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SAMPLE PREPARATION FOR SEMIVOLATILE ORGANICS
ANALYSIS OF HANFORD SINGLE-SHELL TANK WASTE WITH
HIGH NITRATE/NITRITE AND WATER CONTENT

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EXECUTIVE SUMMARY

The analysis of single-shell tank (SST) samples for semivolatile organic compounds by gas chromatography with mass spectrometric detection (GC/MS) often has problems with low recovery of a few acid surrogate and matrix spike compounds. Additionally, the GC column performance degraded because of the analysis of some of these samples. Analysis of some samples with low recoveries of acid surrogate and matrix spike compounds showed the presence of nitrated products of those acids. Poor acid recoveries were observed for other samples, but with no evidence of nitrated acid spike compounds. In addition, an immiscible second organic phase was formed in the process of concentrating the organic solvent used for extracting a number of the samples. Poor chromatography usually occurred when the second organic phase was noted during the concentration step. These problems often resulted in failed quality control parameters and time consuming instrument recovery operations. Difficult sample matrices and the inability of the sample preparation procedures to properly process these samples resulted in the problems. The procedures are based on the U.S. Environmental Protection Agency (EPA), Contract Laboratory Program, Statement of Work (CLP SOW).

A project was initiated to determine the source of these problems, and to establish conditions to minimize them. Most of the work was performed using a simulated drainable liquid modeled after SST core samples for which analysis had demonstrated the problems described. Analysis of these simulant extracts also resulted in virtually all the major problems observed with actual samples. Some experiments, as well as method validation, were performed using actual SST samples. Because nitration of the aromatic acid surrogate and matrix compound spikes (observed in analysis of both the samples and simulant) would be expected to occur primarily at low pH, the effect of the sample pH on acid spike compound recoveries was investigated using the simulant.

The pH-acid recovery studies demonstrated that the USEPA procedures allowed a much too large pH range for SST solid/sludge samples extracted with the organic solvent. The recommended CLP SOW sample pH range is 5 to 11 (or 5 to 9 in the more conservative previously used Pacific Northwest Laboratory (PNL) procedure) compared to a range of 6 to 7 recommended from the work in

this project. Below a pH of about 6, nitration reactions with some acid compounds occur. Above a pH of about 7, some acid compounds form salts that do not extract well into the nonpolar solvent. Some basic compounds used to spike samples formed salts at pHs below about 6, and did not extract well. Inhomogeneity and the carbonate and oxide content of the sample make sample pH adjustment within the pH range of 6 to 7 very difficult when using the preparation method that was designed for the hot cell. Consequently, a new method for sample pH adjustment was developed. The new method uses potassium monobasic phosphate to adjust the pH, and utilizes the native sodium hydroxide, and the sodium sulfate that is normally used to remove free water, to form a buffer in the desired 6 to 7 pH range. The buffering accommodates considerably more sample inhomogeneity than the conventional method in which sulfuric acid is used to adjust sample pH. Although using the phosphate buffer is of most value in the pH adjustment of solid/slurry samples, it can also be used to adjust the pH of liquid samples.

The formation of the second organic phase was determined to be mainly a function of the methanol concentration in the extract and the water content of the sample. This phase is an azeotrope that boils at $>85^{\circ}\text{C}$. GC/MS analysis of the azeotrope showed increased presence of the nitrated acids, and a decrease in two or more of the internal standards. Analysis of this extract also resulted in a significant increase in the chromatographic baseline, and column degradation products were observed in the mass spectra of the raised baseline region of the chromatograms. Formation of the azeotrope has been virtually eliminated by decreasing the amount of methanol used in the extraction process. This reduction was accomplished by a minor modification of the procedure allowing for a higher concentration of the surrogate and spike compounds in their methanol solvent.

Validation of the sample preparation procedure resulting from the work on this project was performed using SST samples spiked with the full list of USEPA CLP SOW 2/88 target compounds. No problems were observed in the GC/MS analysis of any of the SST samples following this procedure. The data from the validation analyses provide advisory control limits for the surrogate and matrix spike recoveries. When sufficient SST sample analyses have been performed on a variety of SST samples, true method quality control limits can be implemented.

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INTRODUCTION

The Organic Analysis Group in Pacific Northwest Laboratory's (PNL's)^(a) Analytical Chemistry Laboratory section has analyzed a variety of Hanford Site samples containing radionuclides. Most of the samples have been wastes from the single-shell tanks (SST) used to store radioactive wastes underground; some are from the double-shell tanks. Many analyses have been difficult, especially the analysis for the semivolatile organic compounds. This analysis consists of a complex, labor-intensive sample preparation process followed by analysis using gas chromatography with mass spectrometric detection (GC/MS). A majority of the samples are highly radioactive; thus, the initial stages of the sample preparation are performed remotely in the Shielded Analytical Laboratory (SAL) hot cells, further complicating the sample preparation process. Waste tanks are sampled using a coring technique that produces segments 19 in. long by 1 in. diameter that require extensive chemical and physical characterization. Radioactivity and limited sample availability govern the choice of the sample preparation method, and result in small sample size for the analysis. Because of these limitations, decreased analytical sensitivity is often an issue.

Sample preparation and the GC/MS analysis can be strongly affected by sample matrices. A litany of problems often results in analyzing samples with the difficult matrices. Sample pH, which is usually basic, is adjusted before extracting the organics into an organic solvent. Some samples vigorously effervesce when acid is added. Precipitation may occur in liquid samples. Small additions of acid to reduce pH in some samples may result in large pH changes, making hot cell pH adjustments difficult. Sludge and solid sample consistency may make homogeneous pH adjustment difficult, while extracts from other samples have fine particulates that cannot be filtered from the extract. Another problem is the occasional formation of an immiscible second phase during evaporation of the extract. The second phase was initially thought to be aqueous, and that many of the problems were a consequence of the water.

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However, this phase was later determined to be primarily organic, and appears to be an azeotrope. Poor chromatography was observed when the second organic phase was noted during the extract evaporation step. Samples with problem matrices that were difficult to prepare often resulted in GC/MS instrumentation problems. The GC column performance was degraded because the column stationary phase was destroyed while analyzing some samples. Quality control parameters were compromised analyzing a significant number of samples. Recoveries of both the surrogate and matrix spike acid compounds, all of which are phenolic compounds, are poor in analyzing extracts from some samples--most notably for analyzing SST sludge and drainable liquid samples. This is not surprising for the liquid samples, but is surprising for the solid and sludge samples. Nitration products of some acid spike compounds (both surrogate and matrix spikes) have been found in waste sample extracts dating back to the earliest sample analyses in 1989. A less frequent problem, but just as important, has been poor response for the internal standards perylene-d12 and chrysene-d12, which results in poor quantitation.

Loss of acid spike compounds usually occurs along with most of these problems, all of which probably result from the nature of the matrix. Consequently, the assumption was made that by minimizing acid spike losses, other problems would probably also be diminished. Two approaches were considered as a means to correct or compensate for acid spike losses: 1) develop a cleanup method to separate matrix problems from the sample, and 2) develop a sample preparation procedure that minimizes the problem. Initially, development of a cleanup procedure for these samples was considered the best approach. Preliminary experiments performed to remove "water" from sample extracts did not improve results, nor diminish the problems. Thus, development of a new preparation method became more attractive.

Because SST material was limited in availability and usually highly radioactive, the development work was performed using simulated SST material. Experience with analysis of the SST samples had shown that all of the problems described had, at one time, resulted from the analysis of the drainable liquid samples. The SST drainable liquid was also attractive because a simulant would be relatively simple to prepare and use as a medium for sample

preparation parameter studies. Analyses of the simulant drainable liquid sample extracts demonstrated early on that the problems described here could be reproduced in the absence of actual sample matrix. This reinforced the decision to work toward developing a new sample preparation method, as opposed to a sample cleanup method. Once the preparation parameters are better understood, a better definition of sample cleanup requirements can be made. To develop a new sample preparation procedure, work was directed toward determining the source of the observed problems, and then establishing conditions to minimize them.

A review of the analytical reports and narratives indicated that many of the problems were associated with extracts from samples that contained a relatively large amount of water, extracts from the matrix spiked samples, and extracts that were observed to contain the second phase. The review did not suggest a reason for poor recovery of some acid spike compounds from the solid/sludge samples. Poor acid spike compound recovery was not surprising for aqueous samples because the acid analytes are extracted at pH <2, which results in the sample nitrate/nitrite reacting with the aromatic acid spike compounds. Nitration reactions were not expected for the solids or sludges since they are extracted at neutral or slightly basic pH. The data reviewed also failed to suggest why the low recoveries were associated with the presence of nitrated spike compounds in extracts from some samples, but without the presence of these nitrated acid spikes in extracts from other samples.

These observations can be explained by poor pH control of the solid/sludge samples before they are extracted into the organic solvent. If the pH is adjusted to values too low for samples with high nitrate/nitrite concentration, good probability exists that nitration reactions would occur for aqueous samples resulting in low spike recoveries and the concurrent appearance of the nitrated spikes. If the sample pH remains too high, some of the acids would be in the ionic form and would not extract into the nonpolar solvent. The U.S. Environmental Protection Agency (EPA), Contract Laboratory Program, Statement of Work (CLP SOW) (EPA 1988), on which the PNL extraction procedure is based, allows the pH to be between 5 and 11. The PNL procedure

for solids calls for the pH to be within a more conservative range of 5 to 9. Because it was difficult to believe that pH could not be controlled within this range, a decision was made to investigate spike compound recoveries as a function of pH to determine the acceptable pH range for the extraction, if pH control is truly a problem.

EXPERIMENTAL

SIMULANT DRAINABLE LIQUID

Simulant composition was based on analytical results for SST drainable liquids. No attempt was made to include any of the cations other than sodium, which was the predominant cation in the drainable liquid. The anion concentrations were: nitrate - 0.95M; nitrite - 1.00M; sulfate - 0.11M; phosphate - 0.14M; and hydroxide - 0.51M. Because the sample preparation process for this simulant resulted in the major problems observed for the actual drainable liquid samples, the assumption was made that the nitration reactions were not catalyzed by the presence of any of the trace constituents. Consequently, these constituents were not added to the simulant.

SAMPLE PREPARATION

Current Method

Because of the limited amount of sample and its radioactivity, the method adapted for the hot cell extractions was the CLP SOW, 2/88 medium-level soil extraction, which calls for a 1-g sample. The method was slightly modified to accommodate hot cell operations. Rather than directly measure the pH of each solid/sludge sample during its pH adjustment, a sample acid titer was determined on a sample aliquot. About 1 g of a weighed sample aliquot was equilibrated with 5 mL of water, and the pH was adjusted to within 5 and 9. The amount of acid required for the adjustment was recorded as a function of sample weight. Then the pHs of aliquots from the same sample were adjusted by adding a proportionate amount of acid to the aliquots. After Na_2SO_4 was added to remove free water, and the appropriate quality control spikes (surrogate and matrix spike compounds dissolved in methanol) were added, the samples were extracted into 10-mL solvent. The drainable liquids were also treated as "medium level". Nominal 1-g (or 1-mL) samples were diluted with water in culture tubes, extracted at pH >11 into methylene chloride, and extracted again at pH <2. The extracts were concentrated in a Kuderna-Danish apparatus with a micro-Snyder column.

Very little radioactivity from the samples is extracted into the organic phase, so the extracts were transferred to open-face radiochemistry hoods for further processing. Nearly all of the radioactivity remaining after the extract is concentrated is removed by centrifuging the extract. Extracts from samples containing complexants and a relatively high concentration of methanol usually have higher concentrations of radionuclides, but even those can be processed in the radiochemistry hoods. Aqueous phase samples (drainable liquids) from segments with sufficient liquid are analyzed separately.

Sample Preparation for the pH vs Recovery Studies

The simulated drainable liquid was treated as a "soil" in that extractions were not made on the sample at the basic and acidic pHs. The sample pH was adjusted to that value specified for the experiment, the acid and base/neutral surrogate and matrix spike compounds were added, and the sample was extracted with methylene chloride. The sum of the methylene chloride and the spike volumes was 10 mL. Extract concentration was accomplished as described for the current method. Preparation of samples for the method validation is described in the Appendix.

Reagents

The solvents used were of pesticide quality or its equivalent. The target and spike compounds were prepared from concentrated stock solutions (Supelco Analytical Reference Standards for EPA Contract Laboratory Method mixes). Spike compound stock solutions were prepared by diluting the concentrated stock solutions 10-fold in methanol, resulting in 200 µg/mL acids and 100 µg/mL base/neutrals. The acid and base/neutral spike stock solutions were not mixed. For the method validation analyses, nominal 1-g SST samples from core 52 were spiked with a mix of 50 µg of each of the CLP SOW target list compounds before sample preparation. Additional information is provided in the Appendix.

Apparatus and Materials

The apparatus and materials used in the sample preparation are described in the procedure in the Appendix.

GC/MS ANALYSIS

The procedure for the GC/MS analyses of the extracts (PNL 1989) is based on the CLP SOW 2/88, without modification.

Instrumentation

A Hewlett-Packard system consisting of an HP-5890/5970 GC/MS with an HP-1000 series RTE-A computer, an HP-7673 autosampler, and associated peripherals were used for the analyses.

Analysis Conditions

The GC column was a 30-m by 0.25-mm DB-5 with 0.25 μ m film (J & W Scientific). The GC injection port and transfer line were at 285°C. The initial column temperature was at 40°C for 4 min, ramped at 8°/min to 300°C, and maintained at that temperature for 10 min. Electronic pressure programming was used to provide a pressure pulse of 60 psi during injection and constant carrier gas (He) flow following the pressure pulse.

Calibration

The mass spectrometer mass calibration and tune parameters were confirmed with a decafluorotriphenylphosphine (DFTPP) analysis according to CLP SOW (EPA 1988) specifications. A single-level continuing calibration was performed for CLP target list compounds each day.

DISCUSSION

EFFECT OF pH ON SPIKE RECOVERIES

Effects of sample pH on spike recoveries were studied using the simulated SST drainable liquid. Results of this work are summarized in Figures 1 through 5. Recovery data in these figures are all normalized to the recovery of each of the spiked compounds at pH 7. As shown in Figure 1, the problem acid surrogate spike recoveries were satisfactory for sample pH adjusted to within about 6 to 9. Matrix spike acid compound recoveries (Figure 2) are satisfactory over the pH range of 6 to 7. Above a pH of 7, recoveries of some of the acids are reduced sharply, as would be expected from pK_a values. Below pH of about 6, some acid spike recoveries decreased and nitration products of acid spike compounds were observed (for unknown reasons, concentrations of the nitration products were usually too low to account for spike losses). However, as shown in Figure 2, recovery of the 4-nitrophenol is significantly increased by nitration of phenol. Nitration products of both surrogate and matrix spike compounds observed in the analysis of the simulant are listed in Table 1. These compounds, as well as 2,4-dibromo-4-nitrophenol, are also observed in the analysis of some SST samples.

As expected, recoveries of the neutral spikes were relatively unaffected by sample pH as shown in Figures 3 and 4. The apparent high recoveries of 1,4-dichlorobenzene and 1,2,4-trichlorobenzene below pH 7 are a result of the

TABLE 1. Nitration Products of Acid Surrogate and Matrix Compounds Observed in Extracts from SST Drainable Liquid Simulant at pH 2 and 4

4-nitrophenol-d4
4-nitrophenol
2-fluoro-4-nitrophenol
2-fluoro-6-nitrophenol
2-chloro-4-nitrophenol
4-chloro-3-methyl-2-nitrophenol
4-chloro-3-methyl-5-nitrophenol
2-chloro-6-nitrophenol

FIGURE 1. Acid Surrogate Recovery as a Function of pH

FIGURE 2. Acid Matrix Spike Recovery as a Function of pH

FIGURE 3. Base/Neutral Surrogate Recovery as a Function of pH

FIGURE 4. Base/Neutral Matrix Spike Recovery as a Function of pH

FIGURE 5. Base Analyte Recovery as a Function of pH

normalized recovery data. The base compounds, as shown in Figure 5, are unaffected at pH values above about 6, but recoveries of 3-nitroaniline and 4-chloroaniline are reduced sharply below pH 6 due to salt formation.

Recommended pH

The optimum pH range for extraction of SST and similar samples containing high concentrations of nitrate and nitrite is 6 to 7. Within this range good recovery of acid, base, and neutral compounds will be achieved in the extraction of such samples.

Sample pH Adjustment Problems

Because of difficulties associated with adjusting sample pH in the hot cells, the ability to accurately and reproducibly adjust sample pH may have a greater effect on surrogate and matrix spike recovery than the sample matrix itself, especially for heterogeneous samples. For example, if the acid titer sample contains more inert material than the sample, the amount of acid added for the sample pH adjustment would be too little, resulting in a high pH; or if the sample contained more of the inert material than the acid titer sample,

the resulting pH would be too low. Both cases would result in low acid spike recoveries. Poor basic compound recovery would also result if the sample pH were too low.

Another source of error in pH adjustment is the presence of an oxide or carbonate that reacts slowly with the acid. This results in a low acid titer, causing the pH in the sample aliquots to be too high. Results shown in Table 2 indicate the validity of this concern. Acid titers for core 36 and 47 samples were determined so that the sample pHs would be adjusted to 7 for the extraction. The initial pH values for core 36-5 and -6 titer samples were close to 7, while pH values of core samples 36-1, -2, -3, and -4 were all initially closer to about 8 even though the amount of acid added was based on the titer. The core 47 acid titer sample was adjusted to 7, but the pH drifted to 8.3 after 4 hours. These pH values for the extraction would probably result in low recoveries for 2-fluorophenol and 2,4,6-tribromophenol surrogate spikes and for 4-nitrophenol and pentachlorophenol matrix spikes. The problem would be worse if the samples were extracted at the high end of the method's pH range of 5 to 9. Because most of the drift in pH occurs between 0.3 and 2 hours, the drift problem could be minimized by performing the extraction within 20 min after adjusting the pH.

TABLE 2. Sample pH Adjustment

<u>Acid Titer</u>	<u>pH Values at Approximate Time, Hours</u>				
	<u>0</u>	<u>0.3</u>	<u>2.0</u>	<u>4.0</u>	<u>8.0</u>
Core 36-5	7.0	7.3	7.8	8.0	8.1
Core 36-6	7.0	7.4	7.9	8.1	8.2
Core 47	7.0			8.3	
<u>Sample</u>					
Core 36-1			8.6	8.7	8.8
Core 36-2			8.4	8.6	8.8
Core 36-3	8.3		8.5	8.7	
Core 36-4	8.2		8.6	8.5	

Control of pH in the adjustment of liquid samples is comparatively easy, even in the hot cell operations. The poor acid spike recovery problems observed for the drainable liquid samples resulted from the procedure. The procedure requires an extraction at pH 2, which assures nitration reactions if the nitrate and nitrite concentrations are high enough, which is usually the case. However, if the pH is to be adjusted to within 6 to 7 as it should be, a method to provide improved pH control even for liquid samples was determined to be beneficial.

IMPROVED SOLID/SLURRY SAMPLE pH CONTROL FOR THE EXTRACTION

As seen from the previous discussion, attainment of a proper pH for the sample before extraction is very important for good recovery of the acid and base spikes and analytes. Both mechanical and chemical means were considered for improving pH control. The mechanical approaches considered were related to measuring the pH of each sample during acid addition, thus eliminating the need for the sample acid titer determination. A brief evaluation of several mechanical approaches did not lead to a practical method that would be satisfactory in hot cell operations. The chemical approach to minimize the pH control problem through sample buffering did appear attractive, even though more reagent additions would likely be required.

Buffered Sample Before Extraction

A review of the literature indicated that a buffer of KH_2PO_4 with NaOH should provide a sample pH in the range of 6.5 to 7.5. This buffer is attractive because the NaOH is native to the samples, and the phosphate should be innocuous. To determine the buffered pH range, the drainable liquid simulant was titrated with 1M KH_2PO_4 . Figure 6 shows the results of the titration. The pH does indeed have a buffered region very near the desired range. The buffered pH of the more concentrated simulant was at a slightly higher pH than the dilute one, indicating that achieving a sufficiently low pH could be a problem for highly basic samples.

Figure 7 shows the acid phosphate titration of a core-36 SST sample and the H_2SO_4 titration of another aliquot of the same sample. The buffered titration results in a sample pH in the desired range, but with about a factor

FIGURE 6. Simulant Titration with KH_2PO_4

of 7 more acid than is needed for the H_2SO_4 pH adjustment. However, little buffering exists within the desired pH range in the H_2SO_4 titration, demonstrating one reason for poor sample pH control. The effect of increased sample basicity is shown in Figure 8. Adding the basic simulant to the sample results in a higher buffered pH. Adjusting the pH of samples, as well as the simulant, with a very high concentration of NaOH to less than 7 might be difficult without adding a stronger acid.

Effect of Na_2SO_4 on the Acid Phosphate Titration

Because Na_2SO_4 is used to absorb water in samples, its effect on the phosphate buffered pH was determined. Figure 9 shows the effect of the sulfate on the titration of simulant. Formation of bisulfate decreases the buffered pH by more than one pH unit. The effect of the sulfate on the acid phosphate titration of a nominal 1-g core 36 SST sample, as shown in Figure 10, also shifts the titration curve to lower pHs without significant change of slope in the buffered range. As seen in Figures 7, 8, and 10, adding the sulfate provides the needed shift of the buffered pH range to lower values

FIGURE 7. Single-Shell Tank Sample Titration with H_2SO_4 and KH_2PO_4

FIGURE 8. Single-Shell Tank Sample Titration with KH_2PO_4

FIGURE 9. Effect of Na_2SO_4 on KH_2PO_4 Titration of Single-Shell Tank Simulant

FIGURE 10. Effect of Na_2SO_4 on KH_2PO_4 Titration of Single-Shell Tank Sample

with no loss in buffering; thus less acid phosphate will be needed to adjust the sample pH to less than 7.

The interrelationship of Na_2SO_4 and KH_2PO_4 in the adjustment of the sample pH allows some flexibility in control of the pH. However, Na_2SO_4 is added to all samples, because even dry samples require adding aqueous solution for the pH adjustment. Consequently, the sample water content and added water from the pH adjustment must both be considered in adding the sulfate and acid phosphate to adjust the sample pH. Variability in the initial sample pH does not appear to present any problem to the pH adjustment. Other advantages of the acid phosphate pH adjustment are less effervescence than when adding H_2SO_4 and less drift in the pH than after H_2SO_4 additions.

Recommended pH Adjustment Procedure for Solid/Slurry Samples

As a rule of thumb, 2 g Na_2SO_4 is added for a 1-g SST sample (a ratio of 3:1 Na_2SO_4 to the water in the sample is usually required to produce the desired sandy texture of the mix). In determining the acid titer of the sample, about 1 g of the sulfate is added followed by 5 mL of water. Then, the mixture is titrated with acid phosphate until a pH of about 7, or slightly lower, is reached. The remaining sulfate is added (if the water content is unknown, a total of 2-g of the sulfate is used). The pH of the mixture is again measured, and if necessary, adjusted to about 6.4 with the acid phosphate.

BUFFERED pH ADJUSTMENT OF LIQUID SAMPLES

The same sample pH limits for extractions exist for the liquid samples as for the solid/slurry samples described in the preceding sections. However, an acid titer sample is not used; the pH is adjusted for each sample before its extraction. In the current procedure, 1 g (or 1 mL) of an SST drainable liquid sample is diluted, and the pH is adjusted with H_2SO_4 . The titration curve for the H_2SO_4 pH adjustment of 1 mL of drainable liquid simulant diluted to 10 mL is shown in Figure 11. The titration indicates no buffering for the H_2SO_4 . The titration with KH_2PO_4 shown in Figure 6 suggests that an acid phosphate adjustment might not achieve a low enough pH, so H_3PO_4 was tested as the titrant. As seen in Figure 11, very little buffering exists using H_3PO_4 ,

FIGURE 11. Buffered and Unbuffered Titration of Drainable Liquid Simulant

so 5 and 10 meq (milliequivalents) NaOH were added to the diluent before the titration. This buffering method effectively adjusts the sample pH to within the desired range, and offers flexibility in the adjustment. The slope of the titration curve in the 6 to 7 pH range for the 5-meq NaOH addition is 0.41 pH/meq(acid), and 0.27 pH/meq(acid) for the 10-meq NaOH addition. The buffer capacity is better after the larger NaOH addition. However, because the pH adjustment is relatively simple, and the pH will be measured during the adjustment of each sample to be extracted, the lesser amount of NaOH added is recommended.

The advantages of this approach for nearly all liquid samples are that a well-controlled single pH extraction is utilized with good recoveries achieved for acid, base, and neutral compounds, and a less reactive acid than H_2SO_4 is used for the pH adjustment. In addition, the reagents added should improve extractions from low ionic strength solutions by salting out the analytes to an increased extent.

Recommended pH Adjustment for Liquid Samples

In general, the procedure for the buffered pH adjustment for SST type liquid samples will be to add about 5 meq NaOH to a 1-mL sample, and dilute it to 10 mL. The diluted sample pH will then be adjusted to about 6.5 with 1:5 diluted H_3PO_4 . Extractions from low salt strength samples using this procedure have not been tested, but should not present any problems.

For the liquid samples, this method has not undergone a validation with actual samples because sufficient sample was not available. However, a large number of extractions of selected acid, base, and neutral compounds have been successfully performed using the simulated SST drainable liquid. Thus, no problems with samples are anticipated. Data from analysis of actual samples will be obtained in the future, which will provide a basis for establishing recovery limits for the method.

SECOND ORGANIC PHASE

Second Organic Phase from Sample Extractions

Extracting drainable liquid and sludge samples containing considerable water using methylene chloride with a high concentration of methanol (such as for matrix spiked samples) often result in forming a second organic phase. GC/MS analyses of SST sample extracts that contain the second phase show reduced instrument response or total loss of some internal standards, the presence of the nitrated acid surrogate and matrix spike compounds, and elevated baseline. Mass spectra of the elevated baseline region of the chromatogram show column degradation products, and the GC column usually needs to be replaced after analyses of such samples. Analysis of extracts from some matrix spiked samples, for which the extracting solvent contained a relatively large amount of methanol (40 vol%), resulted in chromatograms with unidentified peaks that are not present in the chromatogram of the unspiked sample. Because of the increased polarity of the methylene chloride/methanol solvent, these peaks may represent compounds that are more polar than are usually extracted in methylene chloride alone. Other less volatile polar compounds extracted in the more polar solvent may well be the cause of column degradation.

Second Organic Phase from Simulant Extraction

The second organic phase was also formed during the extraction of the drainable liquid simulant using extractant with 40 vol% methanol. A series of experiments were performed in which solvents containing 0, 20%, and 40% methanol in methylene chloride were used to extract 1-mL samples with 1%, 10%, and 100% simulant. This phase appears to have properties of an azeotrope, and will be referred to as such in following discussions. The only condition that resulted in consistent azeotrope formation was if the 40% methanol solvent were used to extract the pure 1-mL simulant. If an organic extract obtained under conditions favoring this azeotrope formation is heated extensively at a sufficiently high temperature to evaporate the methylene chloride, an apparently stable azeotrope is formed that boils at $>85^{\circ}\text{C}$. A volatile GC/MS analysis of the azeotrope indicated the presence of about 60% methylene chloride. If the extract is not extensively heated, the second phase can be eliminated with an excess of sodium sulfate and methylene chloride. For the sake of discussion, this organic phase was called the "pre-azeotrope," because the azeotrope composition is yet to be attained during the evaporation.

GC/MS analysis of the azeotrope phase also resulted in the same degraded performance described earlier for the SST samples, except that the column remained usable after analysis even though the base line mass spectrum did show evidence of column decomposition. The internal standards chrysene-d12 and perylene-d12 decreased in abundance by about 99%, and several nitration products of the acid spikes were present.

Figure 12 shows the infrared spectra of the azeotrope and the pre-azeotrope formed after extraction of simulant. The infrared spectra of methanol and methylene chloride are shown in Figure 13. The sharp methylene chloride peak at about 1270 cm^{-1} has disappeared in the spectra of both the azeotrope and the pre-azeotrope, somewhat surprising in view of the GC/MS analysis that indicated methylene chloride to be about 60%. However, that peak may be the broader one at about 1240 cm^{-1} , and the broad peak at about 740 cm^{-1} may be the shoulder on the 820 cm^{-1} in the azeotrope spectrum. The peak at 1650 cm^{-1} is in both the pre-azeotrope and azeotrope spectra, but not in the methylene and methanol spectra. The broad peak at 3310 cm^{-1} in the

methanol spectrum is less symmetric in the pre-azeotrope spectrum and has gained some structure in the azeotrope spectrum. Because the presence of the simulant appeared to be important to the formation of the azeotrope, evidence of the presence of some sort of nitration products of solvent constituents were expected in the spectrum. A review of a library of infrared spectra (Pouchert 1985) did not provide evidence of nitrogen-oxygen absorption frequencies; or for that matter, the review did not reveal plausible functional group identification for the peaks unique to the azeotrope and pre-azeotrope.

Elimination of the Azeotrope Problem

The azeotrope problem can be eliminated, or at least greatly minimized, by reducing the methanol concentration significantly. This is accomplished by not diluting the concentrated stock solutions in methanol, which reduces the maximum concentration of methanol to 4 vol% (4 vol% for matrix spike extractions and 2 vol% from the surrogate spikes for other sample extractions) as compared to the 40% maximum using the dilute stock solutions. Experience with a modified procedure utilizing this stock concentration has verified prevention of the azeotrope formation. Less methanol may also be beneficial in reducing the possibility for ester formation with sample caboxylate compounds.

DIFFERENCES IN THE METHOD

The principal differences from the existing method resulting from this work are steps to improve pH control of the sample before extraction, using a single pH extraction for liquid samples, and using higher concentration spikes to decrease the methanol content in the extract.

pH CONTROL

Solids/Slurry Sample

Control of pH before extraction is important to all samples, but is of particular importance to the high nitrate/nitrite SST samples. Use of a single pH extraction for the solids/slurry preparation method is in the current PNL and EPA methods, but with considerably wider pH limits. The changes recommended from this work decrease the acceptable pH range for the sample extraction, and provide a buffering method to adjust the pH with relative ease.

Liquid Samples

The aqueous samples have traditionally been extracted at two pHs of >11 and <2. The dual pH extraction is not acceptable for SST drainable liquid samples, or other samples containing high concentrations of nitrate/nitrite. In addition, the most recent CLP SOW (EPA CLP 1991) calls for a single extraction at pH 2 at which basic compounds do not extract well. The change recommended from this work is to extract the liquid samples at a single pH in the range of 6 to 7. A method to buffer the liquid samples is also recommended, and described in the procedure. An additional difference for the liquid samples in this procedure is to allow for a medium level 1-mL sample because of the limited sample availability and its radionuclide content.

CONCENTRATION OF METHANOL IN THE EXTRACT

The PNL procedure and CLP SOW specify the surrogate and matrix spike mixtures to be diluted in methanol to concentrations of 200 µg/mL for the acid mixes and 100 µg/mL for the base/neutrals. This results in a total of 2 mL

FIGURE 12. Infrared Spectra of Azeotrope and Pre-Azeotrope Prepared from Single-Shell Tank Simulant Sample

FIGURE 13. Infrared Spectra of Methylene Chloride and Methanol

methanol for all samples except in the matrix spiked samples using the PNL procedure for preparing the SST samples. The matrix spiked samples contain 4 mL methanol. This means that the methanol concentration in the extraction solvent is 40% for the matrix spiked samples. Although extractions of simulant samples did not result in azeotrope formation for extracts of less than 40% methanol, extractions of actual samples with 20% methanol did, but less often. The change recommended from this work is to maintain the spike concentrations at 2000 $\mu\text{g/mL}$ for the acids and 1000 $\mu\text{g/mL}$ for the base/neutrals. Thus, the methanol concentration will not exceed 4 vol%.

METHOD VALIDATION

The method was tested on actual SST samples from core 52. All target, surrogate, and internal standard compounds in the CLP SOW 2/88 were spiked into the samples. The most significant questions about the method to be answered by the validation experiment are related to the ability to control pH by following the procedure and the inertness of the acid phosphate as evidenced by compound recoveries. In addition, out of this set of analyses comes a practical experience preparing actual samples on a routine basis, which will assist in fine-tuning the method.

Results of the analyses are summarized in Table 3. In general, excellent recoveries were obtained. The reason for high recoveries (>110%) for 6 of the compounds is uncertain. Sample unavailability and time did not allow additional SST sample tests. However, the primary goals for the validation were accomplished. No significant loss of any of the spiked compounds resulted from the preparation. The standard deviations (STD) for all sample recoveries were good except for somewhat higher STDs for the compounds with the high recoveries.

Table 3 also shows $\pm 3 \times$ STD values for the surrogate and matrix spike compounds. These values represent the advisory upper and lower control limits for the method surrogate and matrix spike recoveries. After additional samples from a variety of sources are analyzed using this preparation procedure, more valid control limits can be established.

TABLE 3. Percent Recoveries of Full Target List Analyte Spike Following Use of Buffered Sample Preparation

Analyte	Ext 1	Ext 2	Ext 3	Ext 4	Ext 5	Ext 6	Ext 7	Ext 8	Avg	STD	-3xSTD	+3xSTD
1) *1,4-Dichlorobenzene-d4	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	0.0		
2) 2-Fluorophenol	92.4	99.2	112.4	109.2	99.7	84.6	109.1	101.4	101.0	9.3	73	129 #
3) Phenol-d5	95.3	101.4	116.0	113.9	105.2	89.7	111.1	107.5	105.0	9.1	78	132 #
4) Phenol	94.3	99.8	114.7	114.5	104.4	88.9	111.0	106.6	104.3	9.4	76	133 @
5) bis(2-Chloroethyl)ether	94.8	98.7	112.1	110.9	102.5	87.1	108.3	104.5	102.4	8.6		
6) 2-Chlorophenol	92.5	94.5	107.6	103.7	94.3	81.2	100.6	95.4	96.2	8.0	72	120 @
7) 1,3-Dichlorobenzene	91.6	94.7	106.6	101.9	94.6	80.4	100.4	94.0	95.5	7.9		
8) 1,4-Dichlorobenzene	93.9	95.9	108.0	102.0	94.4	81.2	100.1	94.3	96.2	7.8	73	120 @
9) Benzyl alcohol	95.5	101.6	114.7	117.2	104.0	88.9	109.8	107.4	104.9	9.5		
10) 1,2-Dichlorobenzene	92.5	95.1	104.3	101.2	92.2	80.2	96.3	92.4	94.3	7.2		
11) 2-Methylphenol	95.1	100.3	111.2	113.1	98.4	85.3	106.7	103.1	101.7	9.0		
12) bis(2-Chloroisopropyl)ether	95.0	101.4	119.5	122.4	114.0	99.9	126.6	122.5	112.7	12.2		
13) 4-Methylphenol	92.5	98.3	109.1	110.9	96.9	83.2	103.8	99.6	99.3	9.0		
14) N-Nitroso-di-n-propylamine	95.3	104.6	115.7	120.8	106.3	92.8	115.9	110.2	107.7	10.0	78	138 @
15) Hexachloroethane	89.1	92.0	104.3	99.2	88.8	76.3	94.1	88.2	91.5	8.3		
16) *Naphthalene-d8	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	0.0		
17) Nitrobenzene-d5	92.7	95.5	110.6	110.4	98.3	85.7	106.9	102.5	100.3	8.9	74	127 #
18) Nitrobenzene	95.1	95.7	110.7	110.5	99.7	86.3	106.9	104.6	101.2	8.6		
19) Isophorone	93.3	97.9	110.3	114.1	100.4	87.5	108.9	106.0	102.3	9.1		
20) 2-Nitrophenol	97.0	101.1	115.1	117.1	103.2	88.3	113.3	109.7	105.6	10.0		
21) 2,4-Dimethylphenol	85.8	83.7	95.5	94.3	74.1	60.7	81.0	79.4	81.8	11.2		
22) Benzoic acid	92.8	101.7	99.7	98.3	77.4	62.5	97.0	95.5	90.6	13.6		
23) bis(2-Chloroethoxy)methane	96.3	98.6	112.0	115.5	103.0	87.3	109.0	107.9	103.7	9.3		
24) 2,4-Dichlorophenol	92.0	93.0	104.1	102.0	92.6	78.4	96.7	94.9	94.2	7.8		
25) 1,2,4-Trichlorobenzene	90.4	91.2	101.5	100.9	90.4	77.1	95.9	91.9	92.4	7.6	70	115 @
26) Naphthalene	91.5	94.5	105.3	103.7	93.7	80.3	97.9	96.4	95.4	7.8		
27) 4-Chloroaniline	95.4	96.7	108.6	111.5	94.2	80.6	106.9	103.4	99.7	10.0		
28) Hexachlorobutadiene	93.1	88.8	99.4	95.3	85.3	70.9	89.1	85.5	88.4	8.6		
29) 4-Chloro-3-methylphenol	94.6	99.1	108.3	111.0	96.3	83.4	103.3	101.4	99.7	8.6	74	126 @
30) 2-Methylnaphthalene	92.6	92.1	103.3	103.5	89.7	78.3	94.4	93.4	93.4	8.0		
31) *Acenaphthene-d10	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	0.0		
32) Hexachlorocyclopentadiene	87.2	98.9	102.5	111.2	96.4	82.2	105.5	92.6	97.1	9.6		
33) 2,4,6-Trichlorophenol	92.1	98.7	102.4	110.9	89.1	81.7	99.3	96.3	96.3	8.8		
34) 2,4,5-Trichlorophenol	91.5	95.6	101.6	105.1	92.2	81.0	96.2	92.0	94.4	7.3		
35) 2-Chloronaphthalene	91.6	95.6	105.0	106.7	92.9	80.5	97.2	91.4	95.1	8.3		
36) 2-Fluorobiphenyl	94.2	97.0	104.1	106.8	92.2	81.9	98.8	92.8	96.0	7.7	73	119 #
37) 2-Nitroaniline	94.3	101.7	113.1	120.4	102.8	91.3	116.0	109.1	106.1	10.3		
38) Dimethylphthalate	92.7	96.9	102.4	108.4	91.8	79.7	100.0	95.9	96.0	8.5		
39) Acenaphthylene	95.8	100.5	105.3	109.6	91.4	82.4	98.2	96.3	97.4	8.3		
40) 2,6-Dinitrotoluene	94.4	99.5	102.9	108.0	90.6	81.2	98.4	95.7	96.3	8.1		
41) 3-Nitroaniline	94.3	103.7	113.2	122.1	98.0	86.7	111.5	104.7	104.3	11.3		
42) Acenaphthene	94.9	99.7	105.4	106.9	94.4	82.3	100.2	97.2	97.6	7.7	74	121 @

TABLE 3. (contd)

Analyte	Ext 1	Ext 2	Ext 3	Ext 4	Ext 5	Ext 6	Ext 7	Ext 8	AVG	STD	-3xSTD	+3xSTD
43) 2,4-Dinitrophenol	96.0	118.1	125.3	146.7	118.8	94.9	141.6	126.4	121.0	18.7		
44) 4-Nitrophenol	93.2	92.8	95.5	98.8	82.4	72.2	88.9	84.6	88.6	8.6	63	114 @
45) Dibenzofuran	95.1	98.4	105.5	109.2	94.1	83.7	99.7	98.3	98.0	7.7		
46) 2,4-Dinitrotoluene	95.4	99.0	106.8	114.6	95.5	84.2	106.2	102.0	100.5	9.2	73	128 @
47) Diethylphthalate	92.3	96.1	102.6	106.2	90.6	80.7	96.5	94.7	95.0	7.7		
48) 4-Chlorophenyl-phenylether	96.5	100.7	104.7	109.6	94.4	81.3	100.5	98.1	98.2	8.3		
49) Fluorene	93.2	98.3	105.7	107.8	92.4	81.1	98.7	96.3	96.7	8.3		
50) 4-Nitroaniline	94.3	103.8	123.6	152.4	102.9	89.2	140.9	124.9	116.5	22.6		
51) *Phenanthrene-d10	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	0.0		
52) 4,6-Dinitro-2-methylphenol	97.8	117.5	124.6	144.2	119.8	103.7	135.2	131.2	121.7	15.6		
53) N-Nitrosodiphenylamine	89.3	93.1	100.9	105.6	80.0	73.3	94.0	94.4	91.3	10.5		
54) 2,4,6-Tribromophenol	91.8	96.0	97.3	104.7	86.0	74.5	90.7	88.1	91.1	8.9	64	118 #
55) 4-Bromophenyl-phenylether	94.1	98.3	101.3	108.6	90.9	80.7	91.8	94.3	95.0	8.2		
56) Hexachlorobenzene	89.0	94.0	95.6	100.8	84.5	77.1	87.7	89.5	89.8	7.2		
57) Pentachlorophenol	86.5	90.3	96.1	97.0	83.3	71.3	89.5	84.7	87.3	8.2	63	112 @
58) Phenanthrene	89.9	95.7	97.7	106.4	88.0	78.8	93.5	92.7	92.8	8.0		
59) Anthracene	91.3	97.2	99.0	106.6	88.5	79.1	93.5	94.9	93.8	8.1		
60) Di-n-butylphthalate	90.4	95.5	96.0	103.9	88.1	76.0	91.2	91.5	91.6	7.9		
61) Fluoranthene	93.3	96.4	99.6	106.0	89.5	77.0	94.5	91.5	93.5	8.4		
62) *Chrysene-d12	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	0.0		
63) Pyrene	93.5	96.5	109.2	115.2	92.9	82.7	103.9	102.1	99.5	10.3	69	130 @
64) Terphenyl-d14	93.2	99.2	105.6	112.6	90.2	81.5	99.8	98.9	97.6	9.5	69	126 #
65) Butylbenzylphthalate	96.8	102.6	114.6	119.0	97.2	87.5	106.8	105.4	103.7	10.1		
66) 3,3'-Dichlorobenzidine	104.7	115.6	128.2	143.8	122.4	102.6	128.6	121.1	120.9	13.5		
67) Benzo(a)anthracene	92.6	96.1	108.6	114.1	92.3	80.1	100.9	100.9	98.2	10.5		
68) Chrysene	93.4	95.5	106.5	112.4	90.0	80.4	96.7	97.7	96.6	9.7		
69) Bis(2-Ethylhexyl)phthalate	95.7	98.6	110.9	117.0	163.7	140.7	106.6	107.7	117.6	23.2		
70) *Perylene-d12	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	0.0		
71) Di-n-octylphthalate	95.7	99.2	105.1	110.6	94.9	85.1	97.7	97.8	98.3	7.5		
72) Benzo(b)fluoranthene	93.3	95.3	106.6	114.2	94.3	82.9	95.6	96.4	97.3	9.4		
73) Benzo(k)fluoranthene	92.0	94.8	94.5	98.3	83.6	74.9	88.3	92.3	89.8	7.5		
74) Benzo(a)pyrene	93.3	93.8	100.4	105.0	86.0	76.3	92.7	93.2	92.6	8.7		
75) Indeno(1,2,3-cd)pyrene	97.3	114.5	120.2	110.1	105.9	92.4	96.0	109.8	105.8	9.8		
76) Dibenz(a,h)anthracene	95.4	94.3	100.0	106.0	88.3	75.8	93.2	87.8	92.6	9.0		
77) Benzo(g,h,i)perylene	92.2	94.1	100.5	107.2	86.9	76.1	93.6	90.1	92.6	9.2		

* Internal Standard Compounds

Surrogate Spike Compounds

@ Matrix Spike Compounds

STD Standard Deviation

CONCLUSIONS

Sample preparation methods for semivolatile organic analysis of SST and similar solid/slurry and liquid samples have been developed that will allow improved pH control of the sample before its extraction. The improved method will result in the elimination of surrogate and matrix spike compound losses caused by nitration reactions and salt formation, which will decrease quality control parameter failures significantly. Loss of other compounds native to the samples that undergo these reactions will also be reduced. In addition, the cause for the formation of a second organic phase during the organic extraction solvent concentration step has been determined, and procedure steps implemented to minimize its formation.

The preparation method in use is inadequate for the complex matrices of SST samples. Control of the sample pH before extraction is important for these samples because of their high concentrations of nitrate and nitrite. Experiments conducted in this project demonstrated that for samples with pH below about 6, some of the aromatic acid surrogate and matrix spike compounds are nitrated and some basic compounds form non-extracting salts. In samples with pH above about 7, some acids form salts which do not extract in the nonpolar organic solvent. Consequently, to achieve best compound recoveries in the extraction, the sample pH should be adjusted to within the range of 6 to 7. Making this adjustment is difficult, especially in hot cell operations, because the current method for the adjustment does not satisfactorily accommodate sample heterogeneity and carbonate or oxide content. To overcome this problem, a sample buffering technique was developed. KH_2PO_4 is used to adjust the sample pH. This results in the formation of a buffer in the 6 to 7 pH range with the added sodium sulfate (used to absorb free water) and the sodium hydroxide present in the sample. Thus, problems from poor pH control caused by deficient or excess quantities of acid added in the pH adjustment as a consequence of sample heterogeneity are minimized.

A buffering technique for liquid samples was also developed that utilizes an H_3PO_4 -NaOH buffer combination to achieve a sample pH of 6 to 7.

This allows a single pH extraction for liquids, which results in the same improvements as described for the solid/slurry samples.

The second organic phase formed during the evaporation of the solvent extract is an azeotrope that boils at $>85^{\circ}\text{C}$. Its presence in the sample, if injected in the GC/MS, usually results in degraded analytical performance and time-consuming system maintenance including GC column replacement. The azeotrope forms if the sample contains a significant amount of water, and if there is a high concentration of methanol in the solvent. This condition exists for the "medium" level method for which 10 mL solvent containing up to 4 mL methanol is used for the extraction. The methanol is the solvent for both the surrogate and matrix spike standard stock solutions. To minimize the amount of methanol, a slight change in the method was made such that surrogate and matrix spike concentrations in the stock solution are a factor of ten greater. Since this change was implemented, the second organic phase has not been observed.

The new sample pH adjustment procedure and other modifications have been incorporated in the original method for preparing SST samples for semivolatile organics analysis (PNL 1993), which is included in this document in the Appendix. A validation has been performed for the new method on core 52 samples spiked with a full target list of semivolatile compounds. The results in all cases were satisfactory with no evidence of poor recovery of any compound. Advisory limits for surrogate and matrix spike recoveries have been calculated. After additional data are acquired for a variety of SST samples, better definition of the quality control parameters will be established. Although the new method for pH adjustment of liquid samples was not validated because of insufficient sample, experience with the method with simulants does not indicate potential problems. When sufficient data from analysis of actual liquid samples are acquired, recovery control limits will be determined.

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APPENDIX

PNL-ALO-120, PROCEDURE FOR EXTRACTION OF SAMPLES WITH COMPLEX AND REACTIVE
MATRICES FOR THE ANALYSIS OF SEMIVOLATILE ORGANIC COMPOUNDS

TITLE: PNL-ALO-120, PROCEDURE FOR EXTRACTION OF SAMPLES WITH COMPLEX AND
REACTIVE MATRICES FOR THE ANALYSIS OF SEMIVOLATILE ORGANIC COMPOUNDS

APPLICABILITY

This procedure describes the method used for extracting the semivolatile organic compounds from samples with reactive and complex matrices such as single shell waste samples with high concentrations of nitrate and nitrite. Also described is the procedure to prepare the extracts for analysis of these compounds. Steps have been added in this revision of the procedure to prevent loss of aromatic acid compounds due to nitration reactions at low pH and salt formation at high pH by imposing close pH limits for the sample before the extraction, and providing a buffering process to improve pH control during the pH adjustment. Steps have also been added to accommodate liquid samples. Use of the revised portions of the procedure associated with the pH control and buffered pH adjustment will be under direction of the Cognizant Scientist or test instruction. Advisory control limits for surrogate and matrix spike compound recoveries using the revisions are included in the procedure. This procedure may be used to support work performed in compliance with EPA Contract Laboratory Program (CLP) or other projects/programs as elected at the discretion of the Cognizant Scientist.

DEFINITIONS

None

RESPONSIBLE STAFF

Cognizant Scientist

Analyst

PROCEDURE

- 1.0 This procedure is used for extracting nonvolatile and semivolatile organic compounds from liquid, soil, sludge, and other waste samples. The section of the procedure involving extractions with close pH control and use of buffered pH adjustment is particularly useful in the preparation of samples with known nitration reaction with aromatic acid compounds. Such samples include the single shell samples with high nitrate/nitrite content. The method is divided into three sections.

Two are based on the expected concentration of organics in solid type samples (low and medium levels). The third is for liquid samples. The low concentration method (individual extractable organic components ≤ 20 mg/Kg) uses a nominal 30-g sample size and a more rigorous extraction procedure than for the medium level. The medium concentration method (>20 mg/Kg individual extractable organic components) uses a smaller sample, less extraction solvent and is simpler to use, especially for application in a hotcell environment. The medium level method is used for samples with a high levels of radioactivity and of limited quantity.

Two methods are provided for adjustment of pH for the solid samples which do not meet the pH criteria. Both methods involve the use of an acid titer determination in which an aliquot of the solid sample is equilibrated in water. After equilibration the pH is measured, and the amount of acid added to adjust the pH to the specified value is determined. To adjust sample pH before extraction and analysis, a proportionate amount of acid as calculated from the titer is added to each sample aliquot. One method of pH adjustment involves the conventional addition of H_2SO_4 to adjust the pH to the prescribed value. The second method uses a new procedure that buffers the sample to improve control of the pH. This method is particularly useful for samples containing high concentrations of nitrate and nitrite such as SST samples. Without good pH control in preparation of such samples, there is loss of some aromatic acid compounds. If the pH is less than about 6, there is loss due to nitration reactions. At pH greater than about 7, there is loss because of formation of acid salts that do not extract well in the nonpolar solvent. In addition, some basic compounds suffer loss at pH below about 6 because of the formation of non-extracting salts. The buffer pH range in this procedure is 6 to 7, which is optimum for maximum extraction efficiency.

The sonication process for the solids extraction ensures intimate contact of the sample matrix with the extraction solvent. Vortexing is used to provide adequate contact of the extraction solvent with the sample matrix in processing liquids. Extracts are filtered and evaporated to a volume suitable for optional GPC cleanup procedures followed by screening and/or analyses by GC/FID or GC/MS.

2.0 Apparatus

- a) Mortar and pestle.
- b) 1-mm standard sieve.
- c) Sonicator - Ultrasonic cell disrupter: Heat Systems - Ultrasonic, Inc. Model W-385 (475 watt) sonicator or equivalent (power wattage must be a minimum of 375 with pulsing capability) using a number 208 or number 305 3/4" disrupter horn for low level analyses, and a number 200 1/2" tapered disrupter horn and number 419 1/8" standard taper microtip probe.
- d) Oven, drying.

- e) Desiccator.
- f) Pasteur pipets, 1 mL or equivalent.
- g) Beakers, 400 mL.
- h) Pre-cleaned glass vials, ≥ 20 mL, with screw cap and Teflon liners.
- i) Buchner funnel.
- j) Filter paper, Whatman number 41 or equivalent.
- k) Glass conical funnel.
- l) Filter flask, 500 mL.
- m) Concentrator tube, 10, 15 or 25 mL graduated (Kontes K-570050-1025 or equivalent).
- n) Evaporator flask, 500 mL (Kontes K-570001-0500 or equivalent).
- o) Snyder column, 3-ball macro (Kontes K-503000-0121 or equivalent).
- p) Water bath evaporator, 8-position S-evap, SS boiling water bath Organomation Associates Catalog #12020 or equivalent.
- q) N-evap, 12 position with SS water bath Organomation Associates Catalog #11155 or equivalent.
- r) Boiling Chips, 10/40 mesh (silicon carbide or equivalent) solvent extracted or fired at 450°C for 24 hours, cooled in a desiccator and stored in vial with screw cap.
- s) Balance, capable of accurately weighing 0.01 g.
- t) Spatula, stainless steel or Teflon.
- u) Drying column, 10 mm - 20 mm ID. Pyrex® chromatographic column with Pyrex® glass wool at bottom. Note, the glass column may also be fitted with a Teflon stopcock and a fritted glass disc to retain the drying compound. However, they are difficult to decontaminate after used with highly contaminated extracts. Use a small pad of glass wool to retain the drying compound. Prewash the glass wool with acetone followed with elution solvent before packing the column with the drying compound.
- v) Centrifuge, capable of holding vials and reaching 2000 rpm.
- w) pH meter.
- x) Snyder column, 2-ball micro (Supelco 6-4694M or equivalent).

- y) Muffle furnace, capable of maintaining 400°C for several hours.
- z) Separatory funnel, 125 mL with Teflon stopcock.
- aa) Vortex mixer.
- bb) Gas tight syringes; at least 100, 500, and 1000 μ L. Disposable tip type pipettors can also be used.

3.0 Reagents

- a) Sodium sulfate, powdered or granular, anhydrous and reagent grade. Heated at 400°C for at least 4 hours, cooled in a desiccator and stored in a glass bottle. Baker anhydrous powder, catalog #73898 or equivalent.
- b) Extraction solvents (pesticide quality or equivalent).
- c) H_2SO_4 for pH adjustments, for example 1:1, 1:10, 1:20 dilutions of the as-received concentrated ACS reagent grade acid.
- d) KH_2PO_4 for pH adjustment, 1.0 to 1.5M (13.6 to 20.4 g dissolved in 100 mL deionized water). The 1.5M concentration is preferred to minimize the amount of water added.
- e) H_3PO_4 for pH adjustment, 1:5 dilution of the as-received concentrated ACS grade acid. Other dilutions may be required for some samples.
- f) NaOH for pH adjustment, 10N and 5N NaOH for the buffered liquid sample pH adjustment.

4.0 Standards

- a) Base/Neutral Compounds and Acid Compounds.

Surrogate standards are added to all samples, blanks, matrix spikes, matrix spike duplicates, and calibration solutions; the compounds specified are:

<u>Base/Neutrals</u>	<u>Acids</u>
Nitrobenzene- d_5	Phenol- d_5
Terphenyl- d_{14}	2,4,6-Tribromophenol
2-Fluorobiphenyl	2-Fluorophenol

b) Matrix Spike Compounds.

<u>Base/Neutrals</u>	<u>Acids</u>
1,2,4-Trichlorobenzene	Pentachlorophenol
Acenaphthene	Phenol
2,4-Dinitrotoluene	2-Chlorophenol
Pyrene	4-Chloro-3-methylphenol
N-Nitroso-di-n-propylamine	4-Nitrophenol
1,4-Dichlorobenzene	

Additional/different matrix spike and/or surrogate compounds may be specified by the Cognizant Scientist or the test instructions.

Prepare separate surrogate and matrix spiking solutions in methanol at 2000 µg/mL for the acid matrix spike and surrogate compounds and 1000 µg/mL for the base/neutral matrix spike and surrogate compounds. **NOTE:** High methanol concentrations in the sample extracts may cause problems. For example, extraction of some samples such as single shell tank samples with methylene chloride containing 20% methanol has resulted in formation of a second organic phase which causes problems with the GC/MS analysis. Store the solutions at 4°C (±2°C) in amber glass Teflon-sealed containers. The solutions must be replaced after twelve months, or sooner, if comparison with quality control check samples indicate a problem.

5.0 Safety

- a) Observe the general laboratory safety rules.
- b) Follow the requirements of applicable Radiation Work Procedure.
- c) Observe regulations for handling, storage and disposal of hazardous organic chemicals.

6.0 Quality Control

- a) A reagent blank shall be subjected to the same procedure for each set of samples processed at the same time.
- b) A matrix spike and matrix spike duplicate (see section 4.0.b) shall be performed on one sample from each set of samples having the same sample matrix and/or to one sample from each group of 20 samples received as a group and/or originating from the same sample matrix. The matrix spike and matrix spike duplicate samples shall be subjected to the same procedure.

- c) Base/neutral and acid surrogate spikes (see section 4.0.a) shall be added to all blanks, samples, and matrix spiked samples.
- d) Advisory limits for the surrogate and matrix spike compound recoveries for the buffered pH sample extraction method (section 7.3) are shown in tables 1 and 2. These values are based on a single set of samples, and will change as more data are acquired on a variety of SST and SST-like samples.

TABLE 1. ADVISORY SURROGATE RECOVERY CONTROL LIMITS

<u>Surrogate Compound</u>	<u>Level</u>	<u>Recovery Limits(%)</u>
Nitrobenzene-d ₅	50 µg	74-127
2-Fluorobiphenyl	50 µg	73-119
p-Terphenyl-d ₁₄	50 µg	69-126
Phenol-d ₅	50 µg	73-129
2-Fluorophenol	50 µg	78-132
2,4,6-Tribromophenol	50 µg	64-118

TABLE 2. ADVISORY MATRIX SPIKE RECOVERY LIMITS

<u>Matrix Spike Compound</u>	<u>Level</u>	<u>Recovery Limits(%)</u>	<u>RPD Limit</u>
1,2,4-Trichlorobenzene	50 µg	70-115	50
Acenaphthene	50 µg	74-121	50
2,4-Dinitrotoluene	50 µg	73-128	50
Pyrene	50 µg	69-130	50
N-Nitroso-di-n-propylamine	50 µg	78-138	50
1,4-Dichlorobenzene	50 µg	73-120	50
Pentachlorophenol	50 µg	63-112	50
Phenol	50 µg	76-133	50
2-Chlorophenol	50 µg	72-120	50
4-Chloro-3-methylphenol	50 µg	74-126	50
4-Nitrophenol	50 µg	63-114	50

- e) Duplicates are prepared when directed by the Cognizant Scientist or the test instructions.

7.0 Analysis

7.1 Initial Sample Preparation and pH Measurement.

- a) Verify that the sample has been received and logged into the Analytical Chemistry Laboratory.
- b) Grind and/or mix the sample thoroughly. **NOTE:** For preparing liquid samples go to section 7.6.
- c) Weigh a subsample, (weight shall be specified by the Cognizant Scientist) for pH measurement, typically 1 to 2 g.
- d) Add 1-5 mL of water per each g of sample, and stir for 1 hour, or until the pH is stable. Determine pH of the sample using a pH meter and electrode while stirring the sample. **NOTE:** Consult the Cognizant Scientist or the test instruction for the pH requirement. Close pH control to within 6 to 7 is necessary for some samples. If pH adjustment is needed, go to section 7.2 for samples with simple matrices (such as those containing very little nitrate or nitrite), or to section 7.3 for samples containing high concentrations of nitrate and nitrite (such as SST samples).

7.2 pH Adjustment Titer Measurement Using $\text{H}_2\text{SO}_4/\text{NaOH}$

- a) While stirring the sample, add acid or base dropwise until the pH reaches the required value. **NOTE:** Due to sample variability, it is recommended that the sample be adjusted to pH 6 to 7.
- b) Record sample weight, volume of water added to sample, initial and final pH, volume and concentration of acid or base added on the 325-B Hot Cells Sample Preparation Sheet and/or Organic Extraction Bench Sheet.
- c) Dispose of the sample used for the pH and acid/base adjustment measurement.

7.3 pH Adjustment Titer Using $\text{KH}_2\text{PO}_4\text{-Na}_2\text{SO}_4$.

Virtually all tank samples prepared by this procedure are basic, so this section describes an acid addition. In the event of an acidic sample, request direction from the Cognizant Scientist.

The relationship between the initial sample pH, the KH_2PO_4 added, the Na_2SO_4 added, the total amount of water added, and the texture of the final mixture is complex. Consequently, the following steps are guidelines. The shape and slope of the titration curve in the pH range of 6 to 7 will provide guidance for the final amount of sulfate to add, the value of the final sample pH, and

the amount of acid phosphate needed to obtain that pH. The choice of the final pH should allow for sample inhomogeneity and its effect on the amount of acid needed. The relative amounts of the sulfate and acid phosphate used should result in a mix with the sample that is sandy in texture. Because of the complexity of these requirements, more than one sample aliquot may be needed to obtain a good acid titer.

- a) To determine the titer for a nominal 1-g sample with less than about 20% water, add about 1 g of the Na_2SO_4 to the titer sample from step 7.1.d. Using a 500- μL syringe, add 50 to 100 μL increments of the KH_2PO_4 solution, recording the amount added and the pH after each addition. Continue the addition until a pH of 6.8 to 7.0 is reached. Slowly add 1 g Na_2SO_4 to the solution while stirring, and mix thoroughly. Measure the pH. If the pH is 6.4 ± 0.1 , record the amounts of sulfate and acid phosphate used. Continue the titration to at least pH 6, and proceed to the next step. If the pH is greater, more Na_2SO_4 may be needed to compensate for the acid to finish the titration. About 1 g of the sulfate is needed for each 0.5 mL acid added. Add the sulfate and measure the pH. If the pH is still high, add acid phosphate until the pH is 6.4 ± 0.1 , and record the amounts of acid phosphate and sulfate added. Continue addition of the acid phosphate as before until the pH is at least 6. **NOTE:** The titration of the titer sample should be continued past the desired pH to about 6 so that a well-defined slope is obtained. This will be helpful in selecting the amounts of sulfate and acid phosphate to add to the actual sample aliquots while forming a mixture sandy in texture.

To determine the titer for a nominal 1-g sample with about 20 to 60% water, add about 2 g Na_2SO_4 to the titer sample from step 7.2.d. Using a 500- μL syringe, add the acid phosphate until the pH is 6.8 to 7.0 as described previously for the drier sample. Slowly add 1 to 2 g Na_2SO_4 to the solution while stirring, and mix well. Measure the pH, and proceed with this sample as described in the preceding paragraph for the drier sample.

- b) Record sample weight, volume of water added to the sample, measured pH values as a function of acid volume added, and concentration of acid on the 325-B Hot Cells Sample Preparation Sheet and/or Organic Extraction Bench Sheet. Record the acid volume and the Na_2SO_4 amounts selected for the sample pH adjustment on the Organic Extraction Bench Sheet.
- c) Dispose of the sample used for the pH and acid/base adjustment measurement.

7.4 Extraction of Solid Samples for Medium Level Semivolatile Organics

- a) Weigh out a subsample for extraction. The weight shall be specified by the Cognizant Scientist and shall be recorded on the 325-B Hot Cells Sample Preparation Sheet and/or Organic Extraction Bench Sheet. (EPA suggested weight for the sample is 1 g).
- b) Add sample to a 40-mL pre-cleaned vial. If required, add a proportionate amount of acid or base (NaOH) and Na_2SO_4 as determined from sections 7.2 (H_2SO_4) or 7.3 (KH_2PO_4). If the pH adjustment is made according to section 7.2, about twice the sample weight of the Na_2SO_4 is recommended. More or less may be needed to achieve a final mixture that is sandy in texture. If the adjustment is made according to 7.3, use the amount of Na_2SO_4 determined in step 7.3.b. Record the amount. Mix it thoroughly into the sample. If the mix texture is not correct for samples prepared by the buffer method, it will be necessary to repeat section 7.3 with more or less sulfate.
- c) Add 50 μg of the base/neutral and 100 μg of the acid surrogate compounds to the vial (see section 4.0.a). Record all additions.
- d) If the sample is chosen for matrix spike or matrix spike duplicate, add 50 μg of the base/neutral and 100 μg of the acid matrix spike compounds. Record all additions (see section 4.0.b). **NOTE:** Due to high radiation levels, samples extracted in the Shielded Analytical Laboratory may require addition of the surrogates, spikes, and extraction solvent in one step.
- e) Add sufficient volume of methylene chloride to bring the final solution volume to 10.0 mL (considering the added volume of surrogate and matrix spike).
- f) Disrupt the sample with the 1/8-inch tapered microtip ultrasonic probe for 2 minutes at an output control setting 5 in the continuous mode. **NOTE:** Before extraction, mix the sample and make sure any lumps of the Na_2SO_4 are broken up and the mix is free flowing.
- g) Loosely pack a disposable pipet or column with 2 to 3 cm glass wool with 2 to 3 cm of granular anhydrous Na_2SO_4 on top. Do not pre-rinse the column.
- h) Filter the extract through the glass wool and Na_2SO_4 , and collect the extract. Transfer 5.0 mL to a concentrator tube. Record the volume transferred if less than 5.0 mL. Centrifugation may also be used in place of or in conjunction with the filtration.

- i) Place the concentrator tube in the N-evaporator with the water bath at approximately 35°C, and evaporate the solvent to approximately 0.5 mL using a gentle stream of nitrogen gas. The internal walls of the concentrator tube should be washed down with a small volume of methylene chloride during the operation. During the evaporation, the tube solvent level must be kept below the water level of the bath. The extract should never be allowed to become dry.

or

Attach a 2-ball micro-Snyder column, or equivalent, to the concentrator tube which contains the extract, and add a fresh silicon carbide boiling chip to the concentrator tube. Pre-wet the Snyder column with methylene chloride. Place the K-D (Kuderna-Danish) apparatus over a hot water bath at about 80 - 90°C and reduce the volume to approximately 0.5 mL. Remove the apparatus from the water bath, and allow it to cool for approximately 10 minutes.

- j) Transfer the 0.5 mL concentrate to a 2-mL screw top vial and dilute to 1.0 mL with rinsate of the ampule and Snyder column using quantitative transfer. Label the vial with the sample ID.
- k) Submit the sample for GC/FID screening or GC/MS screening and analysis.
- l) Submit a completed organic extraction bench sheet with the sample.

7.5 Extraction of Solid Samples for Low Level Semivolatile Organics

- a) Weigh out a sample specified by the Cognizant Scientist.
NOTE: The EPA protocol recommends a 30-g sample for the low level extraction. Record the sample weight on the Organic Bench Sheet.
- b) Add the sample to a clean 400-mL beaker or equivalent.
- c) If the sample pH determined in section 7.1 is outside the required range, add a proportional amount of acid or base as determined in section 7.2 to obtain the appropriate pH. Mix thoroughly. **NOTE:** The low level method is not expected to be used for the SST type samples, so the buffered acid pH adjustment (section 7.3) would not be necessary. If SST type samples do need to be prepared for analysis at low level, consult the Cognizant Scientist for direction.
- d) Add Na_2SO_4 at approximately twice the combined weight of sample and pH adjustment reagents. For example, add 60 g of anhydrous powdered Na_2SO_4 for 29 g sample with 1 g of

acid added. If more Na_2SO_4 is needed to achieve the desired sandy texture mixture, record the amount added.

- e) Add 100 mL of 1:1 methylene chloride-acetone.
- f) Add 50 μg of the base/neutral and 100 μg of the acid surrogate compounds to the sample (see section 4.0.a). Record all additions.
- g) If the sample is chosen for matrix spike or matrix spike duplicate, add 50 μg of the base/neutral and 100 μg of the acid matrix spike compounds. Record all additions (see section 4.0.c. NOTE: Due to high radiation levels, samples extracted in the Shielded Analytical Laboratory may require addition of the surrogates, spikes, and extraction solvent in one step.
- h) If a sample extract cleanup is to be performed using Gel Permeation Chromatography (GPC), add a volume of spiking solutions specified by the Cognizant Scientist. Record the standards number, volume, and concentration of the spiking solutions on the organic extraction bench sheet.
- i) Place the bottom surface of the 3/4-inch sonicator disrupter-horn about 1/2 inch below the surface of the solvent. Sonicate for 1 1/2 minutes with the W-385 using number 208 3/4-inch standard disrupter horn with the output control knob set at 10 (or number 305 3/4-inch tapped high gain Q disrupter horn at 5) and mode switch on "1 sec pulse" and percent duty cycle at 50%.
- j) Decant the extract through a #41 filter paper, or equivalent, approximately half filled with anhydrous Na_2SO_4 in a glass conical funnel. Centrifugation may also be used instead of, or in conjunction with, the above filtration. A Na_2SO_4 drying column must be used if the funnel drying method is not employed.
- k) Repeat the above extraction 2 times (steps 7.3.e, 7.3.i, and 7.3.j).
- l) Transfer the extracts to a K-D concentrator consisting of a concentrator tube, a 3-ball Snyder column and 500-mL evaporative flask. The concentrator should be pre-cleaned, and just before assembly it should be rinsed with methylene chloride. One or two clean boiling chips should be added to the concentrator tube during the assembly to prevent bumping.
- m) Place the K-D apparatus on a hot water bath at about 80 to 90°C so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the

flask is bathed with hot steam. Pre-wet the Snyder balls by adding a small amount of methylene chloride through the top of the condenser. At the proper rate of distillation the balls of the column will chatter continuously, but the chamber will not flood.

- n) When the volume in the concentrator tube is below 5 mL remove the K-D apparatus from the water bath and allow it to cool approximately 10 minutes.
- o) If screening is required, adjust the volume of the residue to 10 mL. A 1-mL aliquot of the solution in the concentrator tube can be transferred to an autosampler vial, and submitted for GC/FID or GC/MS screening. Normally, low level extracts are concentrated according to the following steps.
- p) Place the concentrator tube in the N-evaporator with the water bath at about 35°C and evaporate the solvent to approximately 0.5 mL using a gentle stream of nitrogen gas. The internal walls of the concentrator tube should be washed down with a small volume of methylene chloride during the operation. During the evaporation, the tube solvent level must be kept below the water level of the bath. The extract should never be allowed to become dry.

or

Attach a 2-ball micro-Snyder column or equivalent to the concentrator tube which contains the extract and add a fresh silicon carbide boiling chip to the concentrator tube. Pre-wet the Snyder column with methylene chloride. Place the K-D apparatus over a hot water bath at about 80 - 90°C, and reduce the volume to approximately 0.5 mL. Remove the apparatus from the water bath, and allow it to cool for approximately 10 minutes.

- q) Quantitatively transfer the 0.5 mL concentrate to a 2-mL screw top vial and dilute the concentrate to 1.0 mL using rinsates from the concentrator ampule and the Snyder Column. Label the vial with sample ID.
- r) Submit the sample with a completed organic extraction bench sheet for GC/FID screening or GS/MS screening or GS/MS analysis.

- 7.6 Preparation and Extraction of Liquid Samples With Relatively Clean and Simple Matrices. Request guidance from the Cognizant Scientist whether to use the method in this section or in section 7.7 for the more reactive samples.

- a) Measure a liquid aliquot into a clean vial or screw-top culture tube (usually 1 mL diluted 10 mL). The amount will be determined by the Cognizant Scientist or test instructions. Do not dilute the sample at this step.
- b) Use acid or base to adjust the pH of the sample to the value provided by the Cognizant Scientist or the test instructions. Because of sample variability, a pH of 6 to 7 is recommended. Record the reagent, its concentration and volume used, and the final pH.
- c) If a precipitate is produced, centrifuge the sample for 15 minutes at approximately 1500 rpm, and remove and save the supernate.
- d) The Cognizant Scientist or the test instructions will indicate if both phases are to be analyzed. If both phases are to be analyzed, proceed to step 7.4.b with the solid portion and to 7.6.f with the entire liquid portion. If solid portion is not extracted, continue with 7.6.e.
- e) Transfer an aliquot of the supernate to a vial (aliquot to be determined by Cognizant Scientist).
- f) Add 50 μg of the base/neutral surrogate compounds and 100 μg of the acid surrogate compounds to each vial. Record all additions.
- g) Add 50 μg of the base/neutral matrix spike compounds and 100 μg of the acid matrix spike compounds to the appropriate vials. Record all additions. **NOTE:** Due to high radiation levels, samples extracted in the Shielded Analytical Laboratory may require addition of the surrogates, spikes, and extraction solvent in one step.
- h) Add methylene chloride to the vial (5 mL is used for 10 mL sample or diluted sample). Extract the sample by vortexing the vial for a minimum of 1.5 minutes, venting as needed to release excess pressure.
- i) Allow the organic layer to separate from the aqueous phase for about 5 to 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, mechanical aids such as centrifuging may be needed to facilitate phase separation. Consult the Cognizant Scientist for direction.
- j) Remove the lower methylene chloride layer containing the semivolatile organic compounds using a pasteur pipet.

- k) Pass the extract through a disposable column (approximately 10-mm column) plugged with glass wool and containing approximately 10 cm of anhydrous Na_2SO_4 .
- l) Repeat the above extraction twice. (steps 7.6.h - 7.6.k).
- m) Transfer the extracts to a K-D concentrator (size dependent on quantity of extract). One or two clean boiling chips should be added to the concentrator tube during the assembly to prevent bumping. Proceed to 7.6.p, if an evaporative flask is not required.
- n) Place the K-D apparatus on a hot water bath at about 80 - 90°C so that the concentrator tube is bathed with hot steam. Pre-wet the Snyder balls by adding a small amount of methylene chloride through the top of the condenser. At the proper rate of distillation the balls of the column will chatter continuously, but the chamber will not flood.
- o) When the volume in the concentrator tube is below 1.0 mL remove the K-D apparatus from the water bath and allow to cool approximately 10 minutes.
- p) Place the concentrator tube in the N-evaporator with the water bath at about 35°C, and evaporate the solvent to 0.5 mL using a gentle stream of nitrogen gas. The internal walls of the concentrator tube should be washed down with a small volume of methylene chloride during the operation. During the evaporation, the tube solvent level must be kept below the water level of the bath. The extract should never be allowed to become dry.

or

Attach a 2-ball micro-Snyder column or equivalent to the concentrator tube which contains the extract, and add a fresh silicon carbide boiling chip to the concentrator tube. Pre-wet the Snyder column with methylene chloride. Place the K-D apparatus over a hot water bath at about 80 - 90°C, and reduce the volume to approximately 0.5 mL. Remove the apparatus from the water bath and allow it to cool for approximately 10 minutes.

- q) Quantitatively transfer the concentrate to a 2-mL screw top vial, and bring the volume to 1.0 mL using rinsates from the concentrator ampule and the Snyder column. Label the vial with sample ID, and submit the sample with a completed organic extraction bench sheet for GC/MS analysis.

7.7 Preparation of Liquid Samples by the Buffered pH Method. All steps in section 7.6 are followed except 7.6.b. This method is used to adjust samples with complex matrices containing high concentrations of nitrate and nitrite such as SST samples.

- a) Follow step 7.6.a. Usually, a 1-mL (or 1-g) sample diluted to 10 mL is used. Do not dilute to 10 mL at this step.
- b) Add 1 mL of the 5N NaOH to the sample from 7.7.a, and dilute to 10 mL. If more than 1 mL sample is used, it may be necessary to add more NaOH. The pH of the diluted sample after NaOH is added should be about 13.2 ± 0.2 .
- c) Add 1:5 H_3PO_4 until the pH is 6.5 ± 0.1 .
- d) Continue following steps 7.6.c through 7.6.q.

8.0 Specific Qualifications

None required. Surrogate and matrix spike standards traceable to nationally recognized standards are used as part of the quality control protocol, and are measured in the self-qualifying procedure PNL-ALO-345.

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