ANALYSIS OF REGULATORY ORGANIC COMPOUNDS IN HANFORD TANK WASTES

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ABSTRACT

At the Hanford Site in southeastern Washington, there are 177 underground storage tanks that contain approximately 54 million gallons of high-level radioactive waste. The U.S. Department of Energy (DOE), Washington State Department of Ecology (WDOE) and the U.S. Environmental Protection Agency (EPA) have entered into the Hanford Federal Facility Agreement and Consent Order (Tri-Party Agreement) under the Resource Conservation and Recovery Act of 1976 (RCRA) and the Washington Hazardous Management Act of 1976 (HWMA) to address the treatment and disposal of these wastes. The tank waste is designated as listed, characteristic, and criteria waste under RCRA and HWMA. To ensure compliant treatment, storage, and disposal of the waste, including requirements for meeting land disposal restrictions, delisting, and risk assessment, characterization data are needed for the tank waste. Through the Data Quality Objectives (DQO) process, DOE and WDOE have defined and documented characterization needs for the single shell tanks (SST) and double-shell tank (DST) waste.

The selection of regulated analytes to be measured in DST and SST waste was included in the DQO process. Through the process, the analyte list was reduced to 125 organic components consisting of volatiles, semivolatiles, PCBs, organic acids, and pesticides. Examples of volatile components on the list include styrene, cyclohexanone, and n-pentane. Pyridine, benzo(a)pyrene, and nitrobenzene are examples of semivolatile components. Aldrin, endrin, and toxaphene are examples of pesticides.

Waste samples from Tanks AN-107 and AW-101 were analyzed for the regulatory organic components In addition, the samples were also analyzed for dioxins and furans. The results of the regulatory analyses and chelator analysis on these tank wastes will be discussed.

INTRODUCTION

The Hanford Site has 177 underground storage tanks that contain approximately 54 million gallons of high-level radioactive waste. The U.S. Department of Energy (DOE), Washington Sate Department of Ecology (WDOE), and the U.S. Environmental Protection Agency (EPA) have entered into the Hanford Federal Facility Agreement and Consent Order (Tri-Party Agreement or TPA) under the Resource Conservation and Recovery Act of 1976 (RCRA) and the Washington Hazardous Waste Management Act of 1976 (HMWA). Under the RCRA and HWMA, the tank waste is designated as listed, characteristic, and criteria waste. Characterization data are needed for the tank waste to ensure compliant treatment, delisting, and risk assessment. The DOE and Ecology through Data Quality Objectives (DQO) process have defined and documented (1) characterization needs for the Hanford Site single-shell tank (SST) and double-shell tanks (DST) waste.

The characterization defined in the Regulatory DQO will require the use of regulator approved methods. Ecology and DOE have agreed to an approach for providing the technical basis required for selection and validation of modified analytical methods. In addition, the DQO also defined the organic and inorganic components for analysis. Through the process, the analyte list was reduced to 125 organic components consisting of volatiles, semivolatiles, PCBs, organic acids, and pesticides. Examples of volatile components on the list include styrene, cyclohexanone, and n-pentane. Pyridine, benzo(a)pyrene, and nitrobenzene are examples of semivolatile components. Aldrin, endrin, and toxaphene are examples of pesticides.

This paper presents the organic analytical results for "as received" AW-101 and AN-107 tank waste materials. The organic analysis results obtained from the "as received" tank waste materials may be used to support the delisting and permitting activities, as well as to provide limited characterization information for subsequent process testing. Based on the sampling and storage history of the samples, preservation or refrigeration of the "as received" samples was not performed. Also, hold times specified by USEPA SW-846 protocols had expired prior to receiving the samples. The method detection limit (MDL) for the analytes of interest was significantly impacted by the limited quantity of sample available for analysis. However, wherever possible the analytical protocols follow SW-846 guidelines. The concentrations of spiking solutions and choice of extraction solvents are based on SW-846 methods.

For each of the tank waste materials, the individual "as received" shipping bottles were composited, homogenized, and sub-sampled for organic, radiochemical and inorganic analysis in the High Level Radiation Facility (HLRF). Three 125-mL glass bottles of each of the tank waste materials were sub-sampled to support organic analysis activities, and transferred under chain-of-custody (COC) to the Shielded Analytical Laboratory (SAL) hot cells for organic analysis preparations and distributions.

The supernatant and solids were analyzed for volatiles, semivolatiles, pesticides, polychlorinated biphenyls (PCBs), organic acids, and dioxins and furans. The analytical methods for analysis followed SW-846 whenever possible.

RESULTS

Volatiles

AW-101

A few target compounds were detected in the AW-101 supernatant. Only 1,4-dioxane, acetone, and tetrahydrofuran were found at levels greater than 150 µg/L. 2-Butanone, 2-butenal and chlorodifluoromethane were detected at trace levels. Chlorodifluoromethane was detected in the storage blank (used as the method blank in the analysis sequence), and is likely due to contamination from the walk-in refrigeration unit that the samples were stored in after removal from SAL. 1-Butanol and 2-ethyl-1-hexanol were detected in the sample and sample duplicate and measured as TICs. These compounds are likely decomposition products of tributylphosphate and bis(2-ethylhexyl)phosphate. These compounds were used at Hanford in the PUREX and B-Plant extraction processes and are common to many of the tank wastes.

The AW-101 solids samples contained a greater number of target analytes. 1,4-Dioxane, acetone, tetrahydrofuran, 2-butanone, 3-heptanone, acetone, butane, heptane, hexane, nonane, octane, pentane were all found at levels greater than 90 µg/kg. 2-Hexanone, 3-methyl-2-butanone, 4-heptanone, 4-methyl-2-pentanone, acetonitrile, benzene, methylcyclohexane, ethylbenzene, xylenes, and chlorodifluoromethane were detected at trace levels. The AW-101 solids had a large number of TICs, including 1-butanol, 2-ethyl-1-hexanol, undecane, dodecane, tridecane, and various other alkanes, alkenes and alcohols. It is interesting to note that the TIC data for AW-101 solids contain 1-butene and 2-methyl-1-propene. Like butane, these compounds are gases at room temperature, and not likely to be retained in the original tank material given its storage history. It is conceivable that these compounds are generated continuously from the breakdown of dodecane, tridecane, tetradecane, tributylphosphate, or 1-butanol.

AN-107

Six target compounds were detected in the supernatant. Only acetone, and acetonitrile were found at levels greater than 70 µg/L. 2-Butanone, 3-heptanone, tetrahydrofuran and chlorodifluoromethane were detected at trace levels. As noted above, chlorodifluoromethane was detected in the storage blank. Butenal and 1-butanol were detected in the sample and sample duplicate and measured as TICs.

AN-107 solids sample results are similar to the supernatant result, but also include 2-heptanone, 2-hexanone, and methylcyclohexane at levels less than 15 g/kg. Tridecane, tetradecane, and 5-tridecanone were detected and measured as TICs in the AN-107 solids.

Instrument tuning check criteria and 12-hour calibration clock window criteria were met (USEPA CLP 3/90 SOW) for all initial calibration and sample analysis sequences.. The initial calibration met the criteria of USEPA SW-846 method 8260B. All five-system performance compounds (SPCC) met the criteria for minimum response factor, and all six calibration check compounds (CCC) met the maximum relative standard deviation (RSD) criteria. Six of the target analytes of interest have RSDs greater than the recommended 15%; however, none exceeded 25%. The continuing calibration check standard met the criteria of USEPA SW-846 method 8260B. All calibration check standards met the SPCC and CCC criteria. However, in comparison of the results for the continuing calibration standards to the initial calibration, a few target analytes of interest exceed the recommended percent difference (%D) of 15%.

The internal standards used in this study were difluorobenzene, pentafluorbenzene, chorobenzene-D_5, and 1,4-dichorobenzene-D_4. The surrogate compounds used were dibromofluoromethane, toluene-D_8, and bromofluorobenzene. These seven compounds were added to each blank, sample, and matrix spike sample analyzed. Evaluation of surrogate recoveries are somewhat difficult in that performance based recovery limits have not been established for this type of sample matrix. Contract Laboratory Program (CLP) limits for low-level soil samples were used as a guide.

Semivolatiles

AW-101

A few target compounds were detected in the AW-101 supernatant. Only N-nitrosodimethylamine and N-nitrosomethylethylamine were found at levels greater than 220 µg/L. Acetophenone, tributylphosphate, 1-naphthalamine, 2,4-dinitrophenol, 2-naphthalamine, biphenyl, N-nitrosopiperidine, and pentachloroethane were detected at trace levels. Pentachloroethane may be a trace contaminant in the methylene chloride extraction solvent, or a methylene chloride reaction product with the sample.

Chloroform and 1,1,2-trichloroethane are reported in the TIC results, and are likely to be reaction products or trace contaminants of the methylene chloride extraction solvent. Tetramethyl silane was found in the samples and blank, and were likely leached from the teflon lined, silicone rubber septum used in the I-Chem bottles that held the sample extracts prior to removal from the SAL. A number of organic acids, alcohols, ether-alcohols, and nitric acid esters were also detected in the AW-101 supernatant samples.

The AW-101 solids samples also contained N-nitrosodimethylamine at a level of 17000 µg/kg. N-Nitrosomethylethylamine, tributylphosphate, 1-naphthalamine, 3,3'-dimethylbenzidine, N-nitrosodibutylamine, N-nitrosomethylethylamine, and pentachloroethane were detected at trace levels.

Tridecane, tetradecane and pentadecane (used in the PUREX and B-Plant extraction processes) were among the TICs reported in the AW-101 solids A number of artifact compounds such as aldol condensation products were reported in the data.

AN-107

Twelve target compounds were detected in the supernatant. Bis(2-Ethylhexyl)phthalate, N-nitrosodimethylamine, tributylphosphate, 1-naphthalamine, 2-methylnaphthalene, 4-aminobiphenyl, biphenyl, diethylphthalate, N-nitrosodiethylamine, N-nitrosomethylethylamine, N-nitrosopiperidine, and pentachloroethane were detected at trace levels.

As with AW-101 supernatant, chloroform and 1,1,2-trichloroethane are reported in the TIC results. AN-107 supernatant TIC results contain a large number of unknowns and N-nitrosoamines. It is not clear whether these N-nitrosoamines are present in the original tank material or formed in the extraction process. Also, as noted previously, nonane was detected in all samples and blanks; however, nonane was used as a solvent for the dioxin spike solution and was added to all samples, spikes, and blanks.

Pesticides/Polychlorinated Biphenyls

No PCBs or pesticides were detected in these samples at levels above regulatory significance. Although florisil column cleanups were performed on the residues, chromatographic resolution

suffered noticeably following a number of sample residue analyses, indicating some column degradation had occurred. The observed peak broadening may have adversely impacted the retention time windows. The high surrogate recoveries for the pesticide/PCB analysis can be attributed in part to interferences. It is likely that the increased sensitivity of this method leaves it vulnerable to additional interferences. These may include the insufficient cleanup of SVOA surrogate compounds, or the addition of other spiking compounds which behavior has not been established for the method, such as octachloronaphthalene. More work is needed to determine what extent of the interferences are introduced by the method. Until then, extractions for this analysis method should be performed separately from the other fractions.

Organic Acids

The only organic acid detected in the AW-101 and AN-107 supernate was formic acid at a concentration of 2.0 mg/mL. The samples were analyzed for oxalate, formate, acrylate, and acetate. Although the samples were analyzed for acetate, acetate coelutes with glycolate and requires the use of an alternate column for separation from glycolate. However, no acetate/glycolate peak was detected in the supernatant. Without additional separation, one can not unequivocally state that the observed peak contains only acetate, only glycolate, a combination of both anions, or a possible contaminant. From tank waste and solubility studies, the results are dependent on tank waste type. In other words, for tanks with different fill histories, the analytical results may be primarily glycolate, primarily acetate, or a combination of both anions (2-6).

Oxalate (11.0 mg/g) and formate (3.1 mg/g) were detected in the AW-101 solids. Only oxalate (22.0 mg/g) was detected in the AN-107 solid samples. No organic anions of interest were detected in the blank samples. Spike recoveries for blank spikes and matrix spikes ranged from 77% to 165% and except for few cases meet the acceptance criteria of the governing QA plan.

Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans Analysis

No dioxins or furans were detected in these samples. This represents the first time high-level tank waste has been analyzed for dioxins and furans.

DISCUSSION

Volatile Analysis

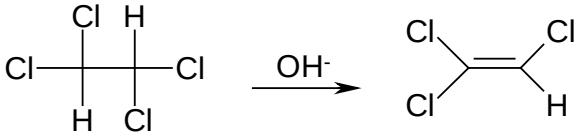
Dibromofluoromethane was poorly recovered from all of the samples, especially the AW-101 samples. It is believed this is due to the reaction of this compound with the sample matrix. The recoveries of the toluene-D_8 and bromofluorobenzene surrogates are somewhat high in all the samples and in one of the storage blanks. The reason for this is not clearly understood, but may be due to the way the spiking solution was handled within the limitations of permissible practices in radioactive contamination area (CA) fume hoods. Some concentration of the surrogate solution may have occurred due to evaporation of the methanol.

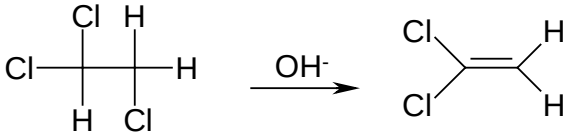
The CLP criterion for internal standard response was used (±50% of the calibration check standard response). Internal standard response met the criteria for all of the AW-101 supernatant

samples spike samples and the blank. The internal standard response for the AN-107 supernatant samples was consistently low for all of the samples and spike samples; however, the blank met the criteria. This may be a matrix effect. Due to the limited quantity of sample available, it was not possible to re-analyze the samples to confirm this effect.

The same effect was observed for the AN-107 solids samples. The AW-101 samples met the internal standard response criteria. Matrix spiking was performed by adding the methanolic calibration solution to the samples at a level of 500 nanograms per compound. The matrix spike revealed some interesting trends. The polar compounds such as acetone, 2-butanone, tetrahydrofuran, 2-pentanone, 3-methyl-2-butanone, 1,4-dioxane, 3-pentanone, 4-methyl-2-pentanone, 2-hexanone, propionaldehyde, 4-heptanone, 3-heptanone, 2-heptanone had high recoveries in the samples. Butylacetate, ethylacetate had variable recoveries. We believed the high recoveries are due to the salting-out effect of the sample matrix, relative to the calibration standard. The calibration standard is prepared using carbon filtered deionized water. Compounds that are completely or partially soluble in water are not completely purged from the aqueous calibration standard solution. Ordinarily this is not a problem as their partial recoveries are reasonably linear with respect to concentration in the solution. Since the samples are a concentrated salt solution (>20% Na^+, >20% NO_3^-), the solubility of partially soluble organics is greatly reduced, increasing their recovery by sparging.

Some chloroalkanes (such as 1, 1, 2, 2-tetrachloroethane and 1, 1, 2-trichloroethane) that were in the matrix spike solution had poor recoveries. Some chloroalkene compounds (such as 1, 1-dichloroethene and 1, 1, 2-trichloroethene) that were in the matrix spike solution had high recoveries. We believe this is due to dehydrohalogenation reactions such as:



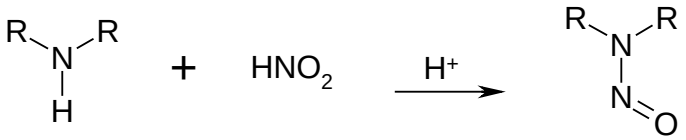


These dehydrohalogenation products were observed and previously reported (7-8).

Acrolein, acrylonitrile, 2-butenal, carbon disulfide, and chloroform had somewhat low and variable recoveries, possibly due to reactivity with the matrix. Cis- and trans- 1,3-dichloropropene had low and variable recoveries. Butylacetate and ethylacetate had variable recoveries, sometimes greater than 100% and sometimes very low. We believe that while the salting-out effect can increase the apparent recoveries of water-soluble compounds, a strong base and catalyst in the matrix may cause these esters to hydrolyze to alcohols and acids.

Semivolatile Analysis

Both AN-107 supernatant and solids samples TIC results contain a large number of nitrogen containing compounds, such as N-nitroso substituted morpholine, piperizine, and piperidine. AN-107 TIC results also contain various nitrate ester compounds, N-nitrosoamines, carboxylic acids, unknown amines, and unknowns. It is not entirely clear as how to interpret the presence of N-nitroso compounds in the samples. Both AN-107 and AW-101 samples contain large quantities of nitrite, 5.8% and 10%, respectively. Adjustment of the sample pH to 6.4 with phosphoric acid in the second part of the extraction procedure was performed in order to protonate phenolic compounds so they were extractable in the solvent. this pH adjustment could have produced some nitrous acid in isolated areas while the acid was mixed into the matrix. Secondary amines, both aliphatic and aromatic, react with nitrous acid to produce N-nitrosoamines:



Primary amines react with HNO_2 to form diazonium salts; however, these tend to be unstable and produce alkenes, alcohols and nitrogen gas.. Nitroso-compounds were also observed as artifacts in the derivatization procedure for the analysis of chelators and chelator fragments (9). The reaction of boron trifluoride (Lewis acid) in the presence of high concentrations of nitrate and nitrite produced nitroso-compounds. Subsequent analysis using thermospray liquid chromatography/mass spectrometry under basic conditions proved, under those conditions, the nitroso-compounds were artifacts produced during the derivatization process.

AN-107 solids sample results are similar to the supernatant results. 1-Naphthlyamine was detected at a level of 3700 µg/kg. Bis(2-Ethylhexyl)- phthalate, N-nitrosodimethylamine, tributylphosphate, 1,3,5-trinitrobenzene, and N-nitrosopiperidine, were detected at trace levels (all found at levels below the MDL). AN-107 solids samples TIC results contain some nitration products of surrogate spike compounds. If the pH is adjusted according to the procedure developed in 1993 by adding the acid prior to the addition of surrogates, then no nitration products were formed (10). We observed at that time nitration occurred if acid were added after the surrogates. We postulated at that time that this was due to the formation of isolated areas within the sample where the pH was too low prior to adequate mixing, particularly important for the solid samples. Analyses of these samples have underscored that requirement by showing the formation of nitrated byproducts.

Instrument tuning check criteria and 12-hour calibration clock window criteria were met (USEPA CLP 3/90 SOW) for all initial calibration and sample analysis sequences. The initial calibration met the criteria of USEPA SW-846 method 8270. All four-system performance compounds (SPCC) met the criteria for minimum response factor, and all 13 calibration check compounds (CCC) met the maximum relative standard deviation (RSD) criteria. Three of the target analytes of interest have RSD greater than the recommended 15%. Hexachlorophene had a low response (0.032) factor and high RSD (81.9%). This compound was measured only

because it was included in the commercial 8270C calibration mixture. The other two targets which had >15% RSDs were both below 30%.

The continuing calibration check standard met the criteria of USEPA SW-846 method 8270C. All calibration check standards met the SPCC and CCC criteria. However, in comparison of the results for the continuing calibration standards to the initial calibration, several target analytes of interest exceed the recommended percent difference (%D) of 15%, but with the exception of Hexachlorophene, all were below 30%.

The internal standards used in this study were 1,4-dichorobenzene-D_4, naphthalene-D_8, acenaphthene-$D_{10,}$ phenanthrene-$D_{10,}$ chrysene-D_{12}, and perylene-D_{12}. An additional internal standard, pyridine-D_5, added to each sample, spike, blank and calibration standard to quantify the earliest eluting peaks. The internal standard area criteria of -50% and +100% were not met for AW-101 supernatant, AW-101 supernatant duplicate, AW-101 solids sample, AW-101 solids duplicate, AW-101 solids matrix spike, and AN-107 solids sample. In each case the perylene-D_{12} area was low, and in some cases the pyridine-D_5 was low or not detected. These sample extracts were reanalyzed on March 3,1999 and in four cases the results were the same. In the two cases where the perylene-D_{12} area met the criteria, it was low and followed the trend of the original analysis. All of these extracts appeared slightly cloudy. We believe the low perylene-D_{12} area is the result of loss of this material due to adsorption by ultra-fine particulates in the sample extracts. These fine particulates are indicative of many tank waste materials containing precipitates. Additionally, some may have been produced by ultra-sonication. Ultra-sonication was used during the extraction of AW-101 supernatant, since the pH adjustment formed a considerable quantity of solids. Ultra-sonication was also used in the extraction of AW-101 and AN-107 solids.

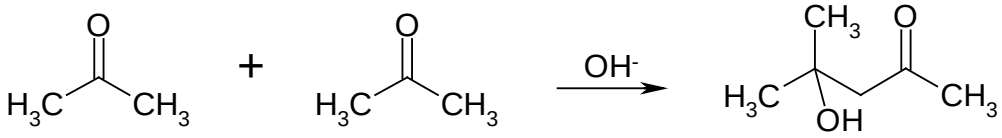
The surrogate compounds used were 2-fluorophenol, phenol-D_5, nitrobenzene-D_5, 2-fluorobiphenyl, 2,4,6-tribromophenol, and terphenyl-D_{14}. Two additional surrogates, 2-chlorophenol-D_4 and 1,4-dichorobenzene-D_4 were also added to each of the samples, spikes and blanks. These two additional surrogates were only advisory and were not included in the calibration mixture. Historical response factors were used to quantify concentrations and recoveries of these additional surrogates. Evaluation of surrogate recoveries are somewhat difficult in that performance based recovery limits have not been established for this type of sample matrix. Contract Laboratory Program (CLP) limits for low-level soil samples were used as a guide.

All phenolic surrogates were poorly recovered from all of the samples, especially the AW-101 samples. It is believed this is in part due to the reaction of these compounds with the sample matrix. One possible reaction of these compounds is the reaction of nitrous acid to form nitration products. Nitrous acid is a relatively weak acid, and some was likely formed when the pH of the samples was adjusted to 6.4 with the addition of phosphoric acid. Nitration products of 2-fluorophenol and 2-chlorophenol-D_4 were identified in the AN-107 solids samples TIC data. However, the quantity of nitration products observed would only account for a small fraction of the surrogate materials which have not been accounted for. It is believed that the majority of the remaining surrogate materials, which were added prior to the pH adjustment, are absorbed onto the relatively large surface area afforded by the precipitate formed during the addition of acid.

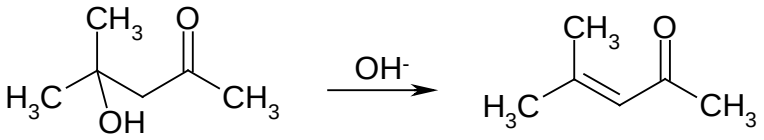
When the pH adjustment is made, a precipitate is formed at the same time acidic ionic organic species are becoming neutral. The resulting neutral species are not soluble in the aqueous environment so they "plate"out by adsorbing to the nearby precipitate. They are later not well extracted from the precipitate because of the large surface area and because they may have been encapsulated by further salt precipiation. The base neutral surrogate compounds all have acceptable recoveries.

The phenolic matrix spike compounds exhibited poor recovery in both the AW-101 solid and supernatant matrix spikes. The AW-101 solids matrix spike data exhibits the greatest number of matrix spike failures. However, performance based recovery limits for these spike compounds need to be established to access these spike recoveries. AN-107 matrix spike recoveries were generally higher. Dinoseb was poorly recovered in the supernatant, and had higher recovery from the solids spike. The phenolic matrix spike compounds exhibited the opposite trend, with higher recoveries in the supernatant.

A 1:1 methylene chloride:acetone solution was used to extract the solids samples. This solvent mixture was used to ensure that all the aqueous-wetted solids particles were wetted with the extraction solvent. Unfortunately, acetone undergoes some reactions in a hydroxide containing solutions, to produce aldol condensation products, notably 4-methyl-4-hydroxy-2-pentanone.



4-Methyl-4-hydroxy-2-pentanone undergoes further dehydration to 4-methyl-3-pentenone. This occurs only in the samples and not the extraction blank.



The presence of these aldol condensation products in the AW-101 solids sample data should not be interpreted as a positive indication of their presence in the tank sample.

The client specified a 32-component SVOA matrix spike. Several of these compounds were not included in the matrix spiking solution for various reasons. A commercial source of the various isomers of pentachloronaphthalene, hexachloronaphthalene, and heptachloronaphthalene could not be found, however octachloronaphthalene was included in the spiking solution. Equal amounts of 2-, 3-, and 4-methylphenol were used to represent cresol [CAS 1319-77-3]. Some difficulties were encountered in preparing the multi-component spiking solution. The solvent initially used to prepare the spiking solution was methanol, which is completely miscible with the aqueous sample matrix. Unfortunately, several of the spike compounds have limited solubility or are insoluble in methanol. Other solvents were added, and solvent "cocktail"

consisting of methanol, methylene chloride, diethyl ether, and acetone was used to dissolve the various compounds. After the additions of each octachloronaphthalene, pentachloronitrobenzene and dinoseb, crystallization occurred. The relative amounts of the various solvents used were adjusted in order to get the crystals back into solution. A decision was made to limit the number of components in this spiking solution in order to avoid further problems with recrystallizations from the solution. The samples were spiked with 16 of the analytes specified in the test plan, plus an additional seven that were part of the commercially available acid and base/neutral matrix spiking solutions.

ACKNOWLEDGMENTS

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CONCLUSIONS

The analytical techniques used in this study were similar to those of SW-846. However there were problems with various analytes including methylhydrazine and 1,1-dimethyl-hydrazine. Other components, such as picric acid and ammonium perflurooctanoate were also on the DQO list of analytes. Methods need to be developed and validated for these analytes. Considerable analytical methods development must be performed.

FOOTNOTES

[1] This work was conducted by Battelle Memorial Institute under contract to BNFL Inc and supported by the Department of Energy under contract DE-AC06-76RLO 1831. Battelle operates the Pacific Northwest National Laboratory for the Department of Energy.

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EXPERIMENTAL

A total of five 125-mL glass bottles of AW-101 and six 125-mL glass bottles of AN-107 were received by the SAL following compositing, homogenizing, and sub-sampling of the "as received" material in the HLRF. Of these bottles, three from each tank waste material were allocated for organic analysis. Following receipt of the samples, the contents of each of the bottles was phase separated so that organic analyses could be performed on each phase (i.e., supernatant and solids). The phase separation was performed by centrifuging and decanting the supernatant, since previous experience indicated that filtering of the samples would be extremely difficult. Each sample was centrifuged in its original bottle, and following centrifuging the supernatant was decanted to pre-labeled teflon bottles (i.e., the solids remained in the original bottle). Table I details the quantity of supernatant and solids collected from each sub-sample. The weight percent supernatant and solids values are used to recombine the results from the supernatant and solids phases into the total organic results per gram (or mL) of original tank waste slurry.

Due to the viscous nature of the tank waste material, all supernatant samples were processed by weight (i.e., sample aliquots taken by weight instead of by volume). Table II provides the density results obtained by the SAL on AW-101 and AN-107 supernatants following phase separation.

Table I. Supernatant and Solids following Phase Separation

Sample [(1)]	Lab ID	Total Mass [(2)]	Supernatant Mass (g)	Wt% Supernatant	Wet Solids Mass (g)	Wt% Wet Solids
AW-101 Comp (C)	99-0648 Supernatant 99-0650 Solids	188.2	157.6	83.7	30.6	16.3
AW-101 Comp (D)		190.7	160.0	83.9	30.7	16.1
AW-101 Comp (E)		190.1	159.3	83.8	30.8	16.2
AN-107 Comp (C)	99-0649 Supernatant 99-0651 Solids	170.4	151.2	88.8	19.2	11.2
AN-107 Comp (D)		170.8	151.4	88.6	19.4	11.4
AN-107 Comp (G)		162.5	143.4	88.2	27.4[(3)]	11.8

[(1)] Suffix ( ) represents individual bottle identification number
[(2)] Total mass remaining following phase separation activities in the SAL.
[(3)] Weights include 8.27g from stir bar. Stir bar weight subtracted prior to Total & Wt% calculation.

Table II. Density Results for AW-101 and AN-107 Supernatants

Sample [(1)]	Lab ID	Sample Density (g/mL)	Duplicate Denisty (g/mL)	Average Density (g/mL)
AW-101 Comp (C)	99-0648	1.487	1.480	1.484
AN-107 Comp (C)	99-0649	1.421	1.418	1.420

[(1)] Suffix ( ) represents individual bottle identification

Volatile Analysis

Supernatant and solids from AW-101 and AN-107 were prepared in the SAL by accurately weighing 0.3 to 1.4 g of sample into pre-cleaned, disposable, 40-mL purge vessels and adding 4 to 5 mL of water diluent. Samples, duplicates, matrix spikes, matrix spike duplicates and blanks were prepared in this manner in the SAL. Immediately following transfer under COC from the SAL to the analytical laboratories, all samples were refrigerated for preservation purposes. Prior to analyzing for volatile target compounds, spikes, internal standards, and surrogates were added

to each sample, as appropriate. Once the spikes and standards were added, the samples were loaded into the VOA autosampler for purging.

The analytical instrumentation used for VOA consists of an autosampler (Dynatech, Model PTA-30) purge and trap system (OI, Model 4560), and gas chromatograph mass spectrometer system (HP Model 5890II/5989A).

Semivolatile Analysis

Prior to performing the single extraction process for the SVOA, PCB/Pest, and Dioxin/Furans, the aliquots of the supernatants from AW-101 and AN-107 and the solids (mixed with deionized water) were titrated with phosphoric acid. The resulting titration curves are used to establish the quantity of phosphoric acid required to adjust the extracting pH to level defined by the procedure (approximately 6.5). The resulting titration curves are shown in Figure 1.

For each supernatant sample of AW-101 or AN-107 extracted, a known quantity (45 to 145 g) of sample was transferred into a teflon separatory funnel. Appropriate spikes, internal standards, and surrogates were added to the samples prior to subjecting the samples to the extraction process. The densities of the AW-101 and AN-107 samples were 1.487 and 1.421 g/mL, respectively. The pH was adjusted prior to extraction of the sample(s) with methylene chloride, but addition of the phosphate did not change the density enough to cause methylene chloride to be heavier than the sample. The extraction process left the sample at the bottom of the separatory funnel in both cases. After each shakeout and phase separation, the sample was drained from the separatory funnel and was collected in a 200 mL-Teflon centrifuge tube. The methylene chloride was then drained through a funnel containing anhydrous sodium sulfate on glass wool and collected in a 250 mL-amber-glass I-Chem bottle. The sample was then poured back into the separatory funnel for subsequent shakeouts, and the process repeated. The process was carried out in two hot cells on two samples at a time. While one separatory funnel was shaking, another was being processed as described above. The cycle time, including transfer to and from the shakeout device was about 15 minutes.

Samples of AW-101 formed significant precipitates that were separated from the supernatant by centrifuging and decanting. The extraction process was repeated on the pH-adjusted supernatant. The solids from AW-101 were further extracted using three 25-mL portions of methylene chloride. All extracts from the supernatant sample were combined and passed through a column containing an anhydrous sodium sulfate desiccant to complete the supernatant extraction process.

For each solids sample of AW-101 or AN-107 extracted, a known quantity (2.6 to 4.8g) of sample was transferred to small Teflon bottle and anhydrous sodium sulfate (pre-dried in a muffle furnace) desiccant added. Appropriate spikes, internal standards, and surrogates were added to the samples prior to subjecting the samples to the ultra-sonication extraction process. Each sample was ultra-sonicated with three 25-mL portions of a 1:1 methylene chloride:acetone mixture. Following this initial extraction, the pH of the solids was adjusted with a predetermined quantity of phosphoric acid and the ultra-sonication extraction process repeated. All extracts from the solids sample were combined and passed through a column containing an anhydrous sodium sulfate desiccant to complete the solids extraction process.

Once the extraction processes were completed in the SAL, the supernatant extracts and the solids extracts were transferred under COC from the SAL to the analytical laboratories and refrigerated prior to subsequent volume reduction processing. During the volume reduction processing, each extract was reduced in volume to 10 mL. Of this 10 mL, 5 mL was used to prepare samples for analysis of semi-volatiles. (The remainder of the extract was used preparing samples for PCB/Pest, and Dioxin/Furan analyses. The SVOA aliquot was further reduced in volume to 1 mL, and refrigerated until analysis was performed.

PCBs and Pesticides

From the original 10 mL of extract residue, a 2-mL aliquot was used for the analysis of PCB/pesticides. Additional cleanup of the 2-mL aliquot of the extract residue was performed following exchange into hexane. When residues to be analyzed by this method are splits from semivolatile extractions or are samples suspected of containing substantial interferences, then additional cleanup is performed. These are typically columns employing silica gel, alumina, or Florisil. In this case, Florisil (SW-846 Method 3620) cleanups were used. Florisil cleanup was selected because of the ease of use. Batch to batch variation in the composition of the Florisil or overloading the column may cause a change in the distribution patterns of the organochlorine pesticides. The lot number of cartridges used for this cleanup was evaluated for recovery of pesticides and PCBs and removal of unwanted polar materials before processing samples. The resulting Florisil cleaned residues were concentrated to 1 mL.

The instrumentation used for the analysis of pesticides and PCBs consists of a gas chromatograph (HP 5890) equipped with two electron capture detectors (ECDs). Both of the detectors were operated at 300° C. Injections were made on-column onto a 5 m fused silica retention gap, which was split between two analytical columns: a) 0.32 mm X 30 m DB-17 (0.25 µm phase) and b) 0.32 mm X 30 m DB-1701 (0.25 µm film thickness)

Organic Acids

Tank samples from AW-101 and AN-107 were prepared in the SAL. For the supernatants, a 1-mL sample was accurately weighed and then passed through a column of cation exchange resin to reduce the radioactivity level. Similarly for the solids, an approximate 1-g sample was accurately weighed, leached with approximately 5 mL of distilled water for 12 hours, and then filtered prior to passing the resulting solution through a cation exchange column. The activity reduction was performed according to previously published procedures. The treatment within the SAL resulted in an approximate 10-fold to 12-fold dilution (weight/weight) into a dilute caustic matrix that is not significantly different from the caustic matrix of the original sample. An additional 300-fold dilution was performed to dilute the major inorganic ions (nitrate and nitrite) to levels that prevent overloading the capacity of the analytical column. Previous experience has demonstrated that ion-exchange sites within the IC column apparently do not recover quickly from an overload of these inorganic species, which results in a non-uniform elution of the weakly retained analytes (e.g. acetate and formate).

Blank spikes, blank spike duplicates, matrix spikes, and matrix spike duplicates were prepared in the laboratory after elution through the cation exchange resin. (11). Previous studies on samples

from these two tanks have shown that organic material was neither introduced nor removed with the use of cation exchange resin. Spiking solutions were prepared using oxalic acid, sodium formate, and sodium acrylate in deionized water.

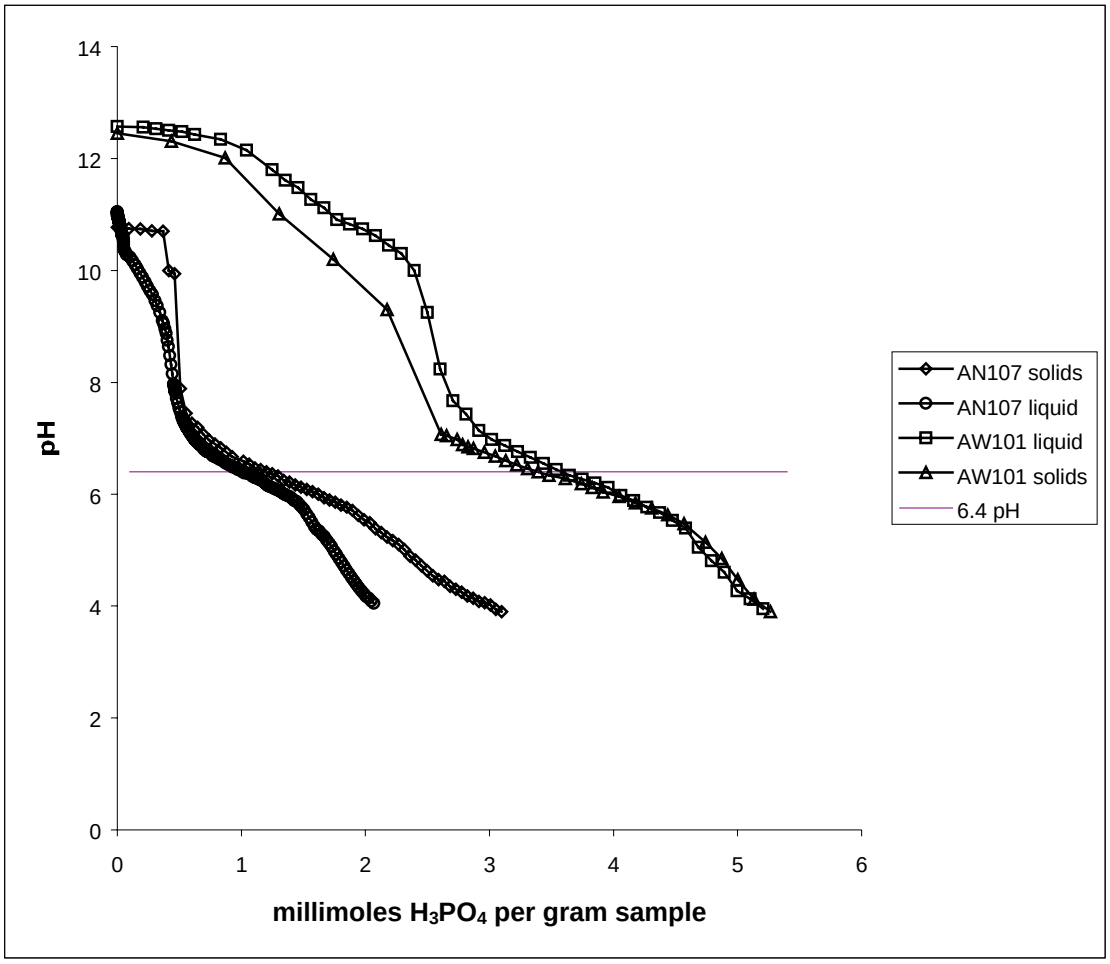

Figure 1. Phosphoric Acid Titration Curve

The analytical instrumentation used for SVOA consists of an autosampler-injector (HP 7673) and gas chromatograph (HP 5890II) mass spectrometer system (HP 5972).

The analytical instrumentation utilized for the analysis of low molecular weight organic acids consisted of an ion chromatography unit (Dionex, 500 DX) equipped with a conductivity detector (Dionex CD20). A Dionex AS-11 column and AG-11 guard column were used at ambient temperature with a 25-µL sample loop. An anion suppressor was used. The flow rate of the mobile phase was 2.0 mL/min

The IC gradient conditions were: (a) 0.0 min 0% 100 mM NaOH, 98.1% deionized water and 1.9% 5 mM NaOH, (b) 6.4 min 0% 100 mM NaOH, 0% deionized water and 100% 5 mM NaOH, and (c) 18.4 min 35% 100 mM NaOH, 0 % deionized water and 65% 5 mM NaOH. The mobile phase contained a gradient of deonized water and a weak solution of NaOH .

Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans

The methylene chloride extracts, the sub-sample fractions for dioxins/furans analysis, were exchanged in hexane. The hexane residues from both the supernatant samples and the solids samples were then processed through an extensive cleanup procedure to remove potential interfering components, primarily PCBs. The hexane extracts were first washed with sulfuric acid, KOH, and 5% NaCl in a separatory funnel. The washed hexane extract was passed through a column of anhydrous sodium sulfate. Following this water removal step, the hexane extract was applied to the top of a silica gel column and eluted with hexane. The eluate was concentrated to approximately 1 mL using a Kuderna-Danish (K-D) apparatus, and added to an alumina column. The concentrated solution was then eluted with 60% methylene chloride in hexane (v/v) and collected. The resulting eluate was concentrated to approximately 1 mL using a K-D apparatus, and then reduced to a final volume of 200 µL using nitrogen blow-down techniques for subsequent analysis using HRGC/LRMS according to SW-846 Method 8280.

The analytical instrumentation used for the analysis of dioxins and furans consists of a gas chromatograph (HP 5980)equipped with a 5 m X 0.32 mm HP retention gap (uncoated and deactivated) column followed by a RTX-5 (60 m X 0.25 mm, 0.25 µm film thickness, Restek) column. Analyses were performed using on-column injection techniques and auto sampler injections. The JEOL high-resolution mass spectrometer (HRMS) system was operated in the low-resolution mode.