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Sample preparation techniques for determining semi-volatile organic compounds in nuclear defense materials production waste

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Abstract

Extraction techniques for semi-volatile organic compounds in caustic and high-ionic-strength nuclear defense material production waste stored is presented. It was demonstrated that the nitrite ions in extracts caused degradation of chromatographic columns. Liquid–liquid extraction, ion-exchange and two types of solid-phase extraction (SPE) adsorbent supports were investigated in this study. The SPE media were styrene–divinylbenzene and alumina. Three classes of compounds were used: acids, base/neutral, paraffinic hydrocarbons and alkyl phosphates. SPE was able to extract semi-volatile organic compounds in simulated waste samples without significant carry-over of nitrate ion. Extraction yields ranged from 2.3 to 97.6% (12% R.S.D.). The range of yields for each chemical class was 0–4.1%, 6.4–79.9%, 14.3–68.3% and 91.1–97.6% for the acid, base/neutral, paraffinic hydrocarbons and alkyl phosphate compounds, respectively. Compounds of regulatory interest, organic semi-volatile acid and base neutral compounds were found to be unstable in the waste samples.

Keywords: Nuclear waste; Sample preparation; Extraction methods; Phenols; Chlorophenols; Aromatic compounds; Hydrocarbons; Alkyl phosphates

1. Introduction

The Hanford Nuclear Reservation in Eastern Washington State USA was one of the USA's primary sites for nuclear defense materials production. Nine nuclear reactors were built at the site between 1944 and 1964 for this purpose. The reactors were used to irradiate nuclear fuel and convert the uranium fuel to plutonium. After discharge from the Hanford reactors, the irradiated fuel was cooled for several weeks. The cooled fuel was dissolved in acid and the resulting solution was processed to separate the plutonium from other fission products and the remaining uranium fuel. The high-level radioactive by-products from this and

other processes were disposed of at Hanford in underground storage tanks. Hanford's high-level radioactive wastes are stored in 177 underground storage tanks which were built between 1943 and 1966. These tanks have capacities from 2000 m³ (550 000 gallon) to more than 3800 m³ (1 million gallon). The total volume of waste stored at Hanford is approximately 227 000 m³ (61 million gallon).

The chemical and radiochemical compositions of waste stored in individual waste tanks vary greatly depending on the waste's origin, subsequent processing and the degree of mixing and subsequent reactions with other waste streams. In addition to wastes from four different plutonium separation processes, the complexity of the tanks' contents is

further increased by the long period over which the waste was collected and intermittent waste treatments over the years. The waste was treated to reduce both radioactivity and volume, and to recover usable isotopes. Precipitation reactions were used to remove certain active isotopes such as ^{137}Cs . Evaporation of water was used to reduce the volume of the waste. In many cases the waste is now so concentrated that it is no longer liquid, but rather sludge and salt cakes.

Most of the organic materials contained in the waste tanks are solvents and chelating reagents that were used in the several production processes. The tanks also received waste streams which contained organic compounds, such as degreasers and cleaning solvents, from other operations at Hanford. Due to regulatory and safety considerations, the characterization of the waste tanks' contents is essential before the waste can be processed for final disposal. However, no satisfactory method has been found for all compounds from all waste tanks.

The characterization of nuclear materials production waste is challenging. Existing analytical procedures must be extended and modified, or whole new methods must be developed, to meet both chemical and radioactivity challenges. Analytical methods must meet the usual criteria of accuracy, precision, cost effectiveness and ability to defend legally other analytical methods. Procedures that are applied to radioactive waste must contain special steps and precautions to ensure that operators are not exposed to excessive levels of ionizing radiation or hazardous chemicals, and to minimize the volume of mixed radioactive/hazardous waste generated during analysis. It is also desirable that the methods include precautionary measures that reduce the amount of radioactive contamination of expensive instruments. Frequently, the methods must be performed on waste samples that are chemically aggressive and physically difficult to manipulate.

During earlier waste tank characterization efforts, samples were evaluated for organic content by standard US Environmental Protection Agency (US EPA) gas chromatographic methods [1]. Others have investigated the determination of regulated organic compounds in radioactive waste samples at other sites [2,3]. However, the chemical nature of nuclear defense materials production waste varies so greatly

that these methods are not always applicable [4]. While performing US EPA Contract Laboratory Program procedures for the evaluation of organic compounds, two characteristics of Hanford waste samples were apparent during chromatographic evaluation: destruction of acid surrogate analytes, and shifting of chromatographic retention times to longer retention times for some compounds [5]. As per standard US EPA analytical procedure, surrogate analytes were added to the sample prior to extraction to evaluate extraction efficiency. The loss of surrogate analytes, which include 2-fluorophenol and [$^2\text{H}_5$]phenol (phenol- d_5), has been attributed to nitration of the surrogate during extraction [6]. This was attributed to the high nitrate and nitrite content of the sample. Some of the nitration products have been identified. The shift in chromatographic retention times, however, did not seem to be directly related to the nitration of the analyte, even though some of the compounds that are affected were also nitrated. The retention time shift was attributed to material present in the sample which caused the effect when introduced into the analytical instrumentation.

An example of these effects can be found in the determination of the surrogate phenol- d_5 . A surrogate in this sense is a compound, which behaves like the compounds of interest, added to the sample to evaluate the extraction efficiency. In some samples, the nitration of phenol- d_5 to 2-nitrophenol- d_4 occurred, eliminating the GC-MS response for phenol- d_5 . Chemical degradation of the analyte by matrix components must be taken into account when determining the efficiency of an extraction technique. An analysis of a phenol standard, after a Hanford waste sample had been run, showed the phenol retention time had increased but the mass spectrum of the phenol was unchanged; indicating the chromatographic system itself had been altered by the components of the extract.

Chemical separation problems associated with organic compound determination are independent of the radioactive nature of the sample. Thus, a non-radioactive analog of the waste was prepared to reduce the exposure incurred by the analyst. The chemical make-up of this simulated Hanford waste (SHW) analog was based on past characterization of the inorganic components of the waste tanks.

The goal of this work was to extract organic compounds from liquid nuclear materials production wastes stored at the Hanford Nuclear Reservation for subsequent analysis. To achieve this goal two criteria, in addition to sufficient extraction of analytes, must be met: avoiding both the nitration of the organic analytes, and the degradation of the chromatographic column. An additional difficulty in the analysis of Hanford defense waste is radioactivity. Sample sizes must be kept small to reduce the dose of ionizing radiation acquired by the analyst. Small sample sizes require that analytical methods employed be sufficiently sensitive.

2. Experimental

2.1. Materials

2.1.1. Simulated Hanford waste

Simulated Hanford waste (SHW) was prepared by dissolving 320 g NaOH (Aldrich, Milwaukee, WI, USA), 840 g $\text{Na}_2\text{Al}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ (Spectrum, Gardena, CA, USA), 1100 g NaNO_3 (GFS, Powell, OH, USA), 770 g NaNO_2 (Mallinkrodt, Paris, KY, USA) in 4 l organic free water. In a separate container, 220 g NaCO_3 (J.T. Baker, Phillipsburg, NJ, USA) was dissolved in 600 ml organic-free water. The solutions were combined, mixed and stored in a polyethylene bottle.

Solutions of saturated NaNO_3 and NaNO_2 were also prepared, using the same materials described above.

The SHW and the saturated salt solutions were spiked with the surrogate and matrix spike organic compounds listed in US EPA SW-846, method 8270A [7]. Standards, analytes and internal standards were obtained from Restek (Bellefonte, PA, USA) as stock solutions (1000, 1500 or 4000 $\mu\text{g}/\text{ml}$) of each of the analyte compounds in either dichloromethane (DCM) or methanol. Compounds were added to the SHW in four mixtures: base/neutrals surrogates (1,2-dichlorobenzene, nitrobenzene, 2-fluorobiphenyl, terphenyl), base/neutral matrix spike compounds (1,4-dichlorobenzene, acenaphthene, N-nitroso-di-*n*-propylamine, 1,2,4-trichlorobenzene, 2,4-dinitrotoluene) both at 1 $\mu\text{g}/\mu\text{l}$ and acids surrogates (2-fluorophenol, phenol, 2-chlorophenol) and acid

matrix spike compounds (phenol, pentachlorophenol, 4-nitrophenol, 4-chloro-3-methylphenol, 2-chlorophenol) both at 1.5 $\mu\text{g}/\mu\text{l}$. The internal standard mixture (1,4-dichlorobenzene, naphthalene, acenaphthene, phenanthrene, chrysene, perylene) was added to each 1-ml extract solution from a 4.0 $\mu\text{g}/\mu\text{l}$ stock solution to the extracts in 10- μl injections with a 10- μl syringe.

Simulated Hanford waste was spiked to a concentration of 20 $\mu\text{g}/\text{ml}$ with standard solutions at concentrations of 50 mg/ml for decane, dibutylbutylphosphonate (DBBP) and tributylphosphate (TBP), and 25 mg/ml for undecane, dodecane, tridecane and tetradecane. Standard solutions of decane, DBBP and TBP were prepared by dissolving 500 mg of each analyte in 10 ml methanol. The standard solutions of undecane, dodecane, tridecane and tetradecane were prepared by dissolving 500 mg of each analyte in 20 ml methanol. These concentrated solutions were used to spike both water and simulated Hanford waste.

2.1.2. Acids and solvents

HNO_3 and HCl, used to titrate and adjust the pH of the SHW, were obtained from J.T. Baker and diluted in deionized water to the desired concentration. Organic solvents were obtained from Aldrich (DCM) and J.T. Baker (methanol, hexanes).

2.2. Methods

2.2.1. Solid-phase extraction

The solid-phase extraction (SPE) materials used were SPE-ed ARP sorbent, (Applied Separations, Allentown, PA, USA) and polydivinylbenzene Empore disks (3M, Minneapolis, MN, USA). SPE-ed ARP is a reversed-phase sorbent designed to resist high pH environments. The sorbent is wide-pore alumina (30–200 nm) coated with a reversed-phase sorbent cross-linked co-polymer, particle size 50 μm . The sorbent was rinsed with methanol and water prior to extraction. The polydivinylbenzene Empore disks were rinsed with DCM, methanol and water prior to extraction. In both cases, the liquids were pulled through the SPE material with a light vacuum. A 5.0-ml sample of SHW was placed on top of the SPE material and drawn through the material

at a rate of 2 ml/min. The solvent rinses and the extracted sample were discarded.

To elute the extract from the alumina material (SPE-ed ARP), the sorbent was extracted with DCM. A test tube was used to collect the extract as it eluted from the SPE material. The Empore disks were extracted with supercritical CO₂. Internal standards were added to the 1-ml extract solutions prior to analysis.

2.2.2. Supercritical fluid extraction

The SFE conditions were: 40.5·10⁶ Pa, 100°C, CO₂ modified with 250 µl DCM. The modifier was placed into the cell along with the sample. The SFE system was an ISCO (Lincoln, NE, USA) SFX with a 260D syringe pump. The extraction cell (10 ml) containing the Empore SPE disk was filled with inert glass beads to fill the remaining space. Extraction times were 5 min static followed by 30 min dynamic with a flow-rate of 0.25 ml/min measured at the pump. Pressure was maintained in the cell with a 20 cm×50 µm fused-silica restrictor. The solvent trap was 1.5–2 ml DCM. The solvent was evaporated to 1 ml with carbon dioxide from the flow restrictor

2.3. Determinations

An Orion Model 93-07 nitrate electrode and an Orion 'sure-flow' Ross reference electrode were used to determine the nitrate concentration before and after the sample was treated with an ion-exchange material. KNO₃ solutions (0.1, 0.1 and 0.01 M; J.T. Baker) were used as standards.

2.4. Quantification

Organic compounds were separated by capillary GC and determined with flame ionization detection (FID). The system, which consisted of an HP 5890 series II GC system with a split-splitless injector, DB-5.625 (J&W Scientific, Folsom, CA, USA), a 30 m×0.32 mm column and an HP 3396A integrator (Hewlett-Packard, Avondale, PA, USA), was calibrated for the semi-volatile surrogates and matrix spike compounds. Chromatographic conditions were: initial column temperature, 40°C held for 5 min, ramp at 4 °C/min to 320°C, He carrier gas at 7 p.s.i.

(1 p.s.i.=6894.76 Pa) head pressure, injector temperature 200°C, detector temperature 275°C. Calibration was based on a single point calibration relative to an internal standard, naphthalene-d₄. The internal standard was present in the calibration mixture and sample at 40 µg/ml. The semi-volatile compounds were present in the calibration mixture at 75 µg/ml and 50 µg/ml for the acids and base neutrals, respectively. The injection volume was 1 µl.

3. Results and discussion

3.1. Titration of simulated waste

The purpose of titrating the SHW was to determine the physical behavior of the waste at various pH levels. Adjustment of pH is standard practice in the extraction of acidic organic compounds from aqueous solutions. A 25-ml aliquot of the SHW was titrated with 8 M HNO₃. The resulting titration curve is shown in Fig. 1. The SHW, as received, was clear and colorless, although somewhat viscous. The pH of the SHW was 13.7. Addition of strong acid (both HNO₃ and HCl) during the titrations caused the evolution of a brown gas, presumably nitric oxides. As the pH was lowered to the 13.5–12.5 range, a white gelatinous precipitate formed. In the pH range 11.5 to 2.0, a white solid precipitate dominated, along with continued evolution of nitric oxides and a colorless gas (presumably CO₂). The amount of solid was so great the solution became a thick slurry. The stirring rate was increased to keep the stir bar in motion. The gas evolution and the thickened solution caused some foaming which required vigorous stirring to control. Below pH 2.5 most gas evolution had stopped and the slurry became milky white and thinner. Below pH 1.5 the solution was clear and slightly blue in color.

The evolution of nitric oxides indicates that the waste sample is a strong nitrating agent in the presence of acids, confirming the earlier observation that acidification and extraction of the sample results in nitration of organic compounds. It is desirable to extract at basic or neutral pH values to avoid nitration of the analytes. The large amount of thick

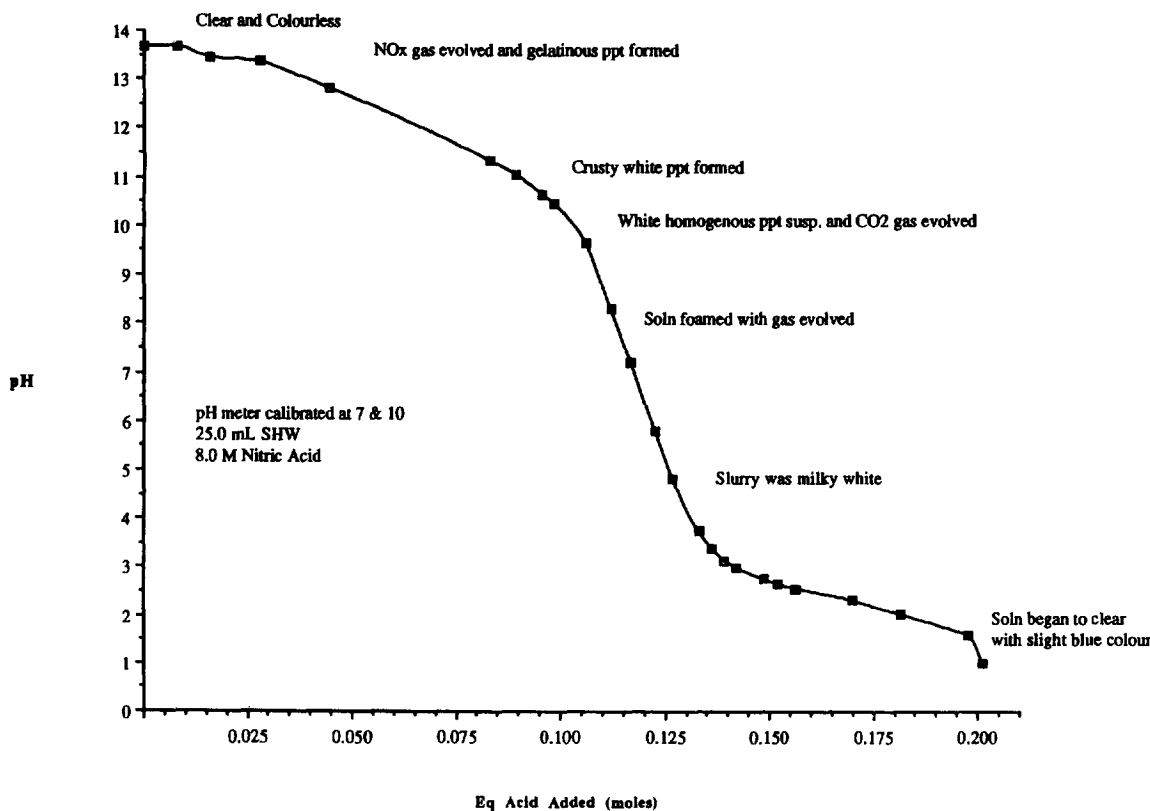


Fig. 1. Titration of a 25 ml aliquot of simulated Hanford waste (SHW) with 8.0 M nitric acid.

precipitate complicated filtration and SPE of the sample at basic and neutral pH values.

3.2. Liquid–liquid extraction

The waste samples contained a high concentration of inorganic salts, which may have contributed to the analytical difficulties discussed above in the background section. To investigate the partitioning of salts into DCM extraction solvent during a liquid–liquid extraction, SHW was extracted, as received (pH > 13) with DCM in a separatory funnel. The contents (25 ml DCM and 25 ml sample) were shaken for 1 min, then allowed to separate into the respective phases, DCM on top. A clear meniscus formed between the two clear phases. The bottom, aqueous phase, was drawn off and discarded, the top DCM layer was drained into a weighed vessel and placed in a 100°C oven for 1 h to evaporate the DCM and leave any dissolved salts. The vessel was

weighed a second time to obtain the mass of the white solid remaining in the vessel. The procedure was repeated with the same results.

The density of the SHW was measured and found to be 1.39 g/ml, indicating 4 g of the original 10-ml waste solution was dissolved material. The data indicated that 3% (120 mg) of the total salt in the SHW sample partitioned into the DCM extract. The organic content of a sample was about 1000 µg (using the semi-volatile surrogates as examples). This meant that the inorganic material transferred from the sample could be present in a 100-fold higher mass than the organic analytes of interest.

This large presence of inorganic species in the DCM extracts could be the source of some of the chromatographic problems seen in previous analyses of Hanford waste samples. If enough of the nitrate and nitrite from a sample was carried by an extract to the analytical column, nitration of the chromatographic stationary phase could have occurred.

3.3. Ion-exchange

Two quaternary amine ion-exchange media were investigated for their ability to remove nitrate ions from the SHW. The first was a Dowex material which consisted of a styrene polymer support to which quaternary amine groups were bound. The strongly basic sample destroyed the styrene material support and flushed the support out of the ion-exchange column. This material was unusable due to degradation of the polymer by SHW samples.

The second material investigated was a silica support to which quaternary amine groups were bound. The nitrate concentration (0.5 M) in the sample was determined to be 40% lower than in the original SHW (0.8 M), after a sample had passed through the ion-exchange material. Although a significant reduction, the inorganic material in a standard liquid–liquid extraction could still be as much as 60-times the mass of organic analytes. The reduction was not judged adequate for the purpose of this investigation.

3.4. Solid-phase extraction

Empore disks have a large surface area (47 mm) compared to the 1 cm diameter syringe barrel which houses the alumina reversed-phase sorbent material. Sample must be acidic to efficiently extract acidic phenols. However, the waste at acidic conditions is a thick slurry. The large surface area of the Empore disk allowed a sample with large amounts of suspended solids to pass through the SPE material without plugging. The lower surface area alumina reversed-phase sorbent SPE cartridge plugged easily when extracting acidic samples with large amounts of suspended solids. However, at acidic pH values Hanford waste is a powerful nitration agent [7].

3.5. Empore SPE disks

Results of three extractions with Empore SPE disks are shown in Table 1: (1) Extraction of an aqueous solution saturated with NaNO_3 at pH 2, (2) SPE of an aqueous solution saturated with NaNO_3 at pH 2 and (3) extraction of SHW adjusted to pH 3. The saturated sodium nitrate solution extract was colorless, as was the disk after extraction, and no

degradation of the disk was observed. The acidic nitrite solution degraded the disk, and the disk turned green as the sample passed through it. Presumably, the green color was due to nitroso compounds formed by the reaction of the acidic and nitrite-rich sample with the styrene based SPE support. The disks were eluted in the same way with supercritical CO_2 and DCM. During elution of the analytes, with both elution solvents, the disk turned orange where it was green before. The liquid extract was also orange. In both cases it was presumably due to nitro compounds. A fine grained precipitate was eluted into the extraction solvent. The fine material was allowed to settle and the supernatant liquid was drawn off with a pipette. The supernatant submitted for GC analysis was clear and orange. An attempt to avoid degradation of the disk by the solution was made by cooling the solution to 10°C before acidification and extraction. However, the effects of the sample on the disk were the same at the colder temperature. The SHW extraction showed the same discoloration effects on the disk as the nitrite solution. The aggressive nature was, in most part, attributed to the nitrite content of the Hanford waste.

The recoveries of the analytes in these extractions are given in Table 1. The recoveries, 47–124% for the acid and 43–115% for base and neutral compounds, easily meet the requirements given in US EPA SW-846 for extraction from the saturated NaNO_3 solution. The precision is also acceptable with a 16.1% relative standard deviation (R.S.D.) for the acids, and 4% R.S.D. for the base/neutral compounds. However, the yields were much lower when a solution which was saturated with NaNO_2 was extracted; 17–85% for the acids and 15–90% for the base/neutral compounds. Almost none of the analytes were recovered in the case of extraction from SHW. Chemical degradation of the disk, as evidenced by the color change, is thought to be the cause. Further, the lower yields in the case of the SHW indicate nitrite is not the only cause of the degradation in this case.

3.6. Reversed-phase sorbent alumina

Initial attempts using silica-based SPE were unsuccessful due to degradation of the silica SPE material by the SHW sample. Alumina is much more

Table 1
Recoveries of acid and base/neutrals compounds with a polydivinylbenzene SPE disk

	Recovery (%)			
	Nitrate solution (pH 2)	R.S.D. ^a (%)	Nitrite solution (pH 2)	SHW (pH 3)
<i>Acids (30.0 µg/ml)</i>				
2-Fluorophenol	89.7	7.9	23.5	N.D. ^b
2-Chlorophenol	124	19	85.2	2
Phenol	68.8	14.4	25.8	1
Phenol-d ₅	70.6	5.0	16.5	N.D.
2-Chlorophenol	101	N.D.	65.6	2
4-Chloro-3-methylphenol	114	25	73.3	7
Pentachlorophenol	46.7	41.1	37.9	5
Average	87.8	16.1	46.8	2
<i>Base/neutrals (20.0 µg/ml)</i>				
1,2-Dichlorobenzene	42.6	8.8	6.0	N.D.
N-Nitro-di-N-propylamine	115	7	9.0	7
Nitrobenzene	72.1	2.6	57.2	5
1,2,4-Trichlorobenzene	52.5	9.3	55.1	N.D.
2-Fluorobiphenyl	77.9	2.1	81.1	4
Acenaphthene	78.1	4.6	62.3	6
2,4-Dinitrotoluene	91.3	2.0	48.5	5
Pyrene	67.4	N.D.	15.6	8
Terphenyl	76.7	N.D.	16.9	8
Average	74.8	4.0	54.1	5

^a R.S.D. (%) for sample $n=3-5$.

^b N.D., not detected.

resistant to basic solutions than silica. Fig. 2 shows a chromatogram of an SPE extract (lower) prepared with the reversed-phase sorbent alumina sorbent relative to a calibration mixture (upper). GC-FID analysis indicated that an average of 3.2% of the eight phenolic acids and an average of 40% of the nine base/neutral compounds were recovered. Table 2 (columns two and three) lists the recoveries and R.S.D. values of the individual compounds. The recoveries were below detection limits; 4% for the acids and 6–80% for base/neutral compounds. The extraction of phenols was not successful. This is likely due to the high pH of the sample. However, the base/neutral compounds were recovered at the high pH in acceptable quantities and with reasonable precision.

The low recovery of phenolic acids is not surprising considering the pH of the sample is higher than 13.5. Attempts to extract the sample at a neutral pH were made. The pH adjustment produced the thick white precipitate seen earlier in the titration of the

waste. At neutral pH values the sample and precipitate slurry was too thick to be drawn through the SPE cartridge. At lower pH values than neutral, nitration of the phenolic compounds has been observed [7]. This nitration defeats the pH adjustment.

Table 3 shows the recovery of the base and neutral compounds, from caustic SHW, compared to the requirements of the US EPA SW-846 method 8270A. The extraction method for the base/neutral compounds meets the criteria in two cases and failed once when compared to the water criteria. The larger and less polar compounds, 2-fluorobiphenyl and terphenyl-d₁₄, were recovered in greatest amounts, presumably due to the lipophilic nature of these compounds.

In addition to the organic compounds addressed thus far in this study, other organic compounds are also of interest in the remediation of the Hanford waste. These compounds include chelators and paraffinic hydrocarbons used in plutonium production and processing. Results of the same SPE procedure

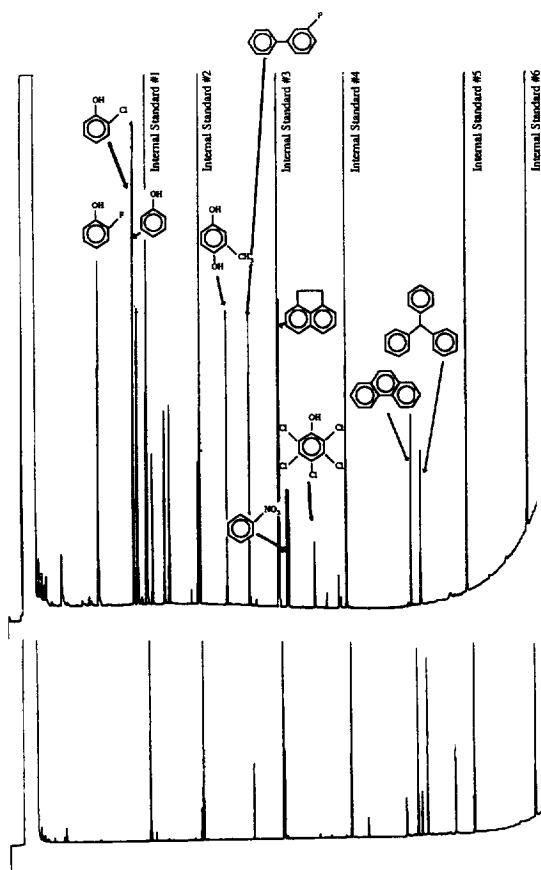


Fig. 2. GC chromatogram of calibration mixture (top) and solid phase extract (bottom) of simulated Hanford waste (SHW). Chromatographic conditions were: initial column temperature, 40°C held for 5 min, ramp at 4 °C/min to 320°C, He carrier gas, injector temperature 200°C, detector temperature 275°C. Calibration was based on a single-point calibration relative to an internal standard, naphthalene. The internal standard was present in the calibration mixture and sample at 40 $\mu\text{g}/\text{ml}$. Analytes were present in the calibration mixture and the SHW at 75 $\mu\text{g}/\text{ml}$ and 50 $\mu\text{g}/\text{ml}$ for the acids and base/neutrals, respectively.

applied to a SHW sample spike with alkanes and alkyl phosphates are given in Table 4. The recoveries were in most part acceptable, although the recovery of the non-volatile alkanes were low. The low recoveries of the light hydrocarbons was attributed to the relatively high volatility. It is possible that they were lost during the drying of the SPE cartridge before elution with DCM solvent. Drying times varied from 15 min to less than 1 min. Little difference in the recoveries was seen. The reversed-phase sorbent coating on the alumina sorbent may

Table 2

Recoveries of acid and base/neutral compounds from SHW using a reversed-phase sorbent alumina SPE cartridge

	Recovery (%)	
	Extraction No. 1	R.S.D. ^a (%)
<i>Acids (75.0 $\mu\text{g}/\text{ml}$)</i>		
2-Fluorophenol	4.1	3.9
2-Chlorophenol	N.D. ^b	
Phenol	N.D.	
Phenol-d5	N.D.	
2-Chlorophenol	N.D.	
4-Chloro-3-methylphenol	2.3	
4-Nitrophenol	N.D.	
Pentachlorophenol	N.D.	
Average	3.2	
<i>Base/neutrals (50.0 $\mu\text{g}/\text{ml}$)</i>		
1,2-dichlorobenzene	12.5	5.7
N-Nitro-di-N-propylamine	6.4	14.4
Nitrobenzene	7.5	2.9
1,2,4-Trichlorobenzene	44.0	2.1
2-Fluorobiphenyl	63.3	6.8
Acenaphthene	79.9	16.4
2,4-Dinitrotoluene	47.0	14.5
Pyrene	39.1	22.5
Terphenyl	62.1	22.6
Average	40.2	11.9

^a R.S.D. (%) for sample $n=3-5$.

^b N.D., not detected.

also not have extracted these light and non-adsorptive compounds efficiently.

3.7. Degradation of organic compounds

The low recoveries may only, in part, be due to poor partitioning of organic compounds into the SPE materials. The chemically aggressive SHW may also have degraded the compounds of interest. A portion of simulated Hanford waste was spiked with acid,

Table 3

Comparison of SPE yields to recovery limits specified in EPA SW-846 Method 8270A

Compound	Recovery (%)	From water	From soil
<i>Base/Neutrals</i>			
1,2-Dichlorobenzene	12.5	—	20–130
Nitrobenzene	7.5	35–114	23–120
2-Fluorobiphenyl	63.3	43–116	30–115
Terphenyl-d ₁₄	62.1	33–141	18–137

Table 4
Recovery for SPE from spiked simulated Hanford waste

	Average recovery (%)	R.S.D. ^a (%)
<i>Hydrocarbons</i>		
Decane	14.3	13.3
Undecane	25.8	25.6
Dodecane	46.3	17.9
Tridecane	68.3	6.4
Tetradecane	59.3	11.3
<i>Alkyl phosphates</i>		
DBBP	91.1	13.4
TBP	97.6	12.3

^a R.S.D. (%) for sample $n=3-5$.

and base and neutral compound matrix spike and surrogate compound mixtures. The spiked waste immediately became bright yellow. Mixing tests showed that the yellow color was due to the components of the acid matrix spike mixture (pentachlorophenol, phenol, 2-chlorophenol, 4-chloro-3-methyl phenol, 4-nitrophenol) rather than the other spiking solutions, the methanol solvent they were delivered in, or the Nalgene bottle in which the spiked sample was prepared.

Table 5 shows the results of extraction of freshly spiked SHW compared to the same procedure carried out on the same sample nine days later. If the sample was extracted within a few hours of being spiked with organic compound, extraction recoveries ranged from 6–80% for the base/neutral compounds. However, if the sample is stored for nine days, even at

4°C, few of the base/neutral compounds remain. Of the nine base/neutral compounds, for which reasonable recoveries could be expected, only three were consistently seen after nine days. The three compounds which were seen, acenaphthene, pyrene and terphenyl, are also the most chemically stable analytes, unsubstituted aromatics.

The destruction of the analytes, which were spiked into the waste mixture, by the mixture itself brings up the question of whether these types of compounds can exist in the Hanford tank waste as native analytes. The data presented here indicates that compound classes such as the acid and base/neutral compounds specified in regulatory documents are not stable, even under controlled conditions, in the Hanford waste.

4. Conclusions

Four separation techniques were investigated; liquid–liquid extraction, ion-exchange, and two types of solid-phase extraction. Investigation of liquid–liquid extraction, currently being used for analysis of Hanford waste, indicated that some inorganic material was being partitioned into the organic extract of a liquid–liquid extraction. This inorganic material was then injected into CG columns, destroying them. Ion-exchange columns hold some potential for removing the nitrate ion prior to extraction; however,

Table 5
Effect of aging on the recovery of organic analytes from simulated Hanford waste samples

	Recovery (%)			
	Extraction of fresh SHW	R.S.D. ^a (%)	Ext of aged (9 days) SHW	R.S.D.(%)
<i>Base/ neutrals (50 µg/ml)</i>				
1,2-Dichlorobenzene	12.5	5.7	N.D. ^b	
N-Nitro-di-N-propylamine	6.4	14.4	N.D.	
Nitrobenzene	7.5	2.9	N.D.	
1,2,4-Trichlorobenzene	44.0	2.1	3.5	
2-Fluorobiphenyl	63.3	6.8	N.D.	
Acenaphthene	79.9	16.4	22.4	20
2,4-dinitrotoluene	47.0	14.5	6.0	
Pyrene	39.1	22.5	31.6	30
Terphenyl	62.1	22.6	41.4	0.01
Average	40.2	11.9	11.7	16.7

^a R.S.D. (%) for sample $n=3-5$.

^b N.D., not detected.

the extent of removal is inadequate for protection of the GC column. The best results were achieved with an alumina-based reversed-phase sorbent SPE. This technique recovered the base/neutral analytes, alkanes and alkyl phosphates without co-extracting the inorganic interferences which have caused trouble in the past. No satisfactory separation method was found for the acidic analytes, in part because the compounds specified in regulatory documents are not stable in the Hanford waste.

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