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Analysis of Vapor Samples from the Organic PISA High Level Waste Tanks

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Summary

Analyses for organic materials in vapor samples taken from the eight High Level Waste tanks (26F, 33F, 46F, 11H, 22H, 32H,39H, and 43H) have been completed. Of these tanks, 26F, 33F, and 43H are designated "organic" tanks. Samples were collected on solvent desorption (SD) tubes (containing activated charcoal) from various heights above the tank waste. Tank ventilation was stopped for one hour prior to sampling and was not reinitiated until sample collection was complete. The results indicate that the concentration of organic materials is extremely low in all samples.

Some organic materials were found in the vapor samples but in nanogram/liter (ng/L) quantities. These materials were present in the samples within the practical quantitation limit (PQL), which represents a practical and routinely achievable detection limit with a relatively good certainty that any reported value is reliable. Because of the low levels and the fact that no field background analysis was run (laboratory background analyses were run), the researchers cannot absolutely determine whether the materials were actually taken from the waste tanks or whether they are from environmental background. In any case, the quantities of material found are several orders magnitude below that which would comprise a flammability concern.

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. 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 development of sampling and analysis techniques for this sampling as well as the results of the analyses of vapor samples pulled High Level Waste tanks that were implicated in the organic PISA.

Discussion

Sampling Equipment

Vapor Sampler

The Passive Vapor Sampler uses solvent desorption (SD) tubes for vapor sampling. Selection of a particular SD tube depends upon the chemical species to be detected. Based upon the anticipated chemicals in the vapor space it was decided to use activated coconut charcoal tubes (ORBO 32 Large, Bed Wt.400/200mg), which has been extensively studied and summarized, for use as a general adsorbent for organics. This charcoal adsorbent type is routinely used by Industrial Hygiene field studies to differentiate between methane and other organic vapors. In this method, a survey tool that detects carbon compounds in air is fitted with a charcoal filter that effectively traps all non-methane organics while allowing the methane (only) to pass through the filter for measurement. Appendix 1 gives a description of the standard OSHA method used with this cartridge.

Figure 1 shows a photograph of the Passive Vapor Sampler. The major components are Supelco Air Sampler, flow meters, HEPA filters, solvent desorption (SD) tubes and valves. The entire system is housed in a weatherproof stainless steel cabinet. The Supelco Air Sampler is essentially a vacuum pump controlled by a digital timer. The vacuum pump is capable of drawing two sample streams through two SD tubes. Flow rate of each stream can be controlled individually in the range 0 – 400 (1000) ml/min. The vapor sample from the tank enters the system through a ¼" port on the backside of the system cabinet. Samples were drawn from the tank using a ¼" OD, 50 ft long polyethylene tubing. Upon entering the sampler cabinet, the sample splits into two identical paths leading to two different SD tubes. Note that each SD tube is capable of absorbing a large number of organics and other vapors. In each path, the sample passes through a three-way valve, SD tube, a HEPA filter, flow meter and the vacuum pump. With the help of the three-way valve, the SD tube can be bypassed in order to flush the tubing between the sampling system and the tank vapor space. Typically a 10-minute flush-out will pull a sample volume of about 8 liters (about 100 meters long, 1 cm ID line).

The Supelco Air Sampler can be operated on rechargeable batteries for 12 hours of continuous operation. It can also be operated directly by 115 V supply using a converter.

Detailed operating instructions are documented in a memo SRT-ETF-990001.

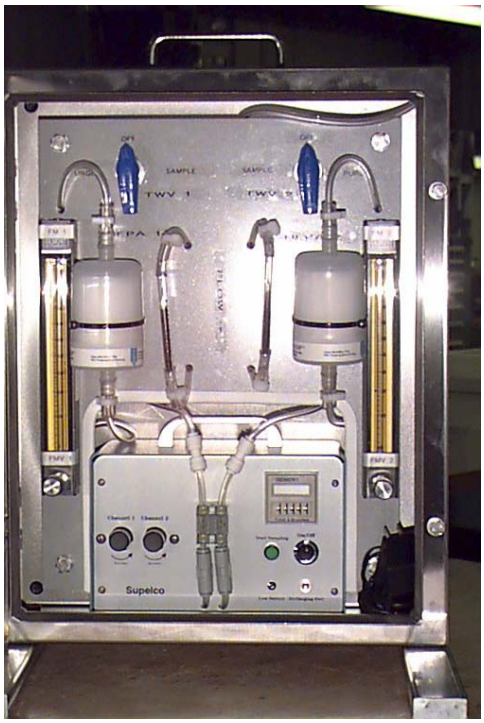

Figure 1. Passive Air Sampler

Sampling Techniques

Sampling was initiated for each tank at 60 minutes after shutdown of tank ventilation systems. The initial (C) was taken at 6 inches from the bottom of the riser, and completed at 160 minutes.

Sample	Sampling location	Sample drawn from tank vapor phase
A	18" from liquid surface	260 minutes to 360 minutes after ventilation shutdown
B	6" from bottom of riser	160 minutes to 260 minutes after ventilation shutdown
C	midpoint between A and B	60 minutes to 160 minutes after ventilation shutdown

Analytical Techniques

Vapor Phase Samples

For vapor samples, a nominal 100 liters of vapor were drawn through the adsorption tube. In the laboratory, the samples were chemically desorbed, and aliquots of the resulting extract were analyzed by GC-MS and/or Ion Chromatography.

Once the vapor phase samples were pulled using the vapor sampler, analysis of the organics captured in the solvent desorption tubes was performed using standard analytical protocols. Analytical Development Section personnel desorbed the organic material from the SD tubes with methanol for analysis for volatile organic materials using Gas Chromatography – Mass Spectrometry (GC-MS). Amines were analyzed in the methanol extract by Ion Chromatography. After methanol desorption, the samples were desorbed with methylene chloride for semivolatile organic analysis by GC-MS.

Volatile Organic Analysis

Volatile organics are those organic compounds with boiling points £ 175°C. Volatile organic analyses were performed by Gas Chromatography - Mass Spectrometry (GC-MS), using ADS method. Samples were concentrated using an OI Analytical model 4460A Dynamic Headspace concentrator (Purge and Trap), using a VOCARBä trap. Separation was performed with a Hewlett Packard 5890 series II gas chromatograph on a 60m x 0.75mm VOCOLä fused silica capillary column with 1 µm film thickness. Quantitation was performed with a Hewlett Packard Model 5970 quadrupole mass spectrometer. The capillary column was directly connected to the inlet into the mass spectrometer. Internal standard compounds were added as specified in the Contract Laboratory Program for volatile organics (SOW 7-93) and used as the basis of calculation for the non-priority pollutant (CLP Target) compounds. While this method is very similar and comparable to the RCRA method, data should be qualified with this basis of origination.

Semivolatile Organic Analysis

Semivolatile organics are organic compounds with boiling points between 150 and 500°C. Preparation for semivolatile analysis involves extraction of organic materials from sample media with methylene chloride. GC-MS analysis is used to identify the organic compounds in the extracted organic material. Analytical separations are completed using a Hewlett Packard 6890 gas chromatograph equipped with a 30 m DB-5 column with 0.25 mm diameter and 0.25 m m film thickness. Quantitation was performed using a Hewlett Packard 5973 mass selective detector. The mass spectrometer tuning was confirmed within 24 hours prior to each measurement using perfluorotributylamine (PFTBA).

Other Analysis

ADS personnel used ion chromatography (IC) to analyze the cations of ammonia and amines captured on the ORBO 32 activated charcoal SD tube.

Analytical Results

Volatile Organic Compounds and Amines

The practical quantitation limit (PQL) for this method, at this particular preparation was 10 ng of volatile compound per liter of gas for most compounds. The compounds listed in Table 1 were detected in the volatile organic chromatographic traces and are corrected for laboratory background levels (if present).

Table 1. Organics and Amines found in High Level Waste Tank Vapor Samples

HLW Tk and Sample		Result Summary
26F	A	Organics not detected (see note 1)
	B	Organics not detected (see note 1)
	C	Organics not detected (see note 1)
33F	A	NBuOH=1.3 µg/L, ammonia=0.26 µg/L [no other Organics detected]
	B	NBuOH=1.3 µg/L, ammonia=0.23 µg/L [no other Organics detected]
	C	NBuOH=1.0 µg/L, ammonia=0.17 µg/L [no other Organics detected]
46F	A	Organics not detected (see note 1)
	B	Organics not detected (see note 1)
	C	Organics not detected (see note 1)
11H	A	Organics not detected (see note 1)
	B	Organics not detected (see note 1)
	C	Organics not detected (see note 1)

22H A	Organics not detected (see note 1)
B	Organics not detected (see note 1)
C	Organics not detected (see note 1)
32H A	Hexanes = 0.15 µg/L (note 2) [no other Organics detected]
B	Hexanes = 0.18 µg/L (note 2) [no other Organics detected]
C	Hexanes = 0.12 µg/L (note 2) [no other Organics detected]
39H A	Organics not detected (see note 1)
B	Organics not detected (see note 1)
C	Organics not detected (see note 1)
43H A	Organics not detected (see note 1)
B	Organics not detected (see note 1)
C	Organics not detected (see note 1)

note 1 No organic compounds were detected in the mass spectral scans, including the alkyl amines.
n-BuOH < 0.1 µg/L
methylamine < 0.2 µg/L
dimethylamine < 0.2 µg/L
trimethylamine < 0.5 µg/L
all other volatile target compounds < 0.01 µg/L
highly water soluble volatile organics (like butanol) would be detected at a level of detection comparable (~10x of targets) to butanol.
semivolatile organic compounds < 0.08 µg/L

note 2 Mixed hexanes consisting of n-hexane and various isomers of methylpentane are commonly used as laboratory extraction reagents. While the presence of laboratory grade hexanes could be attributed to solvents used in the TBP analysis preparation, no QC indicators support contamination by the SRTC labs. Breakthrough indicators were negative, and other samples processed within the prep/analysis batch were also negative. The appearance of mixed hexanes in the vapor could be attributed to field contamination, or actual presence in the tank waste through laboratory operation wastestreams.

Semivolatile Organic Compounds

Twenty-four samples were submitted for semivolatile organic compound analysis. Data indicate that the only detectable semivolatile organics found in the tank vapor samples were organosilicon compounds, specifically short chain polydimethylsiloxanes. The source of the silicon compounds is not clear, however silicone oils and greases are found in a number of lubricating agents, as well as antifoaming products. Since these compounds can be generated as artifacts of gas chromatographic analysis, no quantitation was carried out for the materials.

Sample Preparation

Volatile Organics

Solvent desorption tube samples were prepared by dividing the charcoal from each tube into two parts: A for the front section and B for the back section. Both Each of the twofour parts were extracted with methanol. The extracts were analyzed by GC/MS. For all of the analytes detected in the sample tubes, no breakthrough was observed in any sample. Analysis results that are reported from the vapor tube samples assume that 100 liters of representative tank vapor had been pulled through the tubes. Results are reported as µg analyte per liter of air, e.g. µg n-butanol / liter of tank vapor.

Semivolatile Organics

Preparation for semivolatile analysis was by extracting the SD cartridges into methylene chloride with analysis by GC-MS. The PQL for this analysis is 80 ng/L.

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 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-97-216 (volatile organic analysis), WSRC-NB-98-00287 (semivolatile organic analyses), WSRC-NB-98-00249 (total organic carbon) and WSRC-NB-97-0058 (for ion chromatography methods).

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1. M. Layton, "Contribution of Organics to the Tank Farm Deflagrations," NI-HLW-98-007, Revision 3, July 27, 1999.
2. A. Kisilev, Advanced Chromatography, Volume 4, p. 113 (1967).
3. J. Hassler, Activated Carbon, Chemical Publishing Co., New York, 1963.
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5. "Gas Chromatography/Mass Spectrometry for Volatile Organics: Contract Laboratory Program Methods," Manual L16.1, Procedure ADS-2656, Revision 2, June 1, 1998.
6. "Gas Chromatography/Mass Spectrometry for Semivolatile Organics: Contract Laboratory Program Methods," Manual L16.1, Procedure ADS-2657, Revision 1., January 20, 1997.
7. "Analysis of Solutions by Ion Chromatography," Manual L16.1, Procedure ADS-2306, Revision 7, January 30, 1998.

Appendix 1. Analytical Method for Organic Vapors

METHOD #: 07 (Issue Nov.1979, Last Update Nov. 1989))

TITLE: Organic vapors

ANALYTE: **CAS #**

Allyl chloride	
n-Amyl acetate	
sec-Amyl acetate	
Benzene	71-43-2
Benzyl chloride	100-44-7
Bromoform	75-25-2
2-Butoxyethanol(butyl cellosolve)	111-76-2
Butyl acetate	123-86-4
sec-Butyl acetate	105-46-4
tert-Butyl acetate	540-88-5
Butyl alcohol	71-36-3
sec-Butyl alcohol	78-92-2
tert-Butyl alcohol	75-65-0
n-Butyl glycidyl ether (BGE)	75-65-0
p-tert-Butyltoluene	98-51-1
Camphor	76-22-2
Carbon tetrachloride	56-23-5
Chlorobenzene (monochlorobenzene)	108-90-7
Chloroform (trichloromethane)	67-66-3
Chloroprene (2-chloro1,3-butadiene)	126-99-8
Cumene	98-82-8
Cyclohexane	110-82-7
Cyclohexanol	108-93-0
Cyclohexene	110-83-8
Diacetone alcohol(4-hydroxy-4-methyl-2-pentanone)	123-42-2
o-Dichlorobenzene	95-50-1
p-Dichlorobenzene	106-46-7
1,1-Dichloroethane	75-34-3
1,2-Dichloroethylene	540-59-0
Dichloroethyl ether	111-44-4
1,1-Dichloro-1-nitroethane**	594-72-9
Difluorodibromomethane (F-12-B2)*	75-61-6
Diisobutyl ketone	108-83-8
N,N-Dimethylaniline	121-69-7
Dioxane (diethylene dioxide)	123-91-1
Dipropylene glycol methyl ether	34590-94-8
Enflurane (OSHA method #29)*	13838-16-9
Epichlorohydrin	106-89-8
2-Ethoxyethanol (Cellosolve,)	110-80-5
2-Ethoxyethylacetate (Cellosolve acetate)	111-15-9

ANALYTE:	**CAS #**
Ethyl acetate	141-78-6
Ethyl acrylate	140-88-5
Ethyl alcohol (ethanol)	64-17-5
Ethyl sec-amyl ketone (5-methyl-3-heptanone)	541-85-5
Ethyl benzene	100-41-4
Ethyl bromide	74-96-4
Ethyl butyl ketone (3-heptanone)	106-35-4
Ethylene chlorohydrin**	107-07-3
Ethylene dichloride (1,2-Dichloroethane)	107-06-2
Ethyl ether	60-29-7
Ethyl formate	109-94-4

Glycidol (2,3-epoxy-1-propanol)	556-52-5
Halothane	151-67-7
n-Heptane	142-82-5
Hexachloroethane	67-72-1
n-Hexane	110-54-3
2-Hexanone (MBK)	591-78-6
Hexone (MIBK)	108-10-1
sec-Hexyl acetate	108-84-9
Isoamyl acetate	123-92-2
Isobutyl acetate	110-19-0
Isobutyl alcohol	78-83-1
Isophorone**	78-59-1
Isopropyl acetate	108-21-4
Isopropyl alcohol	67-63-0
Isopropyl ether	108-20-3
Isopropyl glycidyl ether	4016-14-2
Mesityl oxide	141-79-7
2-Methoxyethanol (methyl cellosolve)	109-86-4
2-Methoxyethylacetate (methyl cellosolve acetate)	110-49-6
Methyl acetate	79-20-9
Methyl acetylene-propadiene* mixture (MAPP)	59355-75-8
Methyl acrylate	96-33-3
Methylal (dimethoxymethane)	109-87-5
Methylcyclohexane	108-05-3
Methylene chloride*	75-09-2
Methyl isobutyl carbinol	108-11-2
a-Methyl styrene	98-83-9
Naphthalene	91-20-3
Octane	111-65-9
Pentane	109-66-0
2-Pentanone	107-87-9
Phenyl ether	101-84-8
Phenyl glycidyl ether	122-60-1
n-Propyl acetate	109-60-4
Propyl alcohol	71-23-8

ANALYTE:	**CAS #**
Propylene dichloride	78-87-5
Propylene oxide	75-56-9
n-Propyl nitrate**	627-13-4
Pyridine	110-86-1
Styrene	100-42-5
1,1,1,2-Tetrachloro2,2-difluoroethane	76-11-9
1,1,2,2-Tetrachloro1,2-difluoroethane	76-12-0
1,1,2,2-Tetrachloroethane**	79-34-5
Tetrachloroethylene (perchloroethylene)	127-18-4
Tetrahydrofuran	109-99-9
Tetramethyl succinonitrile	3333-52-6
Toluene	108-88-3
1,1,1-Trichloroethane (methyl chloroform)	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethylene	79-01-6
1,2,3-Trichloropropane	96-18-4
Vinyl chloride	75-01-4
Vinyl toluene	25013-15-4
Xylene	1330-20-7

INSTRUMENTATION: GC

Matrix: Air

Procedure: Collection on charcoal, desorption with an organic solvent, and analysis by gas chromatography with flame ionization detector.

Status of method: This method has been used extensively in the OSHA Analytical Laboratory. With slight modification, this method is a generalized version of validated NIOSH methodology. This method has been revised to include validated OSHA methodology also.

Reference:

5.1 "NIOSH Manual of Analytical Methods", ed. 2 Vol. 1-4 National
Institute of Occupational Safety and Health, U.S. Government Printing Office, Washington, D.C. (1977-78) 07-12