample flowing from the liquid chromatography pump. A needle held at 3 to 6 kV potential creates a corona discharge, producing solvent reactant ions which subsequently ionize the sample by chemical ionization, primarily by proton-transfer reactions. Heated nitrogen gas flows counter to the vaporized liquid flow and aids in removing excess solvent and clustering from the analyte ions of interest. One potential application of atmospheric pressure chemical ionization mass spectrometry is for the analysis of low molecular weight organic acids and their degradation products in tank-waste samples. A typical negative-ion atmospheric pressure chemical ionization mass spectrum of a standard citric acid solution (Figure 2.2) is dominated by the $M-H^-$ ion at

Figure 2.1. Schematic of Atmospheric Pressure Chemical Ionization

Figure 2.2. Negative Ion Atmospheric Pressure Chemical Ionization of Citric Acid Standard

m/z 191. Selected ion monitoring of the $M-H^-$ ion of citric acid at m/z 191 can be used to selectively identify citric acid in a complex mixture. During a selected ion monitoring experiment, the instrument is set up to detect ions only at certain selected m/z values. The selected ion monitoring technique is a MS tool used to select an m/z value for improved sensitivity when the m/z values of ions representative of targeted analytes are known. A preliminary selected ion monitoring experiment of m/z 191 of citric acid with injections of

various concentrations and quantities of citric acid is shown in Figure 2.3. The injection volumes and concentrations are indicated. Under these preliminary conditions, a detection limit of 1 μg of citric acid standard was obtained. This detection limit could be improved with increased optimization of the interface instrument conditions for the atmospheric pressure chemical ionization mass spectrometry experiment. The major advantage to the potential for coupling this MS interface to liquid chromatography separations is the ability to gain molecular-weight information to help identify unknown degradation products of the organic acids and other organics from waste-aging processes.

Figure 2.3. Selected Ion Monitoring of Citric Acid by Atmospheric Pressure Chemical Ionization Mass Spectrometry

2.2 Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry for Non-Volatile Organics

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry is a technique used for obtaining molecular-weight information of non-volatile, thermally labile compounds. The matrix-assisted laser desorption ionization technique desorbs and ionizes these thermally labile compounds followed by time-of-flight mass spectrometry analysis to determine molecular weights of the analyte ions based on their mass-to-charge (m/z) ratios. The samples analyzed by matrix-assisted laser desorption/ionization are mixed uniformly with a matrix substance and applied to a metal slide in microliter amounts. The matrix and analyte solutions are allowed to dry and form uniform crystals. The sample slide is inserted in the vacuum system of the MS, and a laser beam is directed at the sample spot to volatilize the sample. A brief pulse (3 ns) of nitrogen laser light ($\lambda = 337 \text{ nm}$) is directed onto a small target area (about 100 μm in diameter) of the sample/matrix deposited on the sample slide. The matrix rapidly absorbs heat energy from irradiation, inducing vaporization and ionization of itself and the analyte. Common matrices are sinapinic acid (3,5-dimethoxy-4-hydroxycinnamic acid) and 2,5-dihydroxybenzoic acid. When the laser light contacts the matrix and sample, there is localized and rapid (nanoseconds) heating of the matrix and sample. Under

rapid heating conditions, organic compounds favor vaporization reactions over decomposition reactions (Beuler et al. 1972). Matrix-assisted laser desorption/ionization has been shown to be a very useful mass spectrometry ionization technique for biomolecules (Hillenkamp et al. 1991), polymers (Bahr et al. 1992) and other organic molecules (Ligard and Duncan 1995).

Preliminary examples of the capability of matrix-assisted laser desorption/ionization for a variety of organic compounds are shown in Figures 2.4, 2.5, and 2.6. The matrix-assisted laser desorption/ionization technique characteristically provides molecular-weight information for both small and large molecules. While matrix ions are always observed, the $(M+H)^+$ ion dominates the analyte signal in the positive ion mode, and the $(M-H)^-$ ion dominates in the negative ion mode, where M is the intact analyte molecule. Figure 2.4 shows the $(M+H)^+$ ion of histidine (molecular weight = 156) at m/z 157. The matrix ions at m/z 208 and 226 are from the sinapinic acid matrix. Matrix-assisted laser desorption ionization analyses of larger analytes such as the peptide Gramicidin S and polymer Nylon 6 are also readily obtainable. The Gramicidin S spectrum (Figure 2.5) contains the matrix ions in the low m/z range and the $(M+H)^+$ ion in the higher m/z range at m/z 1145. The matrix-assisted laser desorption/ionization polymer spectrum (Figure 2.6) is very representative of the polymer distribution where each ion represents an $(M+H)^+$ or $(M+\text{alkali metal})^+$ ion of the polymer repeating unit. Nylon 6 is a polymer, with an average molecular weight of 2,000, containing a repeating unit of 113 with the formula

Figure 2.4 Positive Ion Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrum of Histidine Using Sinapinic Acid Matrix

The matrix-assisted laser desorption/ionization technique has many potential advantages for analyzing tank waste. It is a very rapid analysis technique (minutes) and thus would be an ideal rapid screening tool for determining non-volatile organics in tank waste if high salt content does not interfere with the analyses. In addition, this technique works best at relatively low analyte concentrations (micromolar), and therefore dilutions can be made to reduce radioactivity levels before sample handling. This technique

would be very simple to implement for radioactive sample analysis. A small drop of sample is deposited on a stainless steel probe, the solvent is dried, and then the probe is inserted onto a probe tip holder for insertion into the vacuum system by remote operation (computer controlled). If sample contamination levels are too high, the benchtop instrument design would be compatible with glovebox or fume hood operations. Efforts are in progress to look at chelators, long chain organic acids, and other nonvolatile species that could be present in tank waste. Preliminary results obtained from Hewlett-Packard during a demonstration of their matrix-assisted laser desorption/ionization instrument indicated that matrix-assisted laser desorption/ionization could be used to identify chelators and other non-volatile compounds. Further studies are being conducted to determine the effects from other sample components, such as nitrates, on these analyses.

Figure 2.5. Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrum of Gramicidin S Using Sinapinic Acid Matrix

Figure 2.6. Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrum of Nylon 6 Polymer Using Sinapinic Acid Matrix

3.0. Development of More Efficient and Effective Analyses for Dibutyl and Monobutyl Phosphate

The organic compounds of most concern to waste tank safety are those with high enthalpy, such as DBP. Dibutyl phosphate has been a problematic organic analyte during analyses of the simulated waste samples as part of the Organic Tanks Safety Waste Aging Task. Many analytical techniques work well for analyzing the standard DBP and monobutyl phosphate (MBP) compounds. However, the complex matrix that is characteristic of tank wastes has proven to be a major challenge for those more traditional organic-analysis techniques. Literature searches revealed two potential candidates for analysis of DBP in nitrate/nitrite containing solutions. One method is based on ion-pair chromatography with refractive index detection (Muller et al. 1985), and the other is based on isotachopheresis (form of capillary electrophoresis) with conductivity detection (Bocek et al. 1980). Preliminary results from using these two techniques for DBP analysis are very encouraging.

3.1 Ion-Pair Chromatography of Dibutyl Phosphate

One method being developed for the detection of DBP in simulant waste mixtures is ion-pair chromatography with refractive index detection (Muller et al. 1985). The ion-pairing agent used is tetrahexylammonium bromide. Details of the experimental conditions are provided in Appendix A. The ion-pair chromatography of a standard solution containing MBP and DBP is shown in Figure 3.1. A good

Figure 3.1. Ion-Pair Chromatography of MBP and DBP Standards with Refractive Index Detection

separation of DBP and MBP is obtained in less than 15 min. The assay has been shown to be linear for standard samples over the working range of DBP in the simulant waste samples (Figure 3.2). Similar linearity was obtained for MBP response in standard solutions (data not shown). Preliminary results obtained with inorganic simulant waste samples spiked with DBP and MBP were very encouraging (Figure 3.3). The DBP could be detected easily and was well separated from peaks due to other waste components. The MBP was frequently lost due to chromatographic interference from co-eluting species, undoubtedly caused by large quantities of nitrates and other salts in the waste matrix. During early attempts to analyze DBP in simulant waste matrices, the retention time for DBP would decrease, perhaps indicating that column sites were being increasingly occupied by other waste species. Detection of a DBP peak and a small MBP peak were obtained in simulated waste containing inorganic and organic components.

Figure 3.2. Calibration Curve for Dibutyl Phosphate in Standard Solutions

Muller et al. (1985) suggested acidifying (pH ~ 2.5) the aqueous-phase solution before analysis. Our initial efforts suggest that acidification results in loss of DBP and MBP. This seems reasonable since an acidic medium would favor MBP to remain as H_2MBP and DBP to occur as $HDBP$, thus making ion pairing with tetrahexylammonium bromide to give neutral species less effective. Therefore, for the remainder of this study, the samples have remained basic.

As a way of removing the waste-sample matrix and improving the baseline stability, work was undertaken to try the preconcentration column procedure described by Muller et al. (1985). The Muller procedure utilizes a preconcentration column to eliminate uranium, plutonium, fission products, nitric, phosphoric and hydrofluoric acids, butanol, hydrazine, etc. before the analysis of DBP and tributyl

Figure 3.3. Ion-Pair Chromatography of Inorganic Simulant Spiked with DBP and MBP

phosphate (TBP). A weaker mobile phase was used to flush out the impurities while retaining DBP and TBP in the pre-column. Then a stronger eluting solvent was used to wash the DBP and TBP onto the analytical column. A similar procedure was followed in these studies for DBP and MBP analysis. The preconcentration column (see Appendix A) was flushed with 1.00 mL of preconcentration mobile phase (35% methanol, 65% water, and 2×10^{-3} M tetrahexylammonium bromide) between each injection. Simulant waste sample (20 μ L) was injected onto this preconcentration column. Then the other waste components were flushed through the preconcentration column and into waste with 1.00 mL of preconcentration mobile phase. Finally, the analytes were flushed off the preconcentration column and onto the analytical column by means of the stronger eluting mobile phase consisting of the 73% methanol, 27% water, and 4.0×10^{-3} M tetrahexylammonium bromide. Adding this preconcentration clean-up step resulted in a much cleaner, more reproducible chromatogram for the simulant waste samples. Figure 3.4 shows the ion-pair chromatography with this preconcentration step for simulant waste spiked with MBP and DBP. The 94C-SIM-101-SY simulant prepared by W. Samuels for the waste aging studies was used (Camaioni et al.

1994). The main interference with the baseline near the elution of MBP was no longer a problem. In addition, the retention times of MBP and DBP stabilized for replicate simulant waste analysis runs at approximately 8 min for MBP and 11 min for DBP. Recovery studies are in progress to determine the quantitation capabilities of this technique.

Figure 3.4. Ion-Pair Chromatography with Preconcentration Clean-up of a Simulant Waste Sample Spiked with DBP and MBP

3.2 Capillary Electrophoresis of Dibutyl Phosphate

Capillary electrophoresis is a process for separating charged molecules based on their movement through a solution under an applied electric field. It is characterized by small sample volumes (less than μL injection volumes), narrow-bore bare fused-silica capillaries (typically 25 to 75 μm inner diameter), small

buffer volume (1 mL), and short analysis times (< 30 min). The instrumentation requirements are relatively simple, and thus transfer of this technique to radiological-sample analysis should be straightforward, once separations development is complete. To perform capillary electrophoresis, both ends of approximately 1 m of bare fused-silica capillary are placed in buffer reservoirs. The buffer must be at the proper pH and provide sufficient conductivity to allow current to pass through the column, which is necessary for the separation. The reservoirs also contain the electrodes necessary to complete the electrical circuit. Sample injection is made by placing one end of the capillary momentarily into a sample reservoir and applying either voltage, external pressure at the inlet, or vacuum at the outlet to inject a small volume (nL) of the sample into the capillary. The capillary end is returned to the buffer vial, and an electric field is applied across the length of the capillary to induce the separation. Several different types of detection mechanisms can be employed. A transparent window can be made in the silica capillary wall for optical-based detection methods, such as ultraviolet (UV). Alternatively, the end of the capillary can be placed into the inlet of a detector, such as into a flowing stream of an electrospray ionization source for MS detection.

Capillary isotachopheresis is a form of capillary electrophoresis where moving boundaries are the mode of separation. Two buffer systems, a leading electrolyte and a trailing electrolyte, are used in capillary isotachopheresis to create separate zones that all move at the same velocity. For anionic capillary isotachopheresis, analyte zones are sandwiched between a leading electrolyte that contains an anion with an effective mobility higher than the solutes and a trailing electrolyte that contains an anion with a lower mobility than the solutes. When the electric field is applied, the anions start to migrate towards the anode. The leading anion, with the highest mobility by design, moves fastest, followed by the anion with the next highest mobility and so on. In capillary isotachopheresis, the analyte anions migrate in discrete zones in close contact with each other with the same velocity. Unlike capillary electrophoresis, only anions or cations (not both) can be separated during a single analysis with capillary isotachopheresis. Comparison of a separation by capillary electrophoresis and by capillary isotachopheresis is shown in Figure 3.5. Capillary zone electrophoresis typically produces very narrow peaks whose height represents concentration. In contrast, analyte plugs whose width represents concentration are typically produced by capillary isotachopheresis.

Figure 3.5 Comparison of Capillary Zone Electrophoresis and Capillary Isotachopheresis

The capillary isotachophoresis technique has previously been applied to the quantitation of DBP and MBP, from relatively clean solutions, using conductivity detection (Bocek et al. 1980). The goal of our efforts is to adapt this method to more complex solutions with UV detection, since conductivity detection is not currently available for the capillary electrophoresis instrument in use for these studies. Preliminary results indicate some difficulty in using UV detection for this separation scheme. A capillary isotachophoresis separation of a mixed MBP and DBP solution is shown in Figure 3.6. This analysis was performed in the reverse anionic form where the trailing electrolyte is placed in the capillary, followed by the sample plug and then the leading electrolyte. A positive voltage is placed on the inlet side. In this mode of capillary isotachophoresis, the analyte ions with lower mobility will elute first followed by the faster moving analyte anions. The trailing electrolyte is 10 mM morpholinoethanesulphonic acid at pH 6 and the leading electrolyte is 10 mM HCl + histidine at pH 6. The sample mixture of DBP and MBP with concentrations ranging from 1 mM to 10 mM were analyzed. A preliminary calibration curve, shown in Figure 3.7, suggests the capability of using capillary isotachophoresis for quantitation purposes. The analytes appear as plugs rather than sharp peaks like more traditional separations. The width of the analyte plug is related to analyte concentration, for a constant injection volume and constant electrolyte concentrations. Comparison of plug widths from DBP and MBP in a variety of known concentration solutions gave the results plotted in Figure 3.7. While preliminary results are encouraging, further studies need to be conducted to determine the robustness of this technique to simulant tank waste samples.

Figure 3.6. Reverse Anionic Capillary Isotachophoresis Separation of DBP and MBP. Trailing Electrolyte: MES, pH 6. Leading electrolyte: HCl + Histidine, pH 6.

Figure 3.7. Concentration vs. Plug Width for Capillary Isotachophoresis Analysis of DBP and MBP Standards
Injection Volume = 0.2 μ L

4.0 Mid-Year Redirection to Functional-Group Analysis

The direction of the work scope was changed mid-year to focus on development of a rapid organic functional group screening tool based on Raman and infrared (IR) spectroscopy to be a complement to the organic speciation capabilities that have been developed (Campbell et al. 1994a, 1994b, 1994c, and 1995a). This screening tool could also be used when complete speciation is not required to provide information relative to tank safety. Proton nuclear magnetic resonance (NMR) spectroscopy is a very powerful functional group technique. However, safety concerns associated with performing nuclear magnetic resonance experiments on radioactive tank waste samples makes it improbable. In addition, sensitivity of NMR in typical tank waste samples may be a limitation. Alternatively, infrared spectroscopy, another functional group technique, has been applied to the analysis of radioactive tank waste samples (Bryan et al. 1995). Infrared and Raman spectroscopy are complementary spectroscopic techniques that are ideally suited for functional group characterization because of the well-established spectral/structure correlations. More detailed explanation of Raman and infrared spectroscopy for functional group analysis was provided in the Analytical Methods Development FY1994 Progress Report (Campbell et al. 1994c). Raman and IR spectroscopy are being developed for functional group determination in combination with DSC analysis to relate functional group analysis and C-H content to sample energetics.

The goal is to develop an integrated approach to determine organic functionality and energetics of waste tank samples. Total organic carbon analysis can give an estimate of the total amount of organics present and functional group analysis (by Raman and/or IR) can provide information about the enthalpy of the organics present in the sample. Camaioni and Samuels have shown there is a correlation between the number of C-H bonds in a molecule and the energy released on oxidation for a wide range of organic compounds typically found in tank waste^(a). Therefore, quantitating the amount of C-H in a given sample should provide information on the energetics of the sample.

With minimal additional analysis cost, the C-O and other carbon containing functional groups can be determined simultaneously with C-H determinations and provide verification of the sample composition. While the number of C-O bonds does not have as clear a relation to energy released upon oxidation, it can provide valuable indirect information on sample enthalpy. For example, if it is determined that 95% of the TOC can be accounted for by C-O bonds, then at most only 5% of the TOC could be C-H. In addition, if a high TOC value is obtained but only a small amount of C-H is determined by Raman and/or IR, determining the other carbon containing functional groups can help verify the high TOC and low C-H numbers.

Several organic species have been identified as of particular interest to the Organic Tank Safety Program. The compounds of interest contain various functional groups that are IR and Raman active and can be semi-quantitatively analyzed by these spectral methods. A list of these compounds is summarized in Table 4.1. The main organic functional groups present are carboxylate and alkyl. These organic compounds will be targeted in the studies under this task. Strategies of Raman and IR spectroscopy and DSC are outlined along with initial results obtained during the early stages of development.

4.1 Raman Spectroscopy

The aim of this work is to develop Raman as a possible means to characterize organic functional groups in tank-waste samples of safety concern. This could potentially yield cost savings and accelerate tank-sample analysis. The initial development plan has three steps. First, Raman spectra of organic compounds expected to be present in tank waste were obtained to develop a spectral library. Second,

(a) D. M. Camaioni, and W. D. Samuels. Task 02-Waste Aging Studies. PNL Waste Tank Organic Safety Project-February, 1995 Monthly Status Report. Richard T. Hallen, Manager, PNL Waste Tank Organic Safety Project, Richland, Washington.

Table 4.1. Model Compounds to be Used for Functional Group Analysis

Organic Compounds for Testing	Functional Groups Present within Target Compound		
	Carboxylate (-CO ₂)	Alkyl (C-H)	Ketone (R-CO-R)
Na ₄ EDTA	√	√	
Na ₃ HEDTA	√	√	
Na ₃ NTA	√	√	
Na ₃ ED3A	√	√	
Sodium glycolate	√	√	
Trisodium citrate	√	√	
Sodium acetate	√	√	
Sodium formate	√		
Sodium succinate	√	√	
Sodium oxalate	√		
Tributyl phosphate		√	
Sodium dibutyl phosphate		√	
Normal paraffin hydrocarbons		√	
Sodium dodecanoate	√	√	
Methyl isobutyl ketone (Hexone)		√	√
Sodium isobutyrate, Sodium butyrate	√	√	

quantitative capabilities of Raman spectrometry for determining organic content (e.g., C-H) in the presence of a complex inorganic matrix were developed. Third, an investigation of interference effects, if any, that could occur due to the complex inorganic matrix was attempted. Preliminary efforts focussed on developing a library of Raman spectra of organic compounds of interest and initial attempts at determining quantitation limits.

The Raman instrument used for these studies is a Fourier transform Raman instrument from Nicolet Instruments with a laser operating at 1064 nm. This long wavelength laser, when used in Fourier transform Raman instruments, is considered to eliminate sample fluorescence, which interferes with analysis. This instrument is also equipped with a fiber optic interface for remote sampling purposes. Thus sampling can be performed remote from the primary optic bench, ideal for analyzing radiological samples.

The first step of compiling a database of Raman spectra of organic compounds expected in the waste tanks has been completed. The database consists of Raman spectra of the sodium salt and acid forms of the chemicals listed in Table 4.1. The spectra of several of the chelator sodium salts were compared to the acid forms. It is interesting to note that the spectra of the sodium forms were generally ten times less intense than the spectra of the acid forms, diminishing the sensitivity of the technique for analysis of carboxylate salts. This could be due to the laser penetration depth, or it could be a real loss of Raman response. This intensity difference suggests that a necessary step of any analytical procedure will be to ensure that the chelators are in a predictable form, either acid or salt. In addition, the response of the section of the Raman spectrum that

arises from the C-H bonds is being evaluated. To date, over 200 spectra are currently in the functional group Raman library. In the near future, these data will be assembled to derive spectral feature/functional-group correlations.

As with any analytical technique, it is necessary to determine the response of an individual component to the analytical technique in addition to the potential interference of the sample matrix. In Raman spectroscopy, the sample matrix affects the volume of the sample that is illuminated and the Raman shifted radiation that escapes to the detector. For much of the tank waste, the matrix is inorganic saltcake consisting of nitrates, nitrites, and hydroxides. To determine the possible effects of this matrix on Raman analysis, a simulated matrix was synthesized which consisted of inorganic components typically found in tank samples in concentrations greater than 5% by weight. A dried sample of the resulting grey material was characterized by Raman spectroscopy. The Raman spectrum of this inorganic matrix sample is shown in Figure 4.1. As can be seen, other than the nitrate band observed at 1000 cm^{-1} , the spectrum is relatively featureless. The majority of the organic-functional-group information of interest will have a Raman shift in the $3400\text{-}2000\text{ cm}^{-1}$ region where clearly no interference occurs from the inorganic matrix components. This is a promising result suggesting that the matrix salt components will cause minimal direct spectral interference during organic analysis by Raman spectroscopy.

Figure 4.1. Raman Spectrum of a Simulated Inorganic Matrix

It is anticipated that many of the actual tank-waste samples received will contain at least 30% water by weight. Water can be problematic when using the 1064-nm laser wavelength, used by the Raman instrument in these studies, because the Raman-shifted radiation can be absorbed by a near-IR water overtone band. This problem was examined by characterizing several ethylenediaminetetraacetic acid (EDTA)/water samples where the water content ranged up to 30% by weight. It was found that the samples containing a small amount of water had spectra similar to the one from a dry sample. When the EDTA sample water content reached approximately 10% by weight, however, the samples apparently decomposed during Raman analysis. It is assumed that heating was responsible for the decomposition, although this is extremely surprising since the melting point of EDTA is approximately 250°C (decomposition is listed as occurring at this temperature). Because the dry and lower water content samples did not decompose, this level of heating can only be accounted for by the water in the sample self-absorbing the radiation. This problem may be minimized by spinning the sample. When the sample is spun, the laser only illuminates a small section of the sample at a given time. Spinning minimizes the heating of the sample by minimizing the time any one portion of the sample is illuminated. This approach is being explored by using a step motor to rotate the sample. One potential problem could be irregularities in the sample surface that cause changes in the detected Raman signal. Depending on the relative rates of sample spinning versus the frequency of data collection, a possible slow signal drift may occur in the interferogram. The use of a step motor will allow the sample spinning to be coordinated with the movement of the interferometer. This may minimize spectral noise caused by irregularities in the sample surface.

Another issue that needs to be addressed during development of the Raman technique for functional group analysis is sensitivity. One of the concerns about Raman is that the volume illuminated by the laser can be affected by parameters such as sample particle size and moisture content. Therefore, the sample matrix must be either controlled or eliminated to remove errors caused by sample matrix differences. One way to do this is to dissolve the sample in a convenient solvent like water. To examine this possibility, several basic solutions of EDTA and citric acid between 1% and 5% w/w were characterized by Fourier transform-Raman. Preliminary results indicated that no organic materials were detected below 4% w/w. To increase sensitivity, the technique of surface enhanced Raman spectroscopy is being evaluated. Surface enhanced Raman spectroscopy is a relatively recent development that increases the Raman response of the analytes. The use of surface enhanced Raman spectroscopy has already been evaluated for a number of compounds (e.g., Wentrup-Byrne et al. 1993). The surface enhanced Raman spectroscopy technique is known to increase Raman sensitivities by several orders of magnitude. The surface enhanced Raman spectroscopy technique requires that metal particles be intermixed with the sample. The theory of surface enhanced Raman spectroscopy is still being explored. Currently, two possible explanations are accepted for the surface enhanced Raman spectroscopy phenomena. In the first, it is thought that the illumination of the metal particles results in an enhancement of the electromagnetic field that is ultimately responsible for the Raman effect. The other possible explanation is that the analyte is absorbed onto the metal surface, which enhances the polarizability of the analyte by increasing the polarizability (Kiefer 1995).

Silver is typically used for surface enhanced Raman spectroscopy, although gold and copper have also been reported as being suitable. The silver can be on the surface of a glass slide, on an electrode surface, on a polymer support, or simply dispersed as a colloid in solution. It is thought that the silver transfers laser energy to the absorbed species, resulting in sensitivities that are on the order of millimolar or lower. The surface enhanced Raman spectroscopy technique was initially evaluated using EDTA tetrasodium salt as a model analyte. The EDTA was mixed with a colloidal solution of silver prepared by reducing silver nitrate with citric acid. Preparing the sample for surface enhanced Raman spectroscopy analysis is simple. An aliquot of the EDTA solution is mixed with an aliquot of the silver colloid solution and allowed to stand for at least 12 h. The sample was characterized by Raman spectroscopy. In this instance, a portion of the silver/EDTA sample solution was removed and placed in a small glass tube before analysis. Several solutions of EDTA were characterized in concentrations ranging from 0.2 M to 0.00032 M (approximately 6% wt to

0.01% wt or 2% TOC to 0.004% TOC, respectively). Using the surface enhanced Raman spectroscopy technique, it was found that indications of EDTA were readily visible in the spectrum to a concentration of 0.00032 M. Figure 4.2 shows a comparison of Fourier transform Raman of a 0.2 M solution of EDTA (top) compared to surface enhanced Raman spectroscopy of a 0.00032 M solution of EDTA (bottom). The enhanced sensitivity of EDTA detection with surface enhanced Raman spectroscopy is very promising for quantitation capabilities. The detection limits obtained with surface enhanced Raman spectroscopy are much lower than that required for addressing a safety issue if the success of this technique shown with EDTA is universal for other organic compounds.

Figure 4.2. Surface Enhanced Raman Spectroscopy of a 0.00032 M Solution of EDTA (bottom) Compared to a Raman Spectrum of a 0.2 M EDTA Solution

4.2 Infrared Spectroscopy

Infrared analysis is able to measure the contribution of organic carbon from each organic functionality present within the waste solution. For example, the fraction of the total wt% of carbon in the form of carboxylate (COO^-) within a sample can be assessed by the total measured absorbance within the region of the IR spectrum corresponding to the C-O stretching frequency (1800 cm^{-1}) of the carboxylic moiety. Infrared spectral analysis will be used to measure the concentration of each functionality present within selected organic waste simulants.

To illustrate the ability of infrared to detect the carboxylate functionality in the model compound EDTA, we have measured the infrared spectra of solutions of the sodium salt of this compound using an attenuated total reflectance infrared sample cell. The spectrum is displayed in Figure 4.3. The asymmetric stretch and symmetric stretch of this functional group is observed in the 1650 to 1540 cm^{-1} and 1450 to 1360

cm^{-1} regions, respectively (Lin-Vien et al. 1991). Either of these bands is suitable for quantitative measurement using standard Beer's Law techniques. Figure 4.4 shows the linear dependence of these two bands as a function of increasing concentration of EDTA added to solution.

Figure 4.3. Infrared Spectrum of EDTA in Aqueous Solution Showing the Carboxylate Region. The concentration of EDTA is 10 wt% as the sodium salt.

The model compounds listed in Table 4.1 will be used for additional experiments. The response of the model compounds listed for each functional group will be compared. It is expected that the extinction coefficient of the functional groups on the various model compounds will be similar. This will allow for the semi-quantitative analysis of waste materials containing unknown quantities of various organics with these organic functionalities on the basis of weight % carboxylate, hydrocarbons, and ketones.

4.3 Energetics Analyses of Surrogate Wastes

To help link the Raman and IR functional group analyses to energetics of Hanford wastes, the energetics of reactions of sodium nitrate with selected organics are being measured (see Table 4.1). DSC is used to investigate the correlation between reaction energetics and the ratios of hydrogen to carbon (H:C) and oxygen to carbon (O:C). In general, as the ratio of H:C increases, the maximum reaction enthalpy is predicted to increase. However, as the ratio of O:C increases, the maximum reaction enthalpy is predicted to decrease.

The reaction enthalpies are measured for 6 mass % TOC mixtures of sodium nitrate and the organics sodium formate, sodium oxalate, sodium tartrate, sodium succinate, sodium isobutyrate, sodium laurate, sodium glycolate, sodium di-2-ethylhexyl phosphate, and sodium glyoxylate. The mixtures have been prepared by mixing the requisite amounts of the ingredients, adding sufficient water to prepare a low water content slurry, air drying at room temperature, grinding with a mortar and pestle to <100 mesh, and vacuum

Figure 4.4 Peak Area of the Carboxylate Asymmetric and Symmetric Bands Versus Concentration of EDTA in Aqueous Solution. The concentration of EDTA is measured as the sodium salt.

drying at 30°C to a constant mass. In addition, the energetics obtained previously for comparable mixtures of sodium acetate, sodium citrate, sodium EDTA, or sodium HEDTA will be added to the data set for the correlation analysis.

Though other organics such as TBP and normal paraffin hydrocarbons (NPH) were present in organic-bearing waste streams, past studies of mixtures of nitrate and/or nitrite with TBP and/or NPH using the DSC and other thermoanalytical methods found little or no reaction between the oxidant and the organic. Since no reaction was observed using DSC, neither TBP nor the volatile hydrocarbons present in NPH are included in this study.

Differential scanning calorimetry analyses of several organic components typically found in tank waste have begun. Preliminary results indicate that the organics exhibit different temperatures at which the reaction is initiated. More analyses are in progress to verify and explain the differences to provide a general relationship between sample energetics and organic functional groups present. Work will continue to help relate functional group analysis by IR and Raman spectroscopy with sample energetics.

4.4 Saltcake Washing Studies

There has been some debate as to whether grab samples taken from the top layer or salt-well of the waste tanks can be analyzed to provide qualitative and quantitative information about the organics present in the waste tanks. Grab sampling of the waste tanks is much cheaper than the alternative auger and core sampling of the waste tanks. Therefore, it would be very cost-effective to determine if sufficient information

can be obtained from grab samples concerning the safety of the tanks due to organic components present or absent. Therefore, a saltcake simulant was chosen to study the correlation between organic content in a grab sample versus what could be present in the actual saltcake of a tank.

Considerable work has been performed by S. Barney of WHC to understand the solubilities of organic compounds in simulant solutions resembling Hanford waste tank supernate solutions (Barney 1994). The solubilities of sodium formate, citrate, EDTA and NTA in simulant tank supernate solutions were in the molar range. It was speculated that these high solubilities would prevent these organic compounds from existing as solids in the saltcake layers of the waste tanks.

A simple experiment was designed to determine the amount of organics partitioning from a tank simulant saltcake phase to the aqueous phase saturated with sodium nitrate. Saltcake spiked with organics was mixed with aqueous concentrated sodium nitrate. Adjustment of the pH (to alkaline) was made periodically. Previous experiments have shown that equilibrium of similar experiments have taken approximately 48 h. The aqueous phase was analyzed for TOC, high-enthalpy organics (tributyl phosphate and dodecane), and organic acids (citric acid, acetic acid, and EDTA). Results from these analyses can be used to estimate the amount of organics partitioning between the solid phase and aqueous phase. Due to the limited scope of this study, only one saltcake simulant preparation and one set of variables was chosen to provide preliminary information on whether grab samples would be sufficient for tank waste organic analysis.

The saltcake was prepared by saturating a 5 M sodium hydroxide, 2M sodium nitrite, and 2M sodium aluminate aqueous solution with sodium nitrate at 90°C to 100°C (Strachan 1975). This solution was cooled to 50°C with constant agitation for 24 h. The resulting mixture was cooled to ambient temperature. The pH of the solution was checked periodically to keep it at a constant value (pH 10 to 11) using NaOH. Tetrasodium EDTA, sodium citrate, sodium acetate, tributyl phosphate, and dodecane, were added to the solution, after it was brought to room temperature, so that their final concentrations were each 1 mM in the saltcake. These organics were chosen to represent the major classes of organic compounds found in the waste tanks; chelators, low molecular weight organic acids, butyl phosphates, and NPH.

The saltcake was washed with three 20 mL aliquots of a saturated sodium nitrate water solution. The aqueous phase filtrate was analyzed for total organic carbon (TOC), high-enthalpy organics (tributyl phosphate and dodecane), and organic acids (citric acid, acetic acid, EDTA). Results from these analyses were used to determine the amount of organics partitioning from the solid phase to the aqueous phase. The moisture content of the saltcake was also determined by drying a small portion of the synthetic saltcake. The analyses and results are summarized below. More details of the experimental procedure, errors of analysis, and results are provided in Appendix A.

Organic analysis of the sodium nitrate filtrate solution provided very interesting, but not surprising, results. These results are summarized in Table 4.2. Ion chromatography was used to analyze for citrate and acetate anions. The amount of acetate and citrate detected in the filtrate solution represented 85% of sodium acetate and 119% of sodium citrate originally added to the saltcake. Essentially all of these two organic acids, originally added to the saltcake, were found in the filtrate solution. The EDTA concentration in the filtrate was determined by ion-pair chromatography using an EDTA anion complexed with copper by employing an excess of 0.05M copper sulfate. Replicate analyses indicated that approximately 50% of the EDTA originally added to the saltcake was found in the sodium nitrate filtrate solution. The concentration of high-enthalpy semi-volatile organics, TBP and dodecane, was determined in the saltcake washing filtrate by using GC-MS. TBP and dodecane were extracted from the aqueous layer using dichloromethane. The extracted solutions were injected along with an internal standard in a GC-MS. Theoretical concentration of semi-volatile organics was calculated by assuming that all the spiked organic is transferred to the liquid

phase when the saltcake is washed with a saturated solution of sodium nitrate. The approximate 10% recovery, shown in Table 4.2, indicates that TBP and NPH did not get transferred efficiently to the aqueous phase from the saltcake.

Table 4.2 Results from Organic Analysis of Filtrate from Saltcake Washing

Analysis	% Found in Filtrate
Tetrasodium EDTA	45
Sodium Acetate	86
Sodium Citrate	119
Tributylphosphate	9
Dodecane	10
Calculated total organic carbon	0.98
Experimental total organic carbon	0.4 ^(a) , 0.65 ^(b)

(a) Hot persulfate wet oxidation method

(b) Dohrman analyzer UV-catalyzed persulfate oxidation method

Total organic carbon analyses of the organic containing filtrate produced questionable results. Several methods were attempted to obtain reasonable TOC numbers for the analysis of this filtrate solution. Due to the complex matrix, no two methods gave consistent results. The hot persulfate wet oxidation method gave approximately 0.40% TOC in the saltcake washing filtrate. The persulfate oxidation method, however, is known to give poor recoveries for some organics, such as NPH (Baldwin 1994). On the other hand, the Dohrmann analyzer UV-catalyzed persulfate oxidation method gave approximately 0.65% TOC in the saltcake washing filtrate. Two other methods, the normal furnace method and the modified dichromate method, were also used, however, TOC results were not available due to poor recovery. Total organic carbon was also calculated based on the results from the organic analyses and was found to be 0.98%. Calculations of the calculated total organic carbon are provided in Appendix A. More TOC can be accounted for based on organic analyses than can be determined by experimental TOC measurements. Part of the observed discrepancy could be due to the dodecane component in the filtrate and the lack of efficient oxidation for hydrocarbons in wet oxidation persulfate TOC measurements.

The results suggest that the highly water soluble organics, such as citrate and acetate, can be washed out of the saltcake layer to a high extent. However, the more highly energetic and less water soluble dodecane and TBP are less likely to be filtered out of the saltcake with an aqueous washing. While this experiment was a crude attempt at modeling the salt-well pumping of waste tanks, these preliminary results may provide some guidance as to the utility of grab sampling for obtaining useful information on organic content of waste tanks.

5.0 Improvement on Existing Organic Analysis Methods

Simulant waste samples were analyzed for organics under the Organic Analytical Support Task to support waste-aging studies and organic concentration mechanisms. The analytical methods used were originally developed under the Organic Methods Development tasks of the Organic Tanks and Flammable Gas Safety programs. (Campbell et al. 1994a, 1994b, 1994c, and 1995a). Fine-tuning and adjustment of these original analysis methods was required to handle the different matrices that interfered with some of the organic analyses. The simulated waste sample used for the waste-aging studies was spiked with the following organic compounds: dodecane, stearic acid, TBP, DBP, hexone, and citric acid. Quantitation of each of these organic starting components was desired. No one analytical method developed to date for waste analysis can analyze for all of these organic compounds simultaneously; thus a combination of techniques is required.

5.1 Simulant Waste Analysis Procedures

Three different analyses are currently being used to obtain quantitative information on the organic starting components in simulated waste following various known amounts of heat and gamma-irradiation treatment (Camaioni et al. 1994, 1995). In addition, some of the degradation products have been identified. Figure 5.1 provides an overall flowsheet of the analysis procedure currently being used. More details of the procedures can be found in Appendix A.

Gas chromatography/mass spectrometry is used to quantitate dodecane, stearic acid, hexone, and TBP. This procedure requires neutralization of the caustic sample with phosphoric acid followed by duplicate extraction of these four organics with dichloromethane (CH_2Cl_2). Two surrogates, dodecane- d_{26} and palmitic acid, are added before extraction to track the efficiency of the sample-preparation procedure. Following extraction, diazomethane is added to methylate stearic acid to enhance its volatility for GC/MS analysis. Analyte recoveries for the CH_2Cl_2 extraction and sample preparation procedure were determined by spiking known amounts of the organic analytes of interest into the inorganic portion of the simulant recipe. Triplicate experiments gave good recoveries for dodecane, TBP, and stearic acid as shown below:

<u>Analyte</u>	<u>Recoveries (%)</u>
Dodecane	102
TBP	96
Stearic Acid	98
DBP	6

Recoveries for DBP with this sample-preparation method averaged only 6%. Therefore, this is not a viable method for DBP. Alternative methods for analyzing DBP in the presence of the complex matrix containing nitrate, nitrite, and numerous metals are being pursued as previously described in this report. Precision of the GC/MS analysis, determined through replicate sample injections, had a standard deviation of less than 2% for all analytes.

Ion-pair chromatography remains the method of choice for the analysis of EDTA and similar chelators. The aqueous layer remaining after extraction of the organics by CH_2Cl_2 for GC/MS analysis is used for EDTA analysis. An aliquot of the aqueous layer is diluted to a concentration within the dynamic range of the ion-pair chromatography technique. Copper sulfate is added to enhance EDTA detection. Error

Figure 5.1. Schematic of the Sample Preparation and Analysis Scheme for Simulant Waste Samples Obtained from the Waste Aging Task

estimates for sampling and analysis were performed under the Flammable Gas Safety Organic Analysis Task, but can be applied here as well. The simulant waste samples have similar inorganic matrix recipes. Replicate sample preparations and instrument injections produced standard deviations of 5% for control simulated waste samples and up to 10% for heated and irradiated simulant waste samples. The increased error in the heated and irradiated samples can be explained by possible incomplete separation of degradation products.

Ion chromatography with conductivity detection is used for citric acid analysis. This technique was developed under the Flammable Gas Safety Organic Analysis Task for detection of low molecular weight organic acids in waste-tank matrices. More details of the development of ion chromatography for organic acid analysis can be found elsewhere (Campbell et al. 1995a). The simulant waste sample is diluted with water. Dichloromethane is added to remove non-polar organics that could interfere with the ion chromatography. Recovery studies of citric acid spiked into the simulant inorganic matrix gave a recovery

of 97%. Triplicate weighing and sample preparation gave a sampling error (standard deviation) of 9%. Multiple injections of the same sample gave a precision of 1%. Therefore, the total error for the ion chromatography analysis was determined to be 10%.

5.2 Identification of Degradation Products

Some degradation products have been identified during analysis of the starting organic components in the Waste Aging studies. Heptadecane, dodecanone isomers, and 3-methyl butanoic acid were identified during GC/MS analysis. Some organic acids, such as succinic acid, glycolic acid, and formic acid, were detected as degradation products during ion chromatography analysis for the starting component citric acid analysis. These degradation products are thought to be primarily from the degradation of EDTA and citric acid. More discussion can be found in Camaioni et al. (1995).

6.0 Real Tank Waste Analysis

A suite of physical and chemical analyses has been performed on waste-tank sludge and saltcake samples from Tanks 241-C-102, 241-C-103, and 241-BY-108 in support of resolving a safety concern regarding the entrainment of organics in waste solids. The analysis program was the result of a Test Plan exercise conducted jointly with staff from WHC and PNL. The tank samples were analyzed for organics, primarily TBP and normal paraffin hydrocarbon (NPH), TOC, percent water, inorganic cations and anions, radionuclides, particle-size distribution, and crystalline and inorganic phases. Preliminary results, a copy of the Test Plan, and the basis for these analyses were previously reported by Campbell et al. (1995b). The majority of the analyses were originally scheduled to be completed by PNL, but temporary closure of the PNL hot cell facilities required that the analyses be transferred to the WHC 222-S laboratory for sample preparation and analysis. Guidance in sample preparation and handling, analytical methods for many of the analyses performed on the tank samples, and interpretation assistance were provided by PNL. Due to changing priorities, some of the analyses of these samples that were originally planned, especially for samples from Tanks BY-108 and C-102, have not been completed. Additional analyses of samples from BY-108 and C-102 were scheduled for completion by PNL. However, efforts to get the radioactive samples delivered from WHC have been unsuccessful. A summary of analyses and results obtained since publication of the preliminary results (Campbell et al. 1995b) are provided in Appendix B. Some of the results presented here were completed by WHC under the characterization program. More detailed explanation of the analyses can be found in the Analytical Services Report 90-Day Safety Screen (WHC 1995) and in Campbell et al. (1995b).

7.0 Future Work

The plan for FY 1996 is primarily to analyze actual tank samples using newly developed analytical methods and screening tools in the most efficient manner to obtain the desired information. In addition, efforts to determine energy-rich organic functional groups by screening methods such as Raman and IR spectrometry, with the support of differential scanning calorimetry and TOC analyses, will continue. Knowledge gained from analyzing simulated waste samples by the functional-group screening-analysis testing will be applied to real waste samples. The goal of these screening tools will be to identify and/or quantify the amount of particular organic functional groups in organic tank wastes with minimal sample preparation and analysis time. Organic speciation will be required to verify the functional-group analysis methods and to provide more detailed organic component information when required for safety reasons. Minimal methods development will occur in FY 1996 and will focus on specific problems that may occur during, or in anticipation of, analyzing real waste samples.

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Appendix A

Experimental Procedures

Appendix A

Experimental Procedures

1.1 Ion-Pair Chromatography with Refractive Index Detection of Dibutyl Phosphate

Details of sample preparation, experimental procedures, and recovery studies for the development of ion-pair chromatography for DBP analysis are provided.

1.1.1 Standards preparation as follows:

Dibutyl phosphate (DBP) was obtained from Pfaltz-Bauer Chemical Co. Commercial DBP is typically 64:36 DBP:MBP when received.

The DBP standards prepared ranged from 0.24 mg/mL to 10.8 mg/mL in water. Above 10 mg/mL, DBP does not dissolve well in aqueous solutions. Calibration graphs of area response vs mg/mL of the analyte were prepared for MBP and DBP using the following standards:

0.24 mg/mL
0.61 mg/mL
1.22 mg/mL
2.44 mg/mL
6.10 mg/mL
10.80 mg/mL

1.1.2 Sample preparation as follows:

1. Weigh 0.5 gram of simulated waste (sample).
2. Quantitatively add 5 mL Mill-Q water.
3. Cap, shake, and vortex the sample tube.
4. Centrifuge for 20 min at 1500 RPM (revolutions per minute).
5. Remove 20 μ L of the aqueous layer and inject into HPLC for analysis.

1.1.3 Instrumental conditions are as follows:

Hewlett Packard 1050 Isocratic HPLC Pump
Waters Associates Differential Refractometer R401
Analytical Column: Brownlee RP18, 25 cm x 4.6 mm, Spheri-5 Monofunctional 5 μ C18
Equivalent guard column
Mobile Phase: 73% methanol: 27% H₂O
Ion-Pair Reagent: 4 x 10⁻³ M tetrahexylammonium bromide (THA-Br)
Data collection: Hewlett Packard HP3396 Series II Integrator

1.1.4 Addition of a preconcentration column to the method:

Preconcentration column: Rainin RP-18, 15 x 3.2 mm, 7 μ m particle size

Column is put in place of the standard 20 μ L sample loop connected to the Rheodyne injector.

Preconcentration mobile phase: 35% methanol, 65% water, and 2.0×10^{-3} M THA-Br

The preconcentration column was flushed with 1.00 mL of preconcentration mobile phase between each injection. 20 μ L of waste sample was injected onto this column. Then the other waste components were flushed off the column with 1.00 mL of preconcentration mobile phase. Finally, the analytes were flushed off the preconcentration column and onto the main column by means of the more eluting mobile phase consisting of the 73% methanol, 27% H₂O, and 4.0×10^{-3} M THA-Br already described.

1.1.5 Recovery Studies

Recovery studies were performed to determine the quantitation capability of this analysis technique for simulant waste samples. Known standard solutions of DBP and MBP were spiked into simulant waste samples that contained only inorganics. The spiked sample was prepared as follows:

1. Weigh 0.5 g of inorganic only simulant into screw top test tube.
2. Add 0.6 mL of standard solution containing 10.1 mg/mL DBP/MBP and 10.23 mg/mL TBP.
3. Add 4.4 mL of Milli-Q water.
4. Cap, shake, and vortex the sample tube.
5. Centrifuge for 20 min at 1500 RPM.
6. Remove 20 μ L of the aqueous layer and inject into the HPLC for ion-pair chromatography analysis.

1.2 Saltcake Washing Studies

Details of the saltcake preparation, experimental design, and calculations of results for the saltcake washing studies described in Section 4.4 are provided.

1.2.1 Saltcake Preparation

saltcake for this work was prepared by saturating a 5M NaOH, 2M NaNO₂, 2M NaAlO₂ solution with NaNO₃ at 90° C to 100° C. This solution was cooled to 50° C with constant agitation for 24 hours. The resulting mixture was cooled to ambient temperature.

The following organic compounds were added to the saltcake mixture after it was brought to room temperature, so that their final concentrations were approximately 1mM in the saltcake:

1. Tetrasodium EDTA
2. Sodium citrate
3. Sodium acetate

4. Tributyl Phosphate
5. Dodecane

1.2.2 Initial Scoping Experiment

An initial scoping experiment was performed to find the problems that may be associated with this experiment. Ninety-nine grams of sodium aluminate was added to 500 mL of Milli-Q water. To this solution, 84.4 g of NaOH was added. This was followed by adding 201 g of sodium nitrate and 69 g of sodium nitrite. This solution was heated to 110 °C and 0.197 g of tetra sodium salt of EDTA was added to the heated solution. This was followed by adding 0.021 g of sodium acetate and 0.118 g of sodium citrate. The volatiles were not added as they would have evaporated at 110 °C. The solution was heated to evaporate almost all the water and then cooled to room temperature. The slurry was transferred to a desiccator to remove any residual water. A saturated solution of sodium nitrate was prepared by adding 369.54 g of NaNO_3 to 500 mL of water. This solution was heated to evaporate approximately half the volume of water. The solution was cooled and 250 mL were added to the saltcake and allowed to stand for 5 days. The saturated solution of NaNO_3 was not able to percolate to the bottom of the saltcake. Therefore, the aqueous phase was forced through the saltcake using a spatula. This solution was allowed to stand for a period of 5 days.

A 10 mL solution of high energy organics was prepared by mixing 6.7 mL of tributyl phosphate and 3.3 mL of dodecane. This solution was added to the "wet" saltcake. The saltcake was wet because it retained approximately 100 mL from 250 mL of aqueous solution of NaNO_3 due to the hygroscopic nature of its constituents. Another batch of saturated solution of NaNO_3 was prepared and added to the saltcake with high energy organics on the surface.

During this scoping experiment, it was observed that the organic layer stayed primarily on the surface of the saltcake and did not percolate to the bottom. Therefore, the aqueous layer would retain all the high energy organic and not necessarily simulate the "salt well" pumping conditions.

The scoping experiment was modified to simulate the salt well pumping conditions. The saltcake was formed in a funnel to allow the washing to filter. Another batch of saltcake was prepared by adding 19.28 g of AlO_2Na , 16.81 g of NaOH, 13.88 g of NaNO_2 and 43.8 g of NaNO_3 to 100 mL (99.4 g) of Milli-Q water. The solution was heated and stirred until all the chemicals were well mixed. To this hot saltcake mixture, 1.01 g of EDTA (tetrasodium salt), 0.041 g of sodium acetate, and 0.99 g of sodium citrate were added. The mixture was cooled and poured into a funnel containing a Whatman # 44 filter paper. The saltcake started forming as the liquid was cooled. A small portion of the saltcake was removed, weighed, and dried in an oven. The dried saltcake was weighed to determine the moisture content of the original saltcake.

Two mL of tributyl phosphate and 2.0 mL of dodecane were added to the top of the saltcake on the filter paper in the glass funnel. This was equilibrated overnight. The saltcake was then washed with three 20 mL aliquots of NaNO_3 saturated water. The aqueous layer was analyzed for all the organics.

1.2.3 Results from Analysis of the Saltcake and Aqueous Filtrate

The results of this study are divided into the following sections:

- **Moisture Content:** The moisture content of the synthetic saltcake was determined by weighing out a small portion of saltcake before and after drying in a desiccator:

Wt. before drying	=	1.1590 g
Wt. after drying	=	0.9406 g
% H ₂ O	=	18.84 %

- **Tetra Sodium EDTA:** The concentration of tetrasodium EDTA was determined in the saltcake washing filtrate by ion-pair chromatography. EDTA was complexed with copper using excess of 0.05M copper sulfate. This analysis was performed in duplicate to verify the recovery results. See Section 1.3.3 in Appendix A for more details of the analysis.

Na ₄ EDTA added to the saltcake	=	1010. mg
Na ₄ EDTA determined in the saltcake filtrate	=	457.15 mg
% accounted for in filtrate	=	45.26 %

- **Organic Acids:** The amount of sodium salts of acetic acid and citric acid in the saltcake washing filtrate was determined by using ion chromatography (see Sections 1.3.4 and 1.3.5 of Appendix A). Recovery for sodium acetate was found to be approximately 85% where as the recovery for sodium citrate was 119%. There may be some impurity in the salts used for the saltcake which may lead to higher recovery for sodium citrate.

Sodium acetate added to the saltcake	=	40 mg
Sodium acetate determined in the saltcake filtrate	=	34.2 mg
% accounted for in filtrate	=	85.5 %
Sodium citrate added to the saltcake	=	990 mg
Sodium citrate determined in the saltcake filtrate	=	1182 mg
% accounted for in filtrate	=	119.39 %

- **Tributyl phosphate (TBP) and dodecane:** The concentrations of high energy semi-volatile organics, TBP and dodecane, were determined in the saltcake washing filtrate by using GC/MS (see Section 1.3.2 of Appendix A). TBP and dodecane were extracted from the aqueous layer using dichloromethane. The extracted solutions were injected along with an internal standard for GC/MS analysis. Theoretical concentration of semi-volatile organics was calculated by assuming that all the spiked organic was transferred to the liquid phase when the saltcake was washed with a saturated solution of sodium nitrate. Approximately 10 % of the original amount of TBP and dodecane added to the saltcake were found in the aqueous filtrate. This suggests the majority of these two organics remained in the saltcake and did not get transferred efficiently to the aqueous phase, or were caught by the filter.

Concentration of TBP originally in the saltcake	=	33.0 mg/mL
TBP concentration in the filtrate determined by GC-MS	=	2.92 mg/mL
% accounted for in filtrate	=	8.85 %
Concentration of dodecane originally in the saltcake	=	25. mg/mL
Dodecane concentration in the filtrate determined by GC-MS	=	2.59 mg/mL
% accounted for in filtrate	=	10.36 %

- Total Organic Carbon (TOC): A 20 mL aliquot of the sample was given to Dave Baldwin for TOC analysis. Several methods were used for TOC analysis in the saltcake filtrate, before and after the washing. Due to the complex matrix, no two methods gave consistent results. The hot persulfate wet oxidation method gave approximately 0.40 % TOC in the saltcake washing filtrate. On the other hand, the Dohrmann analyzer UV-catalyzed persulfate oxidation method gave approximately 0.65% TOC in the saltcake washing filtrate. Two other methods, the normal furnace method and the modified dichromate method, were also used, however, TOC results were not available due to poor recovery. Total organic carbon was also estimated using the results from the organic analyses and was found to be 0.98%. This TOC calculation was determined as follows:

Wt of Na ₄ EDTA in the saltcake filtrate	=	0.45715 g
% C in Na ₄ EDTA	=	31.59 %
Therefore, Wt. of carbon (A)	=	0.144 g
Wt. of Na-citrate in the saltcake filtrate	=	1.182 g
% C in Na-citrate	=	30.52 %
Therefore, Wt. of carbon (B)	=	0.36075 g
Wt. of Na-acetate in the saltcake filtrate	=	0.0342 g
% C in Na-acetate	=	29.28 %
Therefore, Wt. of carbon (C)	=	0.00992 g
Wt. of TBP in the saltcake filtrate	=	0.1166 g
% C in TBP	=	54.14 %
Therefore, Wt. of carbon (D)	=	0.0631 g
Wt. of dodecane in the saltcake filtrate	=	0.10375 g
% C in dodecane	=	84.7 %
Therefore, Wt. of carbon (E)	=	0.0879 g
Density of the saltcake filtrate	=	1.132 g/mL
Therefore, Wt. of 60 mL of aqueous layer	=	67.92 g
Total wt. of carbon (A +B+C+D+E)	=	0.6657 g
Therefore, % TOC	=	0.98 %

Thus, results of TOC analysis reported lower value as compared to the calculated TOC based on the results from organic analysis.

1.3 Simulant Waste Analysis Procedures

The sample preparation procedures in addition to instrumental conditions currently used for GC/MS, IPC, and IC analysis of simulant waste samples are as follows:

1.3.1 Sample Preparation for GC/MS and Ion-Pair Chromatography:

1. Weigh 0.5 gram of sample into screw top test tube.
2. Add 1 mL of dichloromethane (CH_2Cl_2) that contains 2.5 mg/mL of the surrogates dodecane- d_{26} , and palmitic acid. Shake briefly to mix.
3. Add 5 mL of 2N phosphoric acid. A precipitate forms.
4. Cap and shake, carefully release pressure on test tube. There is considerable carbonate in these samples which foams during neutralization.
5. Centrifuge for 20 minutes at 1500 RPM.
6. Remove CH_2Cl_2 layer and run through Na_2SO_4 (anhydr.) into a 100 mL volumetric.
7. Repeat CH_2Cl_2 extraction (using pure CH_2Cl_2 , not the surrogate mix) and transfer.
8. Save the aqueous layer for EDTA analysis. See step 11 below.
9. Add diazomethane solution to the 100 mL volumetric flask containing the CH_2Cl_2 extract until the yellow color persists. This methylates the stearic and palmitic acids and DBP. Dilute to volume with dichloromethane.
10. Transfer 1.5 mL of this solution to an autosampler vial containing 25 μL of 3 mg/mL tridecane internal standard. This sample is ready for GC/MS analysis.
11. Remove 1 mL of the aqueous layer, remaining after step 7 above, and place in a 10 mL volumetric flask. Add 200 μL of 0.5M CuSO_4 and dilute to volume with water. This sample is ready for ion-pair chromatography for EDTA analysis.

1.3.2 Gas Chromatography/Mass Spectrometry Analysis:

The samples were run on a Hewlett-Packard 5970 MSD GC/MS instrument with the following GC and MS parameters:

Analytical Column:	Rtx®-1, 30m x 0.25mm, 0.25 μm film
Head pressure:	5 psi He
Injection Temperature	260°C
Interface Temperature	280°C
Ion Source Temperature	200°C
Oven Ramp:	40°C for 2 minute, ramp to 280°C @ 15°C/min, hold for 2 minutes

The m/z values of the ions chosen for quantitation of each analyte were as follows:

Compound	m/z
Hexone	58
Dodecane- d_{26} (surrogate)	66
Dodecane	71
Tridecane (internal standard)	85
TBP	99
Methyl Palmitate (surrogate)	74
Methyl Stearate	74

1.3.3 Ion-Pair Chromatography Analysis:

This type of liquid chromatography separation was used for the determination of the chelator ethylenediaminetetraacetic acid (EDTA). Copper(II) sulfate was added prior to analysis to enhance analyte detection. A Waters HPLC instrument was used with the following columns and conditions:

Guard column:	Adsorbosphere C-8 cartridge
Analytical Column:	Adsorbosphere C-8 (25 cm x 4.6 mm, particle size 5µm)
Flow:	1.5 mL/min.
Sample Volume:	15 µL
Detection:	UV, 280 nm, as Copper complex
Mobile phase:	0.002M dodecyltrimethylammonium bromide, and 0.05M potassium dihydrogen phosphate, pH 6.5

1.3.4 Sample Preparation for Ion Chromatography:

1. Weigh 0.5 gram of sample into screw top test tube.
2. Quantitatively add 5 mL of Milli-Q water, and about 2.5 mL of CH₂Cl₂.
3. Cap, shake, and vortex the sample tube.
4. Centrifuge for 20 minutes at 1500 RPM.
5. Remove 0.100 mL of the aqueous layer, place in a 10 mL volumetric, and dilute to volume with Milli-Q water.
6. Collect Ion Chromatography data.

1.3.5 Ion Chromatography Analysis:

A Dionex ion chromatograph was used with the following columns and conditions:

Guard column:	Dionex AG11
Analytical Column:	Dionex AS11
Anion Suppressor	SRS 2 mm
Flow:	2.0 mL/min
Detection:	Conductivity, @10µS
Mobile phase:	5 mM NaOH to 38 mM NaOH in 27 min

Appendix B

Details of Tank Waste Analysis

Appendix B

Details of Tank Waste Analysis

1.1 Organic Analyses

Personnel at the WHC 222-S laboratory performed organic analyses on the samples from Tanks C-102 and BY-108 using methods developed by the Advanced Organic Analytical Methods Group (Campbell et al. 1994) and PNL (Pool and Bean 1994). The target organic compounds for these tank waste analyses were TBP and NPH; therefore, GC/MS and GC/FID were utilized. Sample extraction and preparation for organic analysis was performed by WHC 222-S laboratory per Test Plan and instructions by Jim Campbell of PNL {for complete details, see Campbell et al. (1995)}. Between 0.3 g and 0.7 g of sample were weighed into 20-mL glass vials and spiked with 0.5 mg of surrogate (n-hexadecane solution). Dichloromethane was used to extract the volatile and semi-volatile organics from the samples. Aliquots of this extract were analyzed by GC/MS and quantitated by GC/FID. The preliminary results from these analyses were presented in Campbell et al. 1995.

1.2 Preliminary Analyses of Tank C-103 Core Samples 63 and 66

Preliminary results from the analysis of solids and drainable liquids from Tank C-103 are provided in Tables B.1 to B.4. These analyses were performed by WHC but represent analyses that were scheduled to be completed under the joint test plan written by PNL and WHC (Campbell et al. 1995). The analysis methods are briefly described here and can be found in more detail elsewhere.

Particle-Size Distribution

The particle-size distribution of a sampling of sludge (segment 2, core 63 from riser 2 of the tank) from waste-tank 241-C-103 was performed by the Process Chemistry Laboratories of WHC (D. B. Bechtold, WHC Internal Memo 8E110-PCL95-018, 1995). It was observed that the sample was a dark-brown wet sludge-like fine mud with a light yellow-brown clear liquid. The liquid, which contained an appreciable amount of particulate, was used as a blank for background subtraction of the sludge analysis. The number distributions are mostly below 10 μm , while the volume distributions stretch above 100 μm . These values are typical of tank-waste sludges. A multi-modal log-based volume distribution is observed with a minor mode appearing at 4 to 5 μm . The instrument (Brinkmann 2010 analyzer) cannot detect particles below 0.5 μm in diameter, but they are likely present. No particles are indicated above 150 μm in diameter.

Percent Water by Thermogravimetric Analysis

The percent water was determined in the sludge and liquid samples under a nitrogen atmosphere by thermogravimetric analysis (TGA) using WHC procedure LA-560-112, Rev. A-2. In most cases, the water content of the samples was well above the notification limit of < 17% water. Duplicate and triplicate analyses were performed when the first result was below this safety limit of 17% water.

Energetics Content by Differential Scanning Calorimetry

Sample energetics were analyzed by DSC under a nitrogen atmosphere following procedure LA-514-113, Rev. B-1.

Total Organic Carbon

The sludge and drainable-liquid samples were analyzed for TOC by the direct persulfate oxidation method following WHC procedure LA-342-100, Rev. A-0. For comparative purposes, the furnace oxidation method of TOC determination (WHC procedure LA-344-105, Rev. B-3) was also used for the drainable liquids of segments 1 and 2 of core 63.

Nitrate, Nitrite, and Bromide

The concentrations of the nitrate, nitrite, and bromide ions were determined by IC on water digestions of the sludge samples or directly on liquid samples using WHC procedure LA-533-105, Rev. C-2. Concentrations of nitrate were nearly ten times less than nitrite levels for corresponding segment and core samples. Both nitrate and nitrite concentration levels vary with sample depth and core location.

Total Alpha

Fusion digestions of all sludge samples were analyzed for total alpha emissions using WHC procedure LA-508-101, Rev. D-2. All results obtained to date on samples from Tank C-103 are well below the notification limit of 41 $\mu\text{Ci/g}$.

Determination of Metals by Inductively Coupled Plasma

The concentration of Li and other metals such as aluminum, calcium, chromium, iron, potassium, sodium, nickel, zinc, and zirconium were determined by ICP using WHC procedure LA-505-151, Rev. D-1 or LA-505-161, Rev. A-1.

More details of the sample collection, extrusion, and physical nature of the samples can be found elsewhere (WHC-SD-WM-DP-000, 1995).

2.0 References

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Table B.1. Solids Segments for Core 63 of Tank C-103.

Determination	Segment 2 Upper	Segment 2 Lower	Segment 3 Upper	Segment 3 Lower	Segment 4	Units
% Water by TGA using Mettler	62.20	55.34	50.50	37.43(a)	19.92%	%
DSC Exotherm Dry Calculated	284.5	222.5		270.0(a)		Joules/g
DSC Exotherm using Mettler	107.6	99.35	0.00E + 00	168.8(a)	0.00E + 00	Joules/g
TOC by Persulfate Coulometry	8.49E + 03	1.02E + 04	7.60E + 03	8.90E + 03	4.50E + 03	µg/g
TIC by Acid/Coulometry	5.02E + 03	6.57E + 03	5.80E + 03	6.12E + 03	4.49E + 03	µg/g
Strontium 89/90 High Level	4.70E + 03	4.76E + 03	6.76E + 03	7.70E + 03	595.5	µCi/g
Lithium - ICP Fusion	n/a	n/a	n/a	n/a	n/a	µg/g
Cobalt-60 by GEA	2.055	2.340	3.675	2.545	3.49E - 01	µCi/g
Cesium-137 by GEA	132.0	134.5	160.5	192.0	57.2	µCi/g
Europium-154 by GEA	11.47	12.25	20.90	16.45	1.120	µCi/g
Europium-155 by GEA	8.735	9.200	21.15	n/a	1.001	µCi/g
Alpha of Digested Solid	13.25	13.95	19.05	13.80	1.735	µCi/g
Bromide by IC	n/a		n/a		n/a	µCi/g
Chloride by IC	461.5		1.59E + 03		185.5	µg/g
Fluoride by IC	1.08E + 03		1.02E + 03		645.5	µg/g
Nitrite by IC	1.94E + 04		7.38E + 03		2.38E + 03	µg/g
Nitrate by IC	1.70E + 03		665.5		n/a	µg/g
Oxalate by IC	2.66E + 03		1.94E + 03		2.32E + 03	µg/g
Phosphate by IC	3.06E + 03		2.90E + 03		2.52E + 03	µg/g
Sulfate by IC	2.85E + 03		2.01E + 03		1.28E + 03	µg/g
% Water by Gravimetric					25.15	%

(a) Initial analyses performed on sample S95T000046. Repeat DSC and % water were performed in duplicate on sample S95T000566 with the following average results: % water = 35.21%, DSC exotherm dry calculated = 591.5 J/g dry, and DSC exotherm = 383.1 J/g

Table B.2. Drainable Liquids Segments for Core 63 of Tank C-103.

Determination	Segment 1	Segment 2	Segment 4	Units
Tot. Organic Carbon	7.71E + 03	7.61E + 03		µg/mL
% Water by TGA using Mettler	88.43	84.48	79.98	%
DSC Exotherm Dry Calculated			n/a	Joules/g
DSC Exotherm using Mettler	0.00E + 00	0.00E + 00	104.8	Joules/g
TOC by Persulfate Coulometry	7.37E + 03	7.40E + 03	4.55E + 03	µg/mL
TIC by Acid/Coulometry	5.53E + 03	5.48E + 03	9.54E + 03	µg/mL
Lithium - ICP Acid Diltuion	6.56E - 01	3.120	19.90	µg/mL
Bromide by IC	n/a	n/a	n/a	µg/mL
Chloride by IC	424.0	452.0	406.0	µg/mL
Fluoride by IC	1.24E + 03	1.19E + 03	1.24E + 03	µg/mL
Nitrite by IC	2.60E + 04	2.42E + 04	6.26E + 03	µg/mL
Nitrate by IC	2.61E + 03	2.62E + 03	n/a	µg/mL
Oxalate by IC	3.36E + 03		3.36E + 03	µg/mL
Phosphate by IC	2.08E + 03	2.44E + 03	3.14E + 03	µg/mL
Sulfate by IC	3.36E + 03	3.36E + 03	3.27E + 03	µg/mL
Cyanide by Microdistillation & Spec			26.90	µg/mL

Table B.3. Solids Segments for Core 66 of Tank C-103.

Determination	Segment 3 Upper	Segment 3 Lower	Segment 4	Units
% Water by TGA using Mettler	74.14	87.23	74.97	%
DSC Exotherm Dry Calculated				
DSC Exotherm using Mettler	0.00E + 00	0.00E + 00	00E + 00	Joules/g
TOC by Persulfate Coulometry	8.90E + 03	n/a	9.20E + 03	µg/g
TIC by Acid/Coulometry	4.61E + 03		4.40E + 03	µg/g
Strontium 89/90 High Level				µCi/g
Lithium - ICP Fusion	n/a		98.94	µg/g
Cobalt-60 by GEA				µCi/g
Cesium-137 by GEA				µCi/g
Europium-154 by GEA				µCi/g
Europium-155 by GEA				µCi/g
Alpha of Digested Solid	5.850		11.95	µCi/g
Bromide by IC	371.0	n/a	1.71E + 03	µCi/g
Chloride by IC	589.5	380.5	446.5	µg/g
Fluoride by IC	1.44E + 03	1.10E + 03	1.00E + 03	µg/g
Nitrite by IC	2.94E + 04	2.40E + 04	2.16E + 04	µg/g
Nitrate by IC	2.99E + 03	2.37E + 03	2.10E + 03	µg/g
Oxalate by IC	3.92E + 03	2.96E + 03	2.96E + 03	µg/g
Phosphate by IC	4.44E + 03	2.04E + 03	2.86E + 03	µg/g
Sulfate by IC	4.05E + 03	3.12E + 03	3.03E + 03	µg/g
Lithium - ICP Acid Diltuion		22.20		µg/mL

Table B.4. Drainable Liquids Segments for Core 66 of Tank C-103

Determination	Segment 1	Segment 2	Segment 3	Segment 4	Units
% Water by TGA using Mettler	87.94	87.57	87.23	89.44	%
DSC Extherm Dry Calculated					
DSC Exotherm using Mettler	0.00E + 00	0.00E + 00	0.00E + 00	0.00E + 00	Joules/g
TOC by Persulfate Coulometry	n/a	n/a	n/a	n/a	µg/mL
TIC by Acid/Coulometry					µg/mL
Lithium - ICP Acid Diltuion	4.150	2.125	22.20	225.0	µg/g
Bromide by IC	n/a	n/a	n/a	2.82E + 03	µg/mL
Chloride by IC	398.5	377.0	380.5	356.0	µg/mL
Fluoride by IC	1.16E + 03	1.10E + 03	1.10E + 034	973.0	µg/mL
Nitrite by IC	2.42E + 04	2.34E + 04	2.40E + 04	2.25E + 04	µg/mL
Nitrate by IC	2.49E + 03	2.42E + 03	2.37E + 03	2.26E + 03	µg/mL
Oxalate by IC	3.14E + 03	3.10E + 03	2.96E + 03	2.73E + 03	µg/mL
Phosphate by IC	2.00E + 03	1.90E + 03	2.04E + 03	1.82E + 03	µg/mL
Sulfate by IC	3.20E + 03	3.06E + 03	3.12E + 03	2.93E + 03	µg/mL

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