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Environmental Restoration Division
ORNL Environmental Restoration Program

**Investigation of the Organic Matter
in Inactive Nuclear Tank Liquids**

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EXECUTIVE SUMMARY

Environmental Protection Agency (EPA) methodology for regulatory organics fails to account for the organic matter that is suggested by total organic carbon (TOC) analysis in the Oak Ridge National Laboratory (ORNL) inactive nuclear waste-tank liquids and sludges. Identification and measurement of the total organics are needed to select appropriate waste treatment technologies. An initial investigation was made of the nature of the organics in several waste-tank liquids.

Previous work at other laboratories and limited knowledge of the chemicals discharged to the ORNL waste tanks suggested that chelators, extraction and complexing agents, decontamination chemicals, and the known degradation products of all of these could constitute the bulk of the TOC. Considerable effort was applied to the development of derivatization, separation, and quantitation methods. Several such compounds were identified in the samples, and the TOC visualized in the analysis was considerably increased. However, the bulk of the compounds visualized could not be readily identified by gas chromatography/mass spectrometry (GC/MS), and 50 to 75% of the TOC remains unidentifiable and/or irretrievable through this experimental protocol.

Subsequent studies using direct aqueous injection gas chromatography (GC) indicated that small, volatile carboxylic acids ($\sim C_1-C_7$), which had not been detected previously, were not major contributors to the TOC. Other sample semivolatile compounds were screened by temperature-programmed direct probe mass spectrometry (MS) and were not detected.

Laser-desorption Fourier transform MS (FTMS) provided some useful information. The spectra were relatively simple, indicating that the major constituents were relatively small in number. Also, the mass range of the compounds appeared to extend up to the low 700s. Although polymeric matter cannot be excluded, the evidence suggests low-to-moderate molecular weights. Characterization by reverse-phase high-performance liquid chromatography showed a large mass of very polar, relatively low-molecular-weight material.

The results suggest that a large portion of the "unaccounted" TOC is made up of very polar, low-to-moderate-molecular-weight compounds, which are not amenable to analysis by GC methods. It is clear that the characterization of these compounds will require much further work. The derivatization GC method requires additional work that will allow the identification of the TOC that it can visualize. Liquid chromatography and laser desorption FTMS appear to be the best tools for the analysis of TOC that is not amenable to GC. Capillary electrophoretic methods also may be useful.

INTRODUCTION

Thirty-three currently inactive tanks at ORNL were previously used to collect and store radioactive nuclear wastes. Individual tanks have been inactive for periods varying from 1 to 30 years, and most of these contain residual sludge and/or liquids. Because of the diverse nature of research programs, nuclear and/or chemical, from which the wastes were derived and because the tanks were formerly managed by various divisions of the Laboratory, only minimal records exist that could indicate the chemical composition of the residual material.

The Resource Conservation and Recovery Act (RCRA) mandates the analysis of the tank contents for hazardous wastes prior to final closure. Extensive organic and inorganic characterization of 30 of the tanks has been completed. Because standard EPA methods for determination of hazardous waste^{1,2} were not designed for analysis of mixed waste (containing hazardous and radioactive wastes), modifications of some procedures were necessary to reduce the radiation exposure to the analyst.³ The completed analyses provided information that permits classification of the tanks within the guidelines of RCRA, but in most cases <10% of the TOC content has been identified. Studies at the Batelle Pacific Northwest Laboratory (PNL) have shown similar disparities between the results obtained from EPA regulatory analysis and TOC.^{4,5}

Final closure of the inactive tanks requires treatment strategies that meet EPA waste-form criteria. Some treatment strategies that have been considered are in situ grouting, in situ vitrification, incineration, and chemical desorption. The selection of appropriate closure strategies is dependent on the presence or absence of many organics, for example, chelators. In support of treatment strategies, we have begun studies of methods best suited to the isolation and identification of the nonregulatory organics for which no EPA procedures are available.

The organics for which we have not accounted by EPA methods may be from various categories: original source chemicals not determined by EPA regulatory methods, degradation products, or polymers of original source and/or degradation products. Many of these products could be the result of chemical interactions or radiolysis. The nature of the treatment of the tank wastes and the data currently available do not indicate that the unidentified organics are biological intermediates. The probable complexity of chemical contents may require extensive development of methodologies for organic analysis. This report presents the results of our initial investigation into the nature and identity of the nonregulatory components of the TOC.

METHODS AND MATERIALS

SAMPLES

The general characteristics of the waste tank samples are shown in Table 1.³ In addition, the samples contain varying amounts of silver, arsenic, barium, cadmium, chromium, mercury, nickel, lead, selenium, and titanium. Radioactivity is derived from alpha, beta, and gamma emitters, including isotopes of cesium, cobalt, strontium, uranium, and plutonium. Because of the presence of radioactivity in the samples, the quantity used for analysis was often limited to reduce worker exposure.

Table 1. Characteristics of waste-tank samples

Sample identification	pH	NO ₃ (mg/L)	PO ₄ (mg/L)	SO ₄ (mg/L)	CO ₃ (mg/L)	HCO ₃ (mg/L)	Total solids (mg/L)	TOC (mg/L)	TOC accounted by regulatory assays (%)
WC17/L102	7.6	13	<5	98		<0.01	0.7	143	0.8
WC17/L104	7.6	15	<5	82		<0.01	0.5	153	0.6
T2/L112	9.4	8.0	<5	21	0.04	0.09	12.1	1,100	1.0
W3/L017	10.1	<50	600	430	0.02		4.4	790	3.2
W3/L018	11.1	<50	800	620	0.05		8.4	1,500	1.9
TH4/L057	7.6	31,000	<2,500	14,000	0.02		104.1	2,170	0.8

GC OF DERIVATIZED SAMPLES

The derivatized and nonderivatized samples were analyzed using a megabore capillary column GC (Hewlett Packard model 5840) with flame-ionization detection; the carrier was helium at a flow rate of 7 mL/min. The column was 0.53-mm ID by 15-m fused silica with a 1.5- μ m DB-1 bonded phase. The inlet temperature was maintained at 250°C, and the flame-ionization detector, at 280°C. A column temperature program of 100 to 280°C at a rate of 2.5°C/min was used with a 6-min initial isothermal hold and a final isothermal hold of 25 min. Injections of 1.6 μ L were made by an autosampler. Standards were used for spiking at 100 ppm and were routinely run before and after each sample to verify the integrity of the GC. Quantitation was achieved using external standards.

Some analyses were performed with a high-resolution Hewlett-Packard model 5880 GC equipped with a 30-m by 0.25-mm ID fused silica column coated with a 0.25- μ m bonded film of DB-5 and a flame-ionization detector. One microliter of sample was injected via a Grob-type splitless injector. The column temperature program was 100 to 290°C at a rate of 3°C/min with a 10-min initial isothermal hold and a 20-min final isothermal hold. The injector port and detector were maintained at 250 and 300°C, respectively. Helium carrier gas was regulated at 1 mL/min.

GC OF CARBOXYLIC ACIDS

A Perkin Elmer model 3920 GC with a 6-ft by 0.125-in.-ID glass column, packed with 0.3% SP-1000 and 0.3% H₃PO₄ on Carbopack A, was used to analyze for small, polar carboxylic acids. The helium carrier flow was 30 mL/min. The injection port temperature was 150°C, and the column was maintained at an isothermal temperature of 130°C. Manual injections of 3.0 μ L were used. The analyses were quantitated using external standards.

SOLID-PHASE EXTRACTION

Quik-Sep XAD-2 resin columns (5-mL bed volume) were washed with 100 mL of deionized water. Samples of 1 mL were placed on the column, followed by approximately 20 mL of water. The water wash contained most of the inorganic salts and radioactivity and was discarded. The organic components were eluted from the column with 20 mL of acetone. The acetone solution was evaporated under nitrogen, and the residue was derivatized with N-methyl-trimethylsilyl-trifluoroacetamide (MSTFA.) A blank and a standard were extracted in the same manner.

HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

Liquid chromatography was accomplished on a C18 reversed-phase column (packed with Alltech C18, 10 μ m; 4.6 mm ID; 250 mm long) obtained from Alltech Associates, Inc., (Deerfield, Illinois). A water:acetonitrile gradient ranging from 10 to 95% acetonitrile was generated on a Beckman-Altex liquid chromatography system. The system consisted of two Model 110-A pumps controlled by a Model 421 Controller, an autosampler equipped with a 250- μ L loop, and a Model 153 detector equipped with the filters for monitoring absorbance at 254 nm. The specific solvent program was to hold for 9 min at 10% acetonitrile in water followed by a linear gradient to 95%

acetonitrile over the next 48 min (1.8% increase per minute). The 95% acetonitrile eluent was maintained for 16 min; after this time the concentration was reduced to 10% over a 10-min period (8.5%/min). The flow rate was maintained at 1 mL/min, and the average pressure drop across the column was 1000 psi.

GC/MS

GC/MS characterization of trimethylsilyl-derivatized sample extracts was performed on an HP-5895 instrument. One microliter of sample was injected into a 30-m by 0.25-mm-ID fused silica column with a 0.25- μ m bonded film of DB-5. The column was temperature-programmed from 100°C (19-min isothermal hold) to 290°C at 3°C/min. Spectra were recorded at 70 eV ionizing voltage in the electron impact mode with an electron multiplier setting of 2200. The helium carrier gas flow rate was ~1 mL/min.

DIRECT-PROBE MS

The direct-probe MS analyses were conducted using the temperature-programmed direct inlet probe on an HP-5895 quadrupole GC/MS system. Samples were evaporated onto a gold cup under a stream of nitrogen. The cup was placed in the direct inlet probe, inserted into the MS source, and temperature-programmed from 100°C (1-min isothermal hold) to 280°C at 30°C/min. The following instrument conditions were used: 200°C source temperature, 200-eV ionizing voltage, 2400 electron multiplier, positive ion chemical ionization mode with 0.2 torr of methane, and mass range of 50 to 800 amu at 250 to 750 amu/s.

LASER-DESORPTION FTMS

All mass spectra were obtained with a Nicolet FTMS-2000 equipped with a Quanta Ray DCR-11 Nd:YAG pulsed laser. The fundamental line of the laser at 1064 nm was used to desorb and simultaneously ionize the sample. A few micrograms of each sample was placed on the stainless steel tip of a solids probe, which was then used as the laser target inside the vacuum chamber. A complete mass spectrum was obtained for each laser shot; however, because of sample ablation by laser impact, the probe was rotated to a new position after each shot. Each shot ablated ~0.5 mm² of sample area. Two laser powers were used for some samples. "Low power" was ~10⁶ W/cm² of laser power density, whereas "high power" corresponded to ~10⁸ W/cm². Masses 15 to 2000 were scanned in about 200 ms after the laser desorption.

DERIVATIZATION OF SAMPLES

All of the samples to be derivatized were placed in 1-mL crimp-top vials and were evaporated to dryness under a stream of nitrogen. A 0.5-mL aliquot of MSTFA was added to the vial, followed by 0.5 mL of acetonitrile. The vial was capped and then heated at 65°C for 1 h. The derivatized samples were analyzed by GC.

CHEMICALS

All of the standard organics were obtained from Aldrich, Eastman, or Sigma in the highest purity available. The derivatizing agent MSTFA was obtained from Pierce. Quik-Sep XAD-2 resin columns were obtained from Isolab, and the organic solvents acetonitrile, methylene chloride, and acetone were distilled-in-glass grade obtained from Burdick and Jackson.

RESULTS AND DISCUSSION

DETERMINATION OF CHELATORS, EXTRACTANTS, COMPLEXING AGENTS, AND DEGRADATION PRODUCTS

Many components used at ORNL in the Transuranic Processing Plant and Facilities and discharged into the low-level waste (LLW) system (Table 2) are not listed as EPA-regulated chemicals and are not isolated or quantified by regulatory methods. Chemicals similar to those generated at ORNL, in the form of chelators and fragments, have been identified by PNL in commercial nuclear wastes⁶ (Table 3). Other compounds identified by PNL included mono-, di-, and tricarboxylic acids and aromatic acids. Often these compounds cannot be analyzed directly by GC and must be derivatized to increase volatility, increase thermal stability, enhance detectability, or improve separation. PNL's study of chelators indicated the presence in mixed wastes of chemicals that were not observed by GC or GC/MS prior to derivatization.⁴

Two widely used methods for chemical derivatization prior to GC analysis are silylation and alkylation. In silylation, an active hydrogen is replaced by an alkylsilyl group, making the chemical more volatile, less polar, and more thermally stable. Trimethylsilylation is the most widely used alkylsilylation derivatization. Silylation offers an important advantage over all other derivatization reactions: the active hydrogen on nearly every polar group is replaced with a trimethylsilyl (TMS) group. These polar groups include the hydroxyl (OH) group in phenolic, carboxylic, sulfuric, and phosphoric acids and hydroxyl, thiol, and amino groups spanning a wide range of pKs. Alkylation is the addition of an alkyl group to an active functional group such as those found in acids, alcohols, amines, amino acids, and phenols. The most practical alkylation reactions are those that form esters of carboxylic acid groups. We studied the use of two silylating reagents and two alkylating reagents in our attempts to account for the TOC of the waste tanks.

We selected a group of standard chemicals consisting of carboxylic acids, chelators and fragments, extractants, and miscellaneous compounds (Table 4). These chemicals or associated chemicals have been used at ORNL or have been found in commercial nuclear wastes and would normally not be seen by GC or GC/MS analysis. The standards were derivatized individually and as mixtures and analyzed by GC. Our initial derivatization attempts used two alkylating agents, Esterase M and trimethylanilinium hydroxide (Supelco). There was poor recovery of the standards in mixture when they were derivatized with these agents. In addition, the baseline on the GC was not stable and a relatively large number of extraneous peaks were observed in the derivatizing agents. The use of silylation [Hydroxy Sil AQ (Regis) and MSTFA (Pierce)] provided clean peaks that could be well-separated by GC. MSTFA was selected for use in most of our work, based on the results obtained with the mixture of standards (Fig. 1). We were able to separate the TMS derivatives of all of the components listed in Table 4 by high-resolution capillary GC. The

Table 2. Organic chemicals used regularly in the Transuranium Processing Plant (7920) and TURF (7930) and subsequently discharged to the ORNL LLW System

Acetic acid	Ethylenediaminetetraacetic acid (EDTA)
Acetone	2-Ethyl-1-hexanol
Adogen-364 · HP (~trilaurylamine)	α -Hydroxyisobutyric acid
Carbon tetrachloride	Isopropanol
Deodorized mineral spirits (Amsco)	Methanol
2,5-Di-tert-butylhydroquinone	<i>n</i> -Dodecane
Diethylbenzene	<i>n</i> -Paraffin
Diethylenetriaminepentaacetic acid	Oxalic acid
Di-(2-ethylhexyl)phosphoric acid	Thenyltrifluoroacetone
Diisopropylbenzene	Tributylphosphate (TBP)
Ethanol	Trichloroethylene
Ether	Xylene

Table 3. Chelators and fragments identified in commercial nuclear wastes by PNL

Chelating/complexing agents

Citric acid
 Nitrilotriacetic acid
 Ethylenediaminetetraacetic acid (EDTA)

Chelator complexor fragments

N-(dimethyl)iminoacetic acid
N-(ethyl)ethylenediamine-*N*-acetic acid
N-(diethyl)iminocarboxy acid
 Methylenediamine-*N*-carboxy-*N*-acetic acid
 Methylenediamine-*N,N*-carboxyacetic acid
N-(diethyl)iminoacetic acid
 Iminodiacetic acid
N-(2-hydroxyethyl, ethyl)iminoacetic acid
N-(2-hydroxyethyl)iminocarboxypropionic acid
 Methyliminodiacetic acid
N-(ethyl)ethylenediamine-*N*-acetic-*N*-carboxy acid
N-(ethyl)ethylenediamine-*N,N*-carboxyacetic acid
N-(methyliminocarboxy)ethylenediamine-*N*-acetic acid
N-(methylamine)iminodiacetic acid
N-[2-hydroxyethyl-*N'*-carboxy-2-(methylidene)]ethyliminoacetic acid
 Ethylenediaminetriacetic acid
N-(methylamine)-*N'*-(methyl)ethylenediamine-*N',N'*-diacetic acid
N-(2-carboxyethyl)iminodiacetic acid
N-(methylamine)-*N'*-(ethyl)propylenediamine-*N,N'*-diacetic acid

Source: A. P. Toste and T. J. Lechner-Fisk, "Organic Diagenesis in Commercial Nuclear Waste," *Trans. Am. Nucl. Soc.* **56**, 183–85 (1988).

Table 4. Standards used for identification of carbon sources^a

Monocarboxylic acids (carbon No.)	Chelators and chelator/complexor fragments
Lauric acid (12)	Citric acid ^a
Tridecanoic acid (13)	Nitrilotriacetic acid ^a
Pentadecanoic acid ^a (15)	Ethylenediaminetetracetic acid ^a
Palmitic acid (16)	Imidoacetic acid ^a
Heptadecanoic acid (17)	<i>N</i> -(2-hydroxyethyl)ethylenediaminetriicetic acid ^a
Elaidic acid ^b (18)	
Nonadecanoic acid (19)	Extractants
Eicosanoic acid (20)	Tributyl phosphate ^a
Heneicosanoic acid (21)	Di- <i>N</i> -butyl phosphoric acid ^a
Behenic acid (22)	Di-2-ethylhexyl phosphoric acid ^a
Tricosanoic acid ^a (23)	
Lignoceric acid (24)	Expected miscellaneous
Pentacosanoic acid (25)	Benzoic acid ^a
	<i>p</i> -Nitrobenzoic acid
Dicarboxylic acid (carbon No.)	2-Nitrophenol
Oxalic acid ^a (2)	α -Hydroxyisobutyric acid
Malonic acid (3)	2-Ethyl-1-hexanol
Succinic acid (4)	
Tartaric acid (4)	
Glutaric acid ^a (5)	
Adipic acid (6)	
Pimelic acid (7)	
Suberic acid ^a (8)	
Azelaic acid (9)	
Sebacic acid (10)	
Undecanoic acid (11)	

^aA mixture of these chemicals was used routinely for the evaluation of the derivatization, the GC function, and as a spike for selected samples. This mixture was referred to as "selected standards."

^bAll the monocarboxylic acids except elaidic acid are saturated. Elaidic acid has 18 carbons and a carbon-carbon double bond.

Fig. 1. High-resolution capillary column gas chromatogram of derivatized standards of carboxylic acids, extractants, chelators, and chelator fragments.

megabore GC, which was used routinely, provided similar separations with only a few overlapping peaks.

A methylene chloride extraction for semivolatile organic (SVO) compounds in liquids and/or sludges should contain a variety of organic chemicals that are not EPA regulated and may not be seen by the EPA-protocol GC or GC/MS analysis. We derivatized aliquots of the regulatory SVO extracts from the inactive tanks with MSTFA and analyzed them by GC. Some aliquots were spiked with the standards indicated in Table 4 to determine recoveries and the effects of the matrix on the selected standards. The GC results from the derivatized samples were compared with the chromatograms from the nonderivatized SVO extract. Based on total peak area of the chromatograms (solvent peak not included), a large increase in the amount of organic chemicals was observed by GC analysis (Table 5). This increase in peak area of the chromatograms was the result of the appearance of new peaks corresponding to compounds that would chromatograph only after derivatization and did not chromatograph when the underivatized extract was analyzed by GC. Although many of the new compounds in the derivatized aliquots have not yet been identified, tributylphosphate (TBP) and dibutylphosphate (DBP) were present in essentially all of the extracts. This observation indicates that considerably more chemical information can be gained from analysis of the regulatory SVO extracts if they are derivatized. Even though much additional organic matter is visualized (Table 5), quantitative recovery of the TOC is far from complete.

The extraction properties of TBP have been studied since the 1940s, and work at ORNL led to the development of the Purex process.⁷ It has been shown that DBP is a radiolytic and/or chemical degradation product of TBP.⁸ Salts of uranium, zirconium, and ruthenium in the TBP extraction processes increase the release of carbonyl compounds, acids, and esters.⁹ Radiolytic degradation of TBP has also yielded acid lipophilic phosphate esters, carboxylic acids, nitroalkanes, alkyl nitrates, and polymers.^{10,11} It is apparent that many of these classes of compounds not normally seen by GC analysis could account for the increase in organic chemicals observed in the derivatized aliquots of the SVO extracts.

The nature of the potential degradation and/or radiolytic compounds in the inactive tanks and the results obtained from derivatization of the SVO extracts suggested the use of other extraction solvents. We used ethyl acetate, a more polar solvent, and Freon 2, which will solubilize low-molecular-weight polymers, to extract some aqueous waste-tank samples. These extracts were derivatized with MSTFA and analyzed by GC. The derivatized Freon 2 extracts were qualitatively similar to the derivatized SVO extracts; however, some higher-molecular-weight material was observed on the chromatograms. The results of the Freon extraction are presented later in this report. Derivatization of an ethyl acetate extract and subsequent GC resulted in recovery of more peaks than were obtained from Freon 2 or methylene chloride extractions, but the recovery of the selected standards was so poor that calculations of TOC were not feasible. Because some new compounds were obtained, the preliminary studies with ethyl acetate extraction may provide the basis for future studies of extraction methods, but it appears that no single solvent can be used to effectively recover the TOC in liquid/liquid extraction.

The aqueous liquids in the inactive tanks contain various inorganic salts, some of which are present in high concentrations. To determine the effects of these salts on the analysis of organic compounds, we made a salt solution in deionized water that mimicked the high salt content previously reported for one of the tanks. The solution contained 5 mg/mL of nitrate and 2 mg/mL of sulfate at pH 6.1. One milliliter of the salt solution was placed in a crimp-top vial, spiked with 100 ppm of "selected standards" (footnoted in Table 4), and evaporated under a stream of nitrogen. MSTFA and acetonitrile were added to a final volume of 1 mL. The vial was capped and heated at 65°C for 1 h prior to analysis by GC. There was at least 75% recovery of all of the standards,

Table 5. Increase in total GC peak area from TMS-derivatization of regulatory SVO extract

Tank No.	Peak area for sample ^a		Increase in peak area (%)
T2/L112	SVO	4,409	47
	SVO + Der.	8,354	
W3/L018	SVO	451,743	62
	SVO + Der.	734,117	
W3/L017	SVO	232,297	306
	SVO + Der.	943,400	
TH4/L057	SVO	36,404	568
	SVO + Der.	243,154	

^aSolvent peak not included in total peak area.

indicating that simple nitrate/sulfate mixtures would not seriously interfere with the derivatization and analysis of these compounds.

Many of the compounds that do not chromatograph without derivatization are acidic, and most of the aqueous tank solutions are alkaline; therefore, we examined the effect of pH on the recovery of standards from evaporation of spiked salt solutions and derivatization of the dried residues. One aliquot of salt solution containing selected standards was titrated to a pH of 2 with hydrochloric acid, and another aliquot was titrated to a pH of 12 with sodium hydroxide. Each aliquot was placed in a crimp-top vial, evaporated, and derivatized prior to GC analysis. Although the recovery of some of the standards was poor (10%), all of the 12 peaks were present in the alkaline solution. Only 9 of the 12 standards in acid solution could be identified by GC. Because it is possible to have both a pH effect and a matrix effect influencing the recovery of the standards, 33 standards were added to an acidic and a basic salt solution. After evaporation and derivatization, they were analyzed by GC. Twenty-six of the standards were identifiable in the acidic solution, but each of the standards from the basic solution resulted in a peak of sufficient size for quantitation. These results seem to indicate a pH effect, but not necessarily a matrix effect, in the simple salt solution. It is not clear why better recoveries were generally achieved from evaporation of alkaline solutions. Acidic compounds would be present in the residues as alkaline salts, which would not derivatize as readily as would the free acids from evaporation of acidic solutions.

Because the inactive tank aqueous liquids have diverse matrices (Table 1), selected standards were added to acidic and basic pH-adjusted aliquots. Table 6 shows that the best recovery of the standards, in almost every sample, was from basic solutions. One of the extreme differences between the recovery of standards added to acidic or basic aliquots of a sample is shown in Fig. 2. This chromatogram was generated using the megabore GC. Because the recovery of added standards was so varied among the samples, the results clearly indicate both a pH and a matrix effect.

Despite the complexities of pH and/or matrix effects on the recovery of various chemicals, derivatization has been shown to enhance the ability to chromatograph and quantitate several classes of organic chemicals that contribute to sample TOC. Because most of the compounds visualized by the GC have not yet been identified, we estimated the TOC using the selected standards to calibrate the detector response. This is not a standard method for TOC determination. A group of selected standards was used to calculate a flame ionization detector response factor (RF) for micrograms of TOC per milliliter per peak area. The RF was calculated from the following formula:

$$RF = \mu\text{g compound per mL} \times \text{peak area} \times \text{number of C atoms} \times 12 \times MW ,$$

where MW is the molecular weight of the compound.

This value was calculated for each of the selected standards that were run before, between, and immediately after GC analysis of the samples to verify the integrity of the GC column. An average value from all of the standards was used as the RF to calculate the percentage TOC from the derivatized samples. The calculated TOC values and the previously reported TOC for a group of samples are shown in Table 7. The samples were evaporated under nitrogen or extracted with Freon 2 before they were derivatized. Trimethylsilylation of the residual salts and extracts of the aqueous samples showed significant increases in the percentage recovery of TOC. Several previously unreported chemicals were recovered by chromatography of derivatized tank samples (Table 8). The tentative identification of these compounds is based on GC retention time and has

Table 6. Percentage recovery (pH adjusted) of spiked standards from derivatized samples under acidic and basic conditions

Spiked standard	WC17/L02		WC17/L04		W3/L018		TH4/L057	
	Acid	Base	Acid	Base	Acid	Base	Acid	Base
Oxalic acid	0	23	21	31	152 ^a	140 ^a	164 ^a	11
Benzoic acid	0	98	3	80	2	86	13	51
Glutaric acid	0	82	65	97	198 ^a	147 ^a	106	92
Di-N-butyl phosphoric acid	0	160 ^a	0	109	0	12	0	1
Tributylphosphate acid	0	104	64	102	206 ^a	27	51	20
Suberic acid	0	89	52	72	295 ^a	28	26	18
Nitrilotriacetic acid	61	97	118	86	191 ^a	369 ^a	0	122 ^a
Citric acid	0	110	110	108	195 ^a	37	38	25
Pentadecanoic acid	0	111	92	105	205 ^a	164 ^a	111	74
Di-2-ethylhexyl phosphoric acid	0	63	0	9	84	0	81	0
EDTA	0	135 ^a	83	94	200 ^a	128 ^a	131 ^a	66
Tricosanoic acid	0	174 ^a	0	60	177 ^a	0	0	31

^aIn most cases values exceeding 115% were caused by the presence of the tentatively identified chemical in the nonspiked derivatized sample.

Fig. 2. Gas chromatogram of a “spiked” tank sample evaporated and derivatized under basic and acidic conditions. This chromatogram indicates an extreme of pH and/or matrix effects on standard recovery.

Table 7. TOC recovered based on GC peak area from samples extracted or evaporated under different conditions

Tank sample	TOC reported (mg/L)	TOC calculated from GC peak area of derivatized sample (mg/L)	TOC recovery from regulatory assays (%)	TOC recovery after derivatization of evaporated sample (%)
WC17/L102 (basic)	143	159	0.8	111
W3/L018 acid	1500	805	1.9	54
base	1500	853	1.9	57
acid	1500	484	1.9	32
(Freon 2 extract)				
base	1500	592	1.9	40
(Freon 2 extract)				
TH4/L057 acid	2170	305	0.8	14
base	2170	618	0.8	29
acid	2170	622	0.8	29
(Freon 2 extract)				
base	2170	592	0.8	27
(Freon 2 extract)				

**Table 8. Chemicals identified from tank samples
after derivatization and GC**

Monocarboxylic acids	Extractants
Pentadecanoic acid	Tributyl phosphate ^a
Palmitic acid ^a	Dibutyl phosphate ^a
Tridecanoic acid	Di-2-ethylhexyl phosphate ^a
Tricosanoic acid	
	Miscellaneous compounds
Dicarboxylic acids	Benzoic acid
Oxalic acid ^a	2-Ethyl-1-hexanol
Malonic acid ^a	
Suberic acid	
Chelators or fragments	
EDTA	
Nitrilotriacetic acid	

^aConfirmed by GC/MS.

not yet been confirmed by GC/MS for several compounds because the TMS derivative does not produce simple mass spectra. Because the mass spectra of methylated derivatives can be more readily interpreted, further studies of this type of derivatization would be useful for confirmational MS analyses.

SAMPLE PREPARATION USING SOLID-PHASE EXTRACTION

Solid-phase extraction (SPE) is a method of sample preparation that can be used to (1) remove compounds that interfere with analysis and (2) concentrate selected components. The use of SPE often decreases the required sample size and reduces the volume of extracted waste. The basis of the technique is specific interaction between a solid sorbent and a chemical from a sample matrix. Enhancement of specific interactions provides greater recoveries than can be achieved with other methods, such as liquid/liquid extraction. A previous study of SPE in the Analytical Chemistry Division indicated that polycyclic aromatic hydrocarbons and organochlorine pesticides, both neutral classes of compounds, could be extracted with good quantitative recovery from synthetic mixed waste.¹² Recoveries of more-water-soluble phenols were also good. Studies of the use of SPE for regulatory components in drinking water and other matrices have recently been started in several laboratories under the direction of EPA.¹³

Amberlite XAD-2, a synthetic polystyrene polymer, is a hydrophobic adsorbent. Water-soluble organics are selectively adsorbed on the surface of the hydrophobic portion of the resin molecule. Adsorption of the organics permits their separation from inorganic salts. During our studies, we put selected standards through an XAD-2 column and obtained good recovery of the standards and no extraneous peaks in the baseline of the blank. Aqueous tank liquid was placed on the column, which was washed with deionized water, and the organic components were removed with acetone. Calculation of the chromatographic peak area indicated that we had recovered 60% of the TOC. Most of the radioactive material was removed by the water wash; further concentration and analysis could be completed in a conventional, rather than a radiation, laboratory. The results of SPE for use in analysis of EPA-regulated organics seems promising, but further studies of different types of adsorbents and extraction conditions are necessary to optimize the results, particularly for very polar organics.

DETERMINATION OF LOW-MOLECULAR-WEIGHT CARBOXYLIC ACIDS

We confirmed the presence of one carboxylic acid (palmitic) in the inactive-tank samples,³ and several others were identified in the PNL studies.⁴ Additional low-molecular-weight carboxylic acids, not generally detected by regulatory GC/MS methods, could be present in our samples. Carboxylic acids smaller than seven carbons, such as acetic, butyric, valeric, isovaleric, propionic, and heptanoic, would be too volatile to be detected by our derivatization and GC method and would not chromatograph well enough for detection in the regulatory GC/MS method.

A direct-aqueous-injection GC with a column designed to detect low-molecular-weight acids (C_2 to C_7) was calibrated for these analyses. We assayed samples TH4/L057 and W3/L018, which were acidified to maintain the acids in their protonated form. None of the acids was detected with a sensitivity of ~4.0 ppm (each). It is apparent that low-molecular-weight acids do not contribute a significant portion of the TOC for the samples analyzed.

LIQUID CHROMATOGRAPHIC CHARACTERIZATION

High-performance liquid chromatography (HPLC) is more suited than GC for the analysis of highly polar, thermally labile compounds. HPLC was used as a supplement to the GC analysis on one of the regulatory SVO extracts prior to derivatization. The HPLC chromatogram (Fig. 3) shows the early elution of a large mass of relatively low-molecular-weight, highly polar material. The remainder of the chromatogram, which was recorded at ~20-fold-higher sensitivity, shows several other compounds at much lower concentrations. Some of these compounds could be the regulatory surrogate standards or internal standards that were added to the sample. HPLC may prove to be a very useful tool in the analysis of mixed waste, but further studies are needed to develop and evaluate its full potential.

MASS SPECTROMETRIC CHARACTERIZATION

Two mass spectrometric investigations were conducted to expand the organic compound characterization and determine the molecular-weight range of the compounds. The approaches taken were temperature-programmed direct-probe, quadrupole MS, and laser desorption FTMS.

Direct-probe MS was conducted with an HP-5895 quadrupole GC/MS using a direct probe programmed from 100°C (1-min isothermal hold) to 280°C at 30°C/min with positive-ion, chemical-ionization (methane) mode. Mass scans were taken at 250 to 750 amu/s from 50 to 800 amu. A 100 μ L aliquot of W3/L018 (1500 μ g/mL of TOC) was evaporated in the probe-tip cup. Only one peak was present on the mass spectrum prior to the start of the temperature program. The mass spectra resembled those of hydrocarbons with a base peak of molecular weight/charge (M/Z) 57, and major ions at M/Z of 69, 87, 97, 113, 127, 141, 155, and 169. No other peaks were observed on the mass chromatogram. The mass chromatogram of TH4/L057 (217 μ g on probe) was featureless.

The polar organics, EDTA, citric acid, and eicosanoic acid (25 μ g), were individually applied to the probe as standard solutions. All three volatilized easily from the probe tip and appeared early in the mass thermograms. We estimate that quantities as low as 2.5 μ g could be detected; thus, compounds similar to these, if present in the samples, were below this detection limit. Alternatively, the TOC in these samples could be the result of the presence of highly polar compounds not readily vaporized or sublimed from the probe tip.

More-useful characterization was obtained using laser desorption FTMS. The compounds were thermally desorbed from the probe by a laser pulse of 1064-nm light (10^6 W/cm² for "low power" and 10^8 W/cm² for "high power") by the laser. An FTMS was used in place of a quadrupole instrument. Positive- and negative-ion spectra were recorded with the FTMS.

The standards, citric acid (30 μ g), eicosanoic acid (30 μ g), and tetra-sodium EDTA (30 μ g), were analyzed to establish the performance of the system. These standards produced simple negative-ion spectra, in which the molecular ion was readily apparent as the molecular weight of intact compound minus hydrogen ($M - H$)⁻ for citric and eicosanoic acids or as the molecular weight less sodium, ($M - Na$)⁻, for the EDTA salt. For TBP (30 μ g), the negative-ion spectra showed ions at M/Z of 265 ($M - H$)⁻, 209 (M-butyl or dibutyl phosphate)⁻, 153 (M-2 butyl + H or monobutyl hydrogen phosphate)⁻, 125 (unknown), 79 (PO₃)⁻, and 63 (PO₂)⁻. The positive-ion spectra was much more complex, with interpretable ions at M/Z of 267 ($M + H$)⁺, 289 ($M + Na$)⁺, and 305 ($M + K$)⁺. Positive-ion spectra often show the ions ($M + Na$)⁺ and ($M + K$)⁺ as alkali

Fig. 3. Liquid chromatogram that suggests the highly polar nature of the organics not previously observed by GC/MS in an SVO extract of an inactive tank liquid sample.

metal adducts with Na and K, and the molecular weight increased by 23 and 39, respectively. Three other ion pairs detected suggest compounds of molecular weight 270, 398, and 446. Ions at M/Z of 155^+ , 177^+ , and 192^+ were also observed, but we cannot explain their presence or structure.

Sample TH4/L057 was characterized as the neat, evaporated sample and as an XAD-2 extract. Both the positive- and negative-ion spectra of the samples were relatively simple. The spectra were dominated by a half-dozen M/Z , which suggests that the sample is composed of a few major components and that the minor components are very low in relative concentration. Not much can be concluded about the minor components without further study using more concentrated extracts. The positive- and negative-ion spectra of the dried XAD-2 extract are shown in Fig. 4. The corresponding spectra for XAD-2 blank samples were clean, showing that the observed peaks are sample-related. Many of the ions in the negative-ion spectra were TBP-related: $265 (M - H)^-$, 209 (dibutyl phosphate) $^-$, 153 (monobutyl hydrogen phosphate) $^-$, $79 (PO_3)^-$, and $63 (PO_2)^-$. The 62 is $(NO_3)^-$. The positive-ion spectra indicate the presence of compounds with molecular weight up to 721 . Although these could include alkali metal adducts [e.g., $(M + Na)^+$ or $(M + K)^+$], there are no such obvious pairs. The results suggest that macromolecular compounds are not present and that compounds of moderate molecular weight contribute to the bulk of the sample.

TH4/L057 was also analyzed as the dried neat sample, which included considerable inorganic matter not present in the XAD-2 extract. The negative-ion spectrum showed M/Z of $35/37 (Cl)^-$, $42 (NCO)^-$, $46 (NO_2)^-$, $62 (NO_3)^-$, and $127 (I)^-$. The major ions at M/Z of 115 , 131 , 147 , and 303 are unknown. There were no indications of phosphates, and the spectra did not resemble those of the XAD extract, reflecting their different chemical character. Likewise, the positive-ion spectra were different from that of the XAD extract. The high-energy laser pulse revealed ions of M/Z of 237 , 255 (base peak, like that of the XAD extract), and 270 . The low-energy pulse produced a completely different spectrum with major ions at M/Z of 167 , 181 , 195 , 209 , 221 , 236 , and 297 . The interpretation of these spectra will require additional work, including generation of daughter ion spectra from each of these ions.

Sample W3/L018 was analyzed only as a dried residue of the neat liquid. The positive ion spectra from a high-power laser pulse showed ions of M/Z 255 (also seen for TH4/L057) and 289 . The latter is $(M + Na)^+$ for TBP. Ions of M/Z 487 and 483 also were observed. The lower energy pulse yielded major at M/Z of 129 , 181 , 195 , 209 , 236 , 255 , 270 , 289 [$(M + Na)^+$ for TBP], and 357 , which were quite unlike those of the high-energy pulse. The negative-ion spectrum showed major ions at M/Z of $63 (NO_3)^-$, $79 (PO_3)^-$, 100 , 209 (dibutylphosphate) $^-$, and 441 . The spectra were relatively simple, and evidence was found for phosphates and higher-molecular-weight compounds.

Finally, the laser desorption FTMS was applied to a dark material that had been solvent extracted from sludge sample W4/S024 during the preparation of the SVO extract. The spectra were even simpler than those of the preceding samples. The negative-ion spectrum showed ions with M/Z of 127 [exact mass measurement showed this was not $(I)^-$] and 239 . The positive-ion spectrum showed TBP [ions at 289 and 305 corresponded to $(M + Na)^+$ and $(M + K)^+$, respectively], as well as major ions at M/Z of 72 , 89 , 193 , 195 , 220 , and 417 .

MS studies show that the samples contain only a few major compounds that have molecular weights ranging up to ~ 700 . TBP and other phosphates were detected. Considerably more work needs to be done before the unknown ions can be identified; however, this technique has demonstrated its ability to provide additional information on the compounds present in the waste samples.

Fig. 4. Positive (lower spectrum) and negative (upper spectrum) ion spectra from FTMS of an XAD-2 extract of TL4/L57A. These spectra indicate a relatively small number of major organic components and larger numbers of organic in low concentration, with molecular weights ranging up to the low 700s.

CONCLUSIONS

Our studies have shown that a large number of organic chemicals not determined or detected in EPA regulatory methods can be detected and identified using various extraction and/or analytical methods. The exact compounds contributing to the bulk of the TOC remain unidentified. Our analyses suggest that they are highly polar and that several species may have molecular weights ranging up to the low 700s. Compounds associated with nuclear processing, such as chelators, extractants, complexing agents, and their simple degradation products, have been identified, but they do not appear to contribute a major portion of the TOC. Likewise, low-molecular-weight carboxylic acids and EPA Target Compound List chemicals do not appreciably contribute to the TOC. It is speculated that the unidentified TOC is composed of highly complex degradation products of tributyl phosphate and other compounds common to the industry. Degradation may have been induced by radiolysis and chemical reactions within the tanks over the last 30 to 40 years. It is obvious that further research and development are necessary. Some, and perhaps most, of these chemicals will influence the method of final disposition of the inactive mixed tank wastes.

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