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Analysis of Organic Samples from Waste Tanks 26F, 33F, 46F, and 43H - Summer 1999

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SUMMARY

Analyses for organic materials in aqueous samples taken from Waste Tanks 26F, 33F, 46F and 43H and in a floating sample taken from Tank 43H have been completed. The results indicate that the concentration of organic materials is extremely low in all samples.

No quantifiable organics were found in the either the Tank 26F dip (surface) or variable depth sample (VDS - subsurface) samples or the Tank 46F dip samples. The total organic carbon analysis for the two Tank 26F samples indicated the presence of measurable amounts of organic carbon, but no quantifiable individual species were found. Neither semivolatile or total organic carbon analysis could be run on the Tank 46F sample.

The only quantifiable organic species found in the Tank 33F dip and VDS samples were non-volatile formate ion and in the subsurface VDS sample a small amount of normal paraffin hydrocarbon (NPH).

No quantifiable organic species were found in either the dip or VDS samples taken from Tank 43H, though total organic carbon analysis did indicate the presence of measurable organic carbon. Analysis of a floating organic sample taken from Tank 43H indicated the presence of small quantities of a number of volatile and semivolatile organic compounds. Because of the sampling method, converting quantities measured to a meaningful concentration in the tanks is not possible, but it appears that all materials are present in very small quantities in the tanks.

INTRODUCTION

The High Level Waste Tank Farms store and process high-level liquid wastes from a number of sources including F- and H-Canyon, Receiving Basin for Offsite Fuels (RBOF) and the Defense Waste Processing Facility (DWPF). These wastes are made alkaline prior to transfer to the Tank Farm and are subject to acceptance based on their composition. These wastes may contain minor concentrations of organic compounds. The Authorization Basis for the Tank Farms identifies several controls to prevent unwarranted, adverse chemical reactions. However, current analysis of the accident scenarios does not evaluate the impact of the presence of organic compounds. A Potential Inadequacy in the Safety Analysis (PISA) has been declared regarding the issue of organic compounds in the waste.[1] Processing vessels of concern include the pump tanks, waste tanks, and evaporators.

The resolution of this PISA includes sampling and analysis of the processing vessels of concern for organic constituents. This report documents the results of the analyses of liquid samples pulled from Waste Tanks 26F, 33F, 46F and 43H during the spring and summer of 1999.

DISCUSSION

Sampling Equipment

Sampling equipment included standard dip and variable depth samplers used in the Tank Farm. A floating organic sampler that was previously described in Reference 2 was also used.

Analytical Techniques

The analytical techniques used for the samples described in this report were previously described in Reference 2. These included gas chromatography-mass spectroscopy (GC-MS) for both volatile (purgeable from water with a boiling point < 200 °C) and semivolatile (extractable into methylene chloride with a boiling point between 150 and 500 °C) organic components. Scans are run for a spectrum of volatile and semivolatile organic species. With the exception of butanol, which is of particular interest, only those species actually found are reported herein. Ion chromatography (IC) was used to analyze for anions such as dibutyl phosphate (DBP), formate and oxalate and cations such as ammonia and the methylamines. Total inorganic carbon – total organic carbon (TIC/TOC) analysis was used to analyze for overall organic and inorganic carbon species in the liquid phase.

Analytical Results

Tank 26F/46F

Two samples were pulled from Tank 26F: a dip sample and a variable depth sample (VDS). A single dip sample was pulled from Tank 46F. Figure 1 is a picture of all three samples. The sample labeled 1 is the Tank 46F dip sample. The samples labeled 2 and 3 are the Tank 26F dip and variable depth samples, respectively. Both of the dip samples appeared relatively clear with no solids present. The Tank 26F variable depth sample appeared to contain a large amount of sludgy material. No separate organic phase was noted in any of the three samples.

A portion of both Tank 26F samples was extracted into methylene chloride for semivolatile analysis. During the methylene chloride extraction of the Tank 46F sample, the methylene chloride phase was incorrectly identified, and therefore the Tank 46F sample was not analyzed for semivolatile organic compounds. A second portion of all three samples was diluted to allow removal from the Shielded Cells and analyzed for volatile organic compounds, DBP, ammonia and the methylamines, TIC/TOC and formates and oxalates. No TIC/TOC analyses were run on the Tank 46F dip sample because the diluted sample was depleted before the analysis could be run.

No specific organic compounds were detected in either the volatile, semivolatile or ion chromatography analyses for methylamines, DBP, formates or oxalates. Lower limits of detection for generic volatile and semivolatile species as well as for specific species where they different from the generic are given in Table 1. The lower levels of detection are high for the IC analyses because the high salt concentration levels necessitated a large dilution to remove the interfering sodium ion. Though the minimum levels of detection are quite large, we do not believe that actual levels of ammonia and the methylamines are anywhere near these levels. The high salt concentrations of waste tank salt solutions considerably reduces the solubility of and increases the volatility of ammonia in waste tank salt solutions.[3] The methylamines would be expected to behave similarly.

The values given for TOC in for the Tank 26F samples in Table 1 appear quite high. It is believed that these are mostly made up of oxalate and formate that are quite soluble and non-volatile since oxalate is commonly found in Tank Farm salt solutions[4], and formate was found in two of the samples documented herein (Table 3).

Figure 1. Tank 26F Dip and Variable Depth Samples and Tank 46F Dip Sample
(Beaker 1 – Tank 46F Dip Sample, Beaker 2 – Tank 26F Dip Sample, Beaker 3 – Tank 26F Variable Depth Sample)

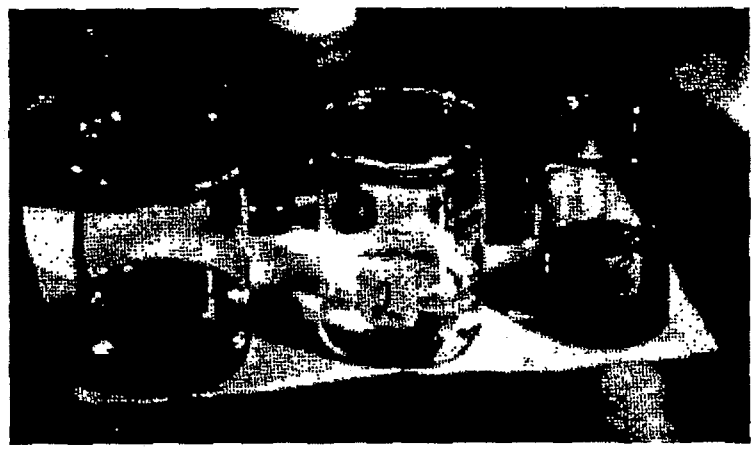


Table 1. Results for Tank 26F and 46F Organic Samples

	Analytical Results (mg/L)		
Species	Tank 26F Dip Sample	Tank 26F Variable Depth Sample	Tank 46F Dip Sample
Ammonium	<4,500	<4,440	<3,090
Methylamine	<4,500	<4,440	<3,090
Dimethylamine	<4,500	<4,440	<3,090
Trimethylamine	<11,300	<11,100	<7,710
Formate	<9,000	<8,880	<6,170
Oxalate	<9,000	<8,880	<6,170
Dibutyl phosphate	<900	<888	<617
Butanol	<20	<20	<20
Miscellaneous Volatile Organics	<0.1	<0.1	<0.1
Miscellaneous Semivolatile Organics	<2	<2	not determined
Total Inorganic Carbon	3,420	3,610	not determined
Total Organic Carbon	1,220	2,500	not determined

Tank 33F

Both a dip and a variable depth sample were pulled from Tank 33F. Figure 2 provides a picture of the two samples. In the picture, the dip sample is labeled 1 and the VDS sample is labeled 2. The VDS appears to be slightly cloudy, perhaps from sludge, but does not contain a significant amount of solids. No separate floating organic phase was noted in either of the samples.

As with the Tank 26F samples, a portion of both Tank 33F samples was extracted into methylene chloride for semivolatile analysis. A second portion of both samples was diluted to allow removal from the Shielded Cells and analyzed for volatile organic compounds, DBP, TIC/TOC and formates and oxalates.

Figure 2. Tank 33F Dip and Variable Depth Samples
(Beaker 1 – Tank 33F Dip Sample, Beaker 2 – Tank 33F Variable Depth Sample)

No volatile organic compounds were found in either of the Tank 33F samples. The lower limits of detection for volatile organics in these samples is given in Table 2. Since butanol is of particular concern in the Tank Farm, the samples were specifically analyzed for that species.

In the semivolatile analysis, nothing was found in the dip sample. Normal paraffin hydrocarbons (NPH) at a concentration of 37 mg/L were found in the VDS sample. The lower limit of detection for other semivolatiles is given in Table 2. The source of NPH in the VDS sample is likely the n-paraffin mixture used by the canyon as a diluent for TBP in the F-Canyon Purex process. The Tank 33F VDS sample was the only sample in which NPH was found, though if it had been present it would have been detected in all of the samples with analytical techniques used. Since the NPH is less dense than supernate salt solution it is unclear why this would be found subsurface and not in a surface sample. One possible explanation is that some of the NPH had adhered to sludge in the bottom of the tank.

The IC analysis indicated the presence of formate but no DBP or oxalate. Some formate was found. No IC-cation analysis (ammonia and methylamines) was requested on these samples. ADS chemists indicate that their experience indicates that these species are not likely present in SRS waste tanks containing high

caustic concentrations (see section on "Future Sample Analyses" below). The high lower limits of detection given for IC results in Table 2 result from the large dilution required to remove sufficient radioactivity from the samples to allow analysis. Additionally, the dilution is required to remove sodium ion that interferes with the IC analysis. The results of the IC and TIC/TOC analyses are given in Table 2. The TOC results appear to be of the same order of magnitude as the analyzed formate concentration and, therefore, are probably comprised largely of soluble nonvolatile formate, as well as oxalate. These species are not a flammability hazard.

Table 2. Results of IC and TIC/TOC Analyses for the Tank 33F Samples.

	Analytical Results (mg/L)	
Species	Tank 33F Dip Sample	Tank 33F Variable Depth Sample
Dibutyl Phoshate	<3,980	<3,750
Formate	1,310	1,350
Oxalate	<398	<375
Total Inorganic Carbon	1,080.	975.
Total Organic Carbon	1,270.	2,250.
Butanol	<20	<20
Miscellaneous Volatile Organics	<0.1	<0.1
Normal Paraffin Hydrocarbons	-	37
Miscellaneous Semivolatile Organics	<1	<1

Tank 43H

Both dip and variable depth samples were pulled from Tank 43H, as well as a floating organic sample. Pictures of the dip and VDS samples are shown in Figure 3. Both samples were clear and neither contained any noticeable solid or organic phase.

Figure 3. Tank 43H Dip and Variable Depth Samples

Figure 4 shows the Tank 43H floating organic sample solid phase extraction (SPE) disk. Figure 5 shows the container which the SPE disk came in. The floating organic sample SPE disk and container both contained specs of a black solid, possibly sludge solids.

Figure 4. Tank 43H Floating Organic Sample SPE Disk.

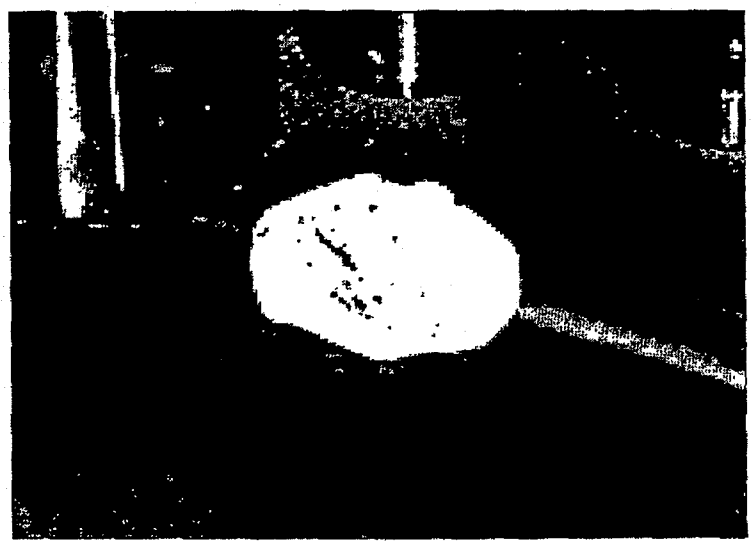
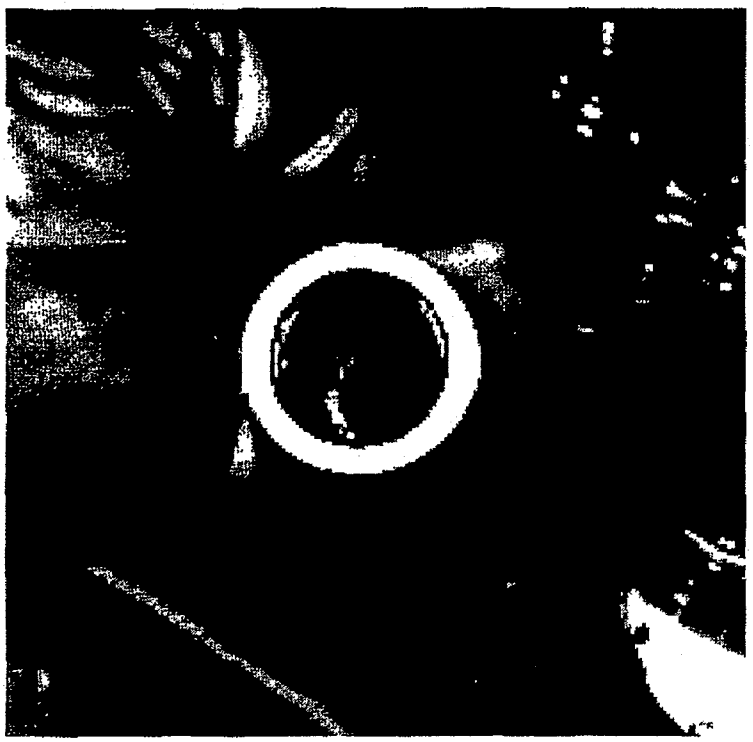


Figure 5. Inside of Tank 43H Floating Organic Sample Container.



No semivolatile organic compounds were detected in either the Tank 43H dip or VDS samples. No DBP, formate or oxalate was detected by IC-anion analysis. No IC-cation (for ammonia and the methylamines) analysis was performed on these samples. The lower limit of detection for the analyses performed are given in Table 3. The results of the TIC/TOC analysis are also give in Table 3. The lower limits of detection given in Table 3 for the IC results are quite high. This is the result of the large dilution required to remove sufficient radioactivity to allow analysis and to eliminate the sodium ion interference. As with the previous samples, the TOC concentration is high. Again, this carbon is believed result largely from soluble, non-volatile formate and oxalate which are known to exist in the Tank Farm.

Table 3. Results of Analyses for Tank 43H Samples

Species	Analytical Results (mg/L) Tank 43H Dip Sample	Tank 43H Variable Depth Sample
Dibutyl Phosphate	<396	<364
Formate	<3960	<3,640
Oxalate	<3,960	<3,640
Miscellaneous Semivolatile Organics	<1	<1
Butanol	<20	<20
Miscellaneous Volatile Organics	<1.8	<2
Total Inorganic Carbon	1,270.	1,090.
Total Organic Carbon	2,930.	182.

The solid phase extraction (SPE) disk with the floating organic sample was found to contain small quantities of a number of semivolatile compounds. These are given in Table 4. Three volatile organic compounds were also found and are given in Table 4. Analysis for ammonia and the methylamines was also completed, but none were found. The lower limits of detection for the methylamines were also documented in Table 4. Because the floating organic sampler is not quantitative, the amounts given in Table 4 represent only the relative amounts of each species found on the SPE disk and do not represent the total amount of material in Tank 43H.

The semivolatile organic compounds found in the Tank 43H floating organic sample appear to be possible decomposition products of ion-exchange resin as well as potential laboratory waste. The volatile organic compounds found in the sample appear to result from laboratory waste.

Table 4. Tank 43H Floating Organic Sample Results

Analyte	Analytical Results (µg/SPE disk)
Semivolatile Organic Compounds	
1-Phenyl-1-butene	4,000
Napthalene	2,600
1-ethenyl-4-ethyl-Benzene	1,300
1,3,5-triethyl-Benzene	1,300
1,4-diethyl-Benzene	720
1,4-dimethyl-2-(2-methyl)Benzene	680
4-tert-Butyltoluene	640
Cyclododecane	620
1,2,4-triethyl-Benzene	480
1,2-diethyl-Benzene	320
Isopthalaldehyde	290
2,2-dimethyl-3-Decene	160
1-ethyl-4-(2-methylpropyl)Benzene	140
1,4-dimethyl-2-(2-methyl)Cyclohexane	96
1-methyl-3-pentyl-Cyclohexane	72
2,2,3,5,6-pentamethyl-3-Heptene	64
1,3-diethenyl-Benzene	63
2-ethyl-1-Hexanol	56
1,1,3,5-tetramethyl-Cyclohexane	44
(1-ethylpropyl)-Benzene	41
Pentamethyl-Pyridine	33
9-Octadecene	32
3,3-diethyl-4,5-dimethyl-4-hexene-2-one	31
(Z)-3-Heptadecene	30
Diisooctyl adipate	25
Cyclopentyl-Benzene	24
8-Heptadecene	22
Volatile Organic Compounds	
Toluene	1,200
p- and m- Xylene	400
Butanol	<2.5
Methylamines	
Ammonia	<800
Methylamine	<800
Dimethylamine	<800
Trimethylamine	<2,000

Future Sample Analyses

Since sampling waste tanks for organic compounds is still a relatively new undertaking, the requested analyses have not always been consistent from sample to sample. A consistent set of analyses needs to be documented. Table 5 provides the set of analyses that will be requested for future analyses. Other analyses, as requested in writing by CSTE may be added to this standard set as needed. ADS chemists indicate that ammonia and methylamine are likely not present in SRS waste tanks containing high caustic concentrations. However, IC analyses for these species will be continued for the present to verify that

they are not present in the waste tanks. Analyses for oxalates and formates are requested for aqueous samples only, since these are non-volatile, water soluble salts. The TIC/TOC analysis is not meaningful in the organic solvents into which the floating organic sample and solvent desorption tubes must be extracted.

Table 5. Standard Analyses for Future Tank Farm Organic Samples

Sample	Analyses to be Requested
Dip and Variable Depth Samples	Volatile Organics Semivolatile Organics IC-Anions (oxalate and formate) TIC/TOC IC-Cations (Ammonia and methylamines) DBP
Floating Organic	Volatile Organics Semivolatile Organics IC-Cations (Ammonia and the methylamines)
Vapor Phase Samples (Solvent Desorption Tubes)	Volatile Organics Semivolatile Organics IC-Cations (Ammonia and the methylamines)

QUALITY ASSURANCE

Analysis of the samples was performed using routine ADS quality assurance protocols. It should be noted that the ADS laboratory is not certified by the South Carolina Department of Health and Environmental Control (DHEC) for the purposes of generating data that is required to demonstrate compliance with a specific permit. The data is qualified for the purposes of establishing knowledge of the process or facility. Any data from this laboratory that is available or submitted to DHEC must be qualified as originating from a non-certified lab.

Data collected from these analyses is kept in laboratory notebooks WSRC-NB-99-00006 and WSRC-NB-99-00228.

During preparation of the Tank 46F sample for analysis, the methylene chloride extract from that sample was lost. The methylene chloride used to extract the organic species is quite dense and would ordinarily be expected to sink to the bottom of the vial during the extraction. In the case of the Tank 46F sample, the sample was a highly concentrated salt solution and was therefore denser than the methylene chloride. The less dense methylene chloride sample was set aside instead of the aqueous phase and ultimately evaporated. ADS has identified a water soluble dye that will be used to color the aqueous phase in future organic sample extractions. This will eliminate the possibility of error due to mistaken phase identification.

ACKNOWLEDGEMENTS

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APPROVALS

Robert F. Swingle II Date: 10/21/99
R. F. Swingle, Author
Waste Handling and Mechanical Processing

D. T. Hobbs Date: 10/21/99
D. T. Hobbs, Design Check per Manual E7, Procedure 2.40
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STI, 703-43A