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Department of Energy
Richland Operations Office
P.O. Box 550
Richland, Washington 99352

95-PCA-200

MAR 08 1995

Mr. David L. Lundstrom
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Nuclear Waste Program
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Department of Ecology
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Mr. Joseph J. Witczak
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Department of Ecology
P.O. Box 47600
Olympia, Washington 98504-7600

Dear Messrs. Lundstrom and Witczak:

DESCRIPTION OF ANALYTICAL TESTING METHOD FOR VOLATILE ORGANICS IN CONCRETE (T-3-1)

The U.S. Department of Energy, Richland Operations Office (RL) and the Westinghouse Hanford Company (WHC) are proposing the use of a sonification/zero headspace procedure to prepare concrete samples for volatile organics analysis (VOA). Enclosed is the procedure for analysis of volatile organics in concrete and a description of the procedure verification process. Transmittal of this procedure and procedure verification is needed to support the 300 Area Solvent Evaporator closure activities. These activities have been previously discussed in various Unit Manager Meetings with Bob Cordts of the State of Washington Department of Ecology.

The use of this procedure covers sonification/zero headspace methodology to prepare concrete samples for VOA. This procedure was developed at WHC because no promulgated analytical method existed for the VOA of concrete samples. The procedure to prepare samples for subsequent analysis uses an existing WHC procedure based on SW-846 Method 8260.

Should you have any questions, please contact Ms. E. M. Mattlin, RL, on (509) 376-2385 or Mr. F. A. Ruck III, WHC, on (509) 376-9876.

Sincerely,

James E. Rasmussen

James E. Rasmussen, Acting Director
Environmental Assurance, Permits,
and Policy Division
DOE Richland Operations Office

EAP:EMM

W T Dixon

William T. Dixon, Manager
Environmental Services
Westinghouse Hanford Company

Enclosure:
Sonification/Zero
Head Space Procedure for
Preparation of Concrete Samples
for Volatile Organics Analysis

cc w/encl:
Admin. Record
EDMC, H6-08
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R. Cordts, Ecology
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Enclosure

Sonification/Zero Head Space Procedure
for Preparation of Concrete Samples for
Volatile Organics Analysis

SONIFICATION/ZERO HEAD SPACE PROCEDURE FOR PREPARATION OF CONCRETE SAMPLES FOR VOLATILE ORGANICS ANALYSIS

The U.S. Department of Energy, Richland Operations Office (RL) and Westinghouse Hanford Company (WHC) propose the use of a sonification/zero headspace procedure developed at WHC to prepare concrete samples for volatile organics analysis (VOA). This procedure is used to prepare samples for subsequent analysis using a WHC procedure based on SW-846 Method 8260. This procedure will be used to prepare samples from concrete as part of the 300 Area Solvent Evaporator Closure Plan activities.

Background

This procedure is being submitted to the Washington State Department of Ecology (Ecology), at the Ecology's Unit Manager's request. This request is documented in the 300 Area Solvent Evaporator (ASE), Unit Managers' Meeting minutes of May 4, 1993. Ecology specifically requested that RL submit the procedure following the Washington Administrative Code (WAC) 173-303-110(5). WAC 173-303-110(5) references the guidelines stated in WAC 173-303-910(2). The description of the procedure will follow the guidelines in WAC 173-303-910(2)b(i) through (v).

The Resource Conservation and Recovery Act (RCRA) closure plan for the 300 ASE includes sampling and analyzing concrete for volatile organic compounds (VOCs). The current acceptable method for volatile organics analysis (VOA) is the SW-846 Method 8260. This method is useful for soils and sediments and is prescribed in WAC 173-303-110. However, this method is not documented for analysis of concrete samples. Because the physical nature and the chemistries of soils and concrete are vastly different, it is unreasonable to expect the SW-846 Method to be suitable for performing VOA on concrete samples.

The proposed sample preparation method (attached) was developed at the WHC laboratories in response to the need for analysis of concrete at the 300 ASE. The proposed procedure was developed after it was determined that no adequate preparative procedure exists for these analytes in a concrete matrix. A detailed literature search covering the last 30 years produced only one documented VOA performed on concrete. Only two VOCs were studied and they were unable to be quantified using the method. Thus, this documented analysis is unsuitable for this task.

The proposed method prepares the sample for analysis by sonification, using WHC procedure LA-523-435. The VOCs are desorbed from the concrete into high purity water. The VOA target compounds are then determined by gas chromatography/mass spectroscopy (GC/MS) using a WHC procedure based on SW-846 Method 8260. This paper describes the sample preparation method, WHC procedure LA-523-435.

WAC 173-303-910(2)

As stated in WAC 173-303-910(2)(a), the proposed method must be demonstrated to be equal to or superior to the corresponding method prescribed in WAC 173-303-110 in terms of sensitivity, accuracy, and precision (i.e., reproducibility).

The requested information for WAC 173-303-910(2)(b) is as listed below:

(i) A full description of the proposed method, including all procedural steps and equipment used in the method;

The WHC procedure is attached and is summarized in the following paragraph.

The concrete is placed into a glass vial with high purity water under zero-headspace conditions. The vial is then sonicated in an ultrasonic bath. Through this process, the VOA target compounds are desorbed from the concrete into the high purity water. The water is then analyzed by GC/MS in compliance with the protocols in SW-846 Method 8260. (The target compounds are determined by GC/MS using WHC procedure LA-523-405, which is based on SW-846 Method 8260.)

(ii) A description of the types of wastes or waste matrices for which the proposed method may be used;

This method will be used to determine VOCs in concrete samples taken from locations where solvents have been stored.

(iii) Comparative results obtained from using the proposed method with those obtained from using the relevant or corresponding methods prescribed in WAC 173-303-110;

There are no comparative data. The standard method is not applicable to analysis of concrete; the physical nature as well as the chemistries of soils and concrete are vastly different. Thus, no comparative data can reasonably be generated.

standard methods:
The unsuitability of direct application of SW-846 was recognized during the preparation of and negotiations concerning the 300 Area Solvent Evaporator Closure Plan. The Sampling and Analysis Plan section of the closure plan (Appendix E) states, "There are currently no EPA protocols for the collection and processing of concrete core samples or the identification of volatile contamination of concrete." The section goes on to state, "the sample preparation and analysis methods for volatile and semi-volatile waste constituents in soils cannot be applied to concrete because sample preparation involving crushing or powdering could severely compromise the integrity of the concrete samples and thus render them useless for regulatory compliance purposes."

As is stated in the closure plan, most sample preparation methods are unacceptable because they involve crushing of the sample. Crushing the sample too finely causes the release of the volatile constituents from accessible pore spaces in the sample before analysis. Headspace and purge and trap techniques will not effectively purge pore spaces of solid concrete. Most fluid extraction methods are inadequate because constituents in the pore volume of the concrete cannot efficiently exchange with the extraction fluid, or because the efficiency of the extraction method is unknown. To efficiently purge the VOCs from the sample, the purge tube must be inserted near the bottom of the purge vessel. This is not physically possible with concrete chips or a concrete core in the purge tube unless the concrete is ground to approximately 1/16-inch diameter. With the proposed method, the only particle size requirement is that the concrete pieces be small enough to fit into the sample container.

An alternate method considered in the closure plan involved laboratory crushing of the concrete to obtain a size fraction about 1/8 inch in diameter. The sample would then be immediately loaded into the

stainless steel sample port of a thermal desorption mass spectrometer and analyzed for organic constituents. This method was tested in the WHC laboratory and gave irreproducible results. It was found that particulates generated from heating the concrete were trapped with the analytes on the trap. During thermal desorption, these particulates would then release into the GC/MS, clogging the jet separator. In addition, the laboratory quality assurance requirements stated in the closure plan (Appendix E) could not be met. Therefore, the thermal desorption method was deemed inadequate.

dry matrix spike recoveries:
For these reasons, comparative data are not obtainable. In addition, there are no concrete standards from which to try to extract VOC to test the proposed method. As part of the development of this procedure, an attempt was made to spike dry concrete with known amounts of specific target analytes (matrix spike) before adding water to the sample. More details on this test are provided in Appendix A of this document.

Based on the amounts of the analytes recovered, it is believed that the method extracts sufficient amounts of the analytes to ensure that the concentrations of concern for the RCRA closure would be detectable. For example, with only a 20 percent extraction efficiency, a detected concentration of 200 parts per billion would correspond to an actual concentration of 1 part per million. Concentrations of 200 parts per billion are detectable with the determinative method and all concentrations of concern for VOCs at the 300 ASE closure area are greater than 1 part per million. Concentrations of concern would be detected; however, they might not be quantified.

It was decided not to test the effect of spiking the concrete before curing. If the concrete is spiked before curing, the constituents would end up within the inner pores of the concrete, which is not representative of the situation in which compounds may be spilled onto the surface of the concrete. If the concrete is mixed or stirred after spiking, the heat generated during curing will result in the loss of the VOCs.

standard method (SW-846 Method 8260) matrix spike recoveries:
However, the proposed method was tested for recoveries using a matrix spike method similar to that used for determining recovery of volatile organics from soils. The matrix spike is added to a vial containing the concrete and water. The sample then undergoes sonification. (This spiking process is described in detail in Section v.) This spiking process demonstrates the effect of sonification of the constituents in water in the presence of concrete on their recoveries. It is believed that the results described herein demonstrate the effectiveness and accuracy of the proposed method.

The precision and accuracy of this method were determined by following the recommended procedure in SW-846 Third Edition, Final Update I, July 1992, Method 8260, Sections 8.3.2.to 8.5.5. These sections suggest using four replicate for each analyte to determine the average recovery and standard deviation. Results of this study are compared with the single laboratory recovery and precision data provided in Table 7 of SW-846 Method 8260. Results are comparable if the calculated relative standard deviation (RSD) of the recovery does not exceed 2.6 times the single laboratory RSD or 20 percent, whichever is greater; and the mean recovery lies within the interval R +/- 3s or R +/- 30 percent, (where R = average recovery and s = standard

deviation of the recovery), whichever is greater. The developmental work was performed within one laboratory (by a single analyst).

Table 1 shows that the RSD and average recoveries are within the RCRA acceptance criteria except for six compounds. Of these six compounds, five involve chemical conversion in the basic matrix. The other, bromodichloromethane, is within 0.2 percent of RCRA comparable based on mean recovery. Table 1 shows good comparability of the results of the proposed method with the single laboratory precision and accuracy shown in Table 7 of the SW-846 Method and demonstrates that the proposed method meets the criteria for VOA comparability.

Tables 1, 2, and 3 give the relevant data from the WHC laboratory. Table 1 shows the accuracy and precision for VOA of concrete samples. These analyses were performed on samples reduced to 1/16-inch . As shown, all but five compounds give good recoveries. These five compounds are discussed further in the following section. Table 2 shows that for analysis of concrete samples of different particle size, the matrix spike recoveries and relative percent differences on duplicates are well within the performance limits for soils. Table 3 shows the method detection limit (MDL) and practical quantitation limit estimations for the volatile organics analyzed. The MDL was determined using the method described in SW-846, Third Edition, Final Update 1, July 1992, page ONE-25 ff.

This matrix spike recovery process indicates that most VOCs are not affected by contact with the concrete (exceptions are discussed in section iv.) Therefore, VOCs are not irreversibly bound to the concrete.

All internal standard results and surrogate recoveries were within quality control (QC) limits.

(iv) An assessment of any factors that may interfere with, or limit the use of, the proposed method;

The factors that may interfere with the proposed method are the same as those for method 8260. However, one limitation on interpretation of the data was noted.

As shown in Table 1, five compounds give poor recoveries. These compounds are as follows:

Compound	Mean Recovery
1,1,2,2-tetrachloroethane	0 %
1,1,2-trichloroethane	28 %
1,1-dichloroethene	173 %
trichloroethene	184 %
vinyl acetate	0 %

After considering the chemistry involved, it is believed that the 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane undergo dehydrohalogenation and are converted into 1,1-dichloroethene and trichloroethene, respectively. These compounds undergo dehydrohalogenation because of the basic pH of the concrete and aqueous solution. The poor recovery of vinyl acetate is believed due to base hydrolysis.

(v) A description of the QC procedures necessary to ensure the sensitivity, accuracy, and precision of the proposed method.

All QC procedures necessary to ensure the sensitivity, accuracy and precision in SW-846 Method 8260 are followed.

The matrix spikes and matrix spike duplicates are prepared as similar to method 8260 as possible. The same compounds are spiked as in method 8260. The spike solution is added directly to a vial containing the sample and water matrix; at minimum, the syringe tip is as close to the concrete surface as possible. If the concrete pieces are small enough, the syringe tip will penetrate the sample pieces. Spiking is done before sonification.

The MDL are improved by the use of a larger sample size than method 8260. This also should reduce sample inhomogeneity effects. In addition, the proposed method does not require purging the sample at 40 degrees C, as does method 8260.

The proposed method provides improved sensitivity because of the larger sample size. Analyte loss during sample preparation is believed to be reduced because of less sample processing during size reduction. The net result is that the proposed method gives higher quality data, improved MDL, less sampling error, and improved instrumental accuracy and precision. The method performance is documented in the attached tables. These data meet the requirements for the SW-846 Method 8260 procedure.

TABLE 1: RCRA Comparability for Volative Organics. Page 1 of 2

Compound	Percent recovery				Mean percent recovery (R)	Standard deviation (s) (df, n-1)	RSD	RCRA comparability based on RSD*		RCRA comparability based on mean recovery	
	Trial 1	Trial 2	Trial 3	Trial 4				RCRA RSD recovery	RCRA comparable	R+/-3S (or R+/-30%)	RCRA comparable
chloromethane	99.9	101.9	93.7	93.9	97.4	4.2	4.3	8.9	Yes	117.9/68.1	Yes
vinyl chloride	103.6	103.5	96.9	96.6	100.2	3.9	3.9	6.7	Yes	117.5/78.5	Yes
bromomethane	95.9	99.1	91.7	94.2	95.2	3.1	3.3	8.2	Yes	118.4/71.6	Yes
chloroethane	102.4	103.1	100.6	101.6	101.9	1.1	1.1	9	Yes	113.0/65.0	Yes
1,1-dichloroethene	175.8	176.1	168.4	171.1	172.9	3.7	2.2	6.7	Yes	112.9/75.1 (122.2/65.8)	No**
carbon disulfide	67.4	67.0	62.4	62.4	64.8	2.8	4.3	--	---	---/---	---
acetone	172.0	127.2	122.6	103.5	131.3	29.0	22.1	--	---	---/---	---
methylene chloride	109.3	109.9	102.2	104.1	106.4	3.8	3.6	5.3	Yes	110.0/80.0	Yes
1,2-dichloroethene	109.0	109.2	101.5	102.9	105.7	4.0	3.8	--	---	---/---	---
1,1-dichloroethane	109.0	110.7	103.6	105.3	107.2	3.3	3.0	5.3	Yes	---/---	---
2-butanone	122.6	92.3	91.8	80.6	96.8	18.1	18.6	--	---	---/---	---
chloroform	105.5	107.9	99.7	102.3	103.9	3.6	3.5	6.1	Yes	106.5/73.5	Yes
1,2-dichloroethane	110.4	108.5	97.6	96.6	103.3	6.6	6.4	6.7	Yes	---/---	---
1,1,1-trichloroethane	102.7	102.9	97.6	97.5	100.2	3.0	3.0	8.1	Yes	121.7/74.3	Yes
carbon tetrachloride	102.1	102.2	96.6	96.9	99.5	3.1	3.1	8.8	Yes	106.2/61.8	Yes
benzene	110.3	109.6	103.5	103.0	106.6	3.9	3.6	5.7	Yes	116.5/77.5	Yes
trichloroethene	192.1	191.2	176.1	175.8	183.8	9.0	4.9	7.3	Yes	109.5/70.5 (117.0/63.0)	No**
1,2-dichloropropane	115.1	111.5	102.8	103.2	108.2	6.1	5.7	6.1	Yes	114.7/79.3	Yes
bromodichloromethane	71.0	68.4	63.8	62.0	66.3	4.1	6.2	6.1	Yes	112.1/77.9 (123.5/66.5)	No
cis-1,2-dichloropropene	114.6	111.4	102.2	99.9	107.0	7.1	6.6	--	---	---/---	---
trans-1,2-dichloropropene	102.7	94.7	90.9	83.9	93.1	7.9	8.5	--	---	---/---	---
1,1,2-trichloroethane	32.8	28.1	25.9	23.4	27.6	4.0	14.4	7.3	Yes	126.8/81.2 (135.2/72.8)	No**
dibromochloromethane	89.6	82.0	78.2	70.3	80.0	8.0	10.0	7	Yes	111.5/72.5	Yes
bromoform	108.4	95.6	89.4	81.4	93.7	11.4	12.1	6.3	Yes	120.2/81.8	Yes
4-methyl-2-pentanone	121.7	112.4	101.4	93.6	107.3	12.3	11.5	--	---	---/---	---

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TABLE 1: RCRA Comparability for Volative Organics. Page 2 of 2

toluene	107.0	111.4	104.6	105.4	107.1	3.0	2.8	8	Yes	126.3/77.7	Yes
tetrachloroethene	106.3	105.1	101.7	104.0	104.3	2.0	1.9	6.8	Yes	107.0/71.0	Yes
2-hexanone	131.1	122.1	105.4	89.5	112.0	18.4	16.4	--	---	---/---	---
chlorobenzene	110.1	114.0	104.2	105.2	108.4	4.5	4.2	5.9	Yes	115.4/80.6	Yes
ethylbenzene	106.6	110.0	105.0	106.0	106.9	2.2	2.0	8.6	Yes	124.2/73.8	Yes
xylene (total)	100.6	102.6	101.2	103.0	101.9	1.1	1.1	--	---	---/---	Yes
styrene	110.6	112.11	104.31	107.11	108.5	3.5	3.2	7.2	Yes	123.9/80.1	Yes
bromofluorobenzene	74.1	75.4	81.0	78.1	77.2	3.0	3.9	--	---	---/---	---
1,1,2,2,-tetrachloroethane	0.0	0.0	0.0	0.0	0.0	0.0	---	6.3	---	108.1/73.9 (118.3/63.7)	No**
vinyl acetate	0.0	0.0	0.0	0.0	0.0	0.0	---	--	---	---/---	No**

Note: Analyses performed on 1/16 inch samples (determined by mesh size). These data were compiled as described in SW-846, third Edition, Final Update, July 1992, Section 8.5. Four replicates were analyzed as per Section 8.5.3.

* RCRA RSD Recovery is from Table 8, SW-846, Third Edition, Final Update 1, July 1992, Method 8260. These values represent single laboratory accuracy and
precision data for volatile organic compounds in water determined with a narrow bore capillary column. RCRA comparability is determined by the method defined in Section 8.5.5 (same reference). Results are comparable if the calculated RSD does not exceed 2.6 times the single laboratory RSD or 20%, whichever is greater, and the mean recovery lies within the interval R+/-3S or R+/-30%, whichever is greater.

**Because of chemical conversion in the basic matrix. 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane are believed to undergo dehydrohalogenation to 1,1-dichloroethene and trichloroethene, respectively. Vinyl acetate is converted to unknown compounds.

RCRA = *Resource Conservation and Recovery Act of 1976*

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TABLE 2 Matrix Spike Recoveries and Relative Percent Differences

Compound Name	Run	Percent Recoveries				
		1/16 inch*		1/8 inch*	1/4 inch*	1/2 inch*
		Trial 1	Trial 2			
1,1-	1	79	89	83	94	82
Dichloroethene	2	106	85	91	97	81
(RPD)#		(29.2)	(4.6)	(9.2)	(3.1)	(1.2)
Benzene	1	86	86	88	112	85
	2	95	91	94	117	85
(RPD)		(9.9)	(5.6)	(6.6)	(4.4)	(0)
Trichloroethane	1	85	93	85	104	83
	2	108	90	89	100	79
(RPD)		(23.8)	(3.3)	(4.6)	(3.9)	(4.9)
Toluene	1	85	92	85	101	88
	2	109	92	90	107	88
(RPD)		(24.7)	(0)	(5.7)	(5.8)	(0)
Chlorobenzene	1	90	93	86	104	91
	2	117	92	91	109	88
(RPD)		(26.1)	(1.1)	(5.6)	(4.7)	(3.4)

* Inches refer to concrete particle size, determined by mesh size. Two runs were performed on the 1/16-inch concrete size. An air bubble biased the first set of data. The information is included here for completeness.

\# Relative Percent Difference (RPD) was determined as described in SW-846, Revision 1, July 1992.
The RPD, when only two samples are available, is:

$$RPD = 100[(x_1 - x_2)/\{(x_1 + x_2)/2\}].$$

Table 3: Method Detection Limits (MDL) and Practicals Quantitation Limits (PQL) for Volitile Organics.

	TRIAL 1	TRIAL 2	TRIAL 3	TRIAL 4	s *	MDL **(ppb)	PQL **(ppb)
COMPOUND	parts per billion (ppb)						
chloromethane	64.9	66.2	60.9	61.0	2.7	12	60
vinyl chloride	67.4	67.3	63.0	62.8	2.6	12	60
bromomethane	62.4	64.4	59.6	61.2	2.0	9	50
chloroethane	66.5	67.0	65.4	66.1	0.7	3	50
1,1-dichloroethene	114.3	114.5	109.5	111.2	2.4	11	60
carbon disulfide	43.8	43.6	40.6	40.6	1.8	8	50
acetone	111.8	82.7	79.7	67.2	18.9	86	430
methylene chloride	71.1	71.5	66.5	67.7	2.5	11	60
1,2-dichloroethene	141.7	142.0	131.9	133.8	5.3	24	120
1,1-dichloroethane	70.9	72.0	67.4	68.5	2.1	10	50
2-butanone	79.7	60.0	59.7	52.4	11.7	53	270
chloroform	68.6	70.1	64.8	66.5	2.3	10	60
1,2-dichloroethane	71.7	70.5	63.4	64.1	4.3	20	100
1,1,1-trichloroethane	66.8	66.9	63.5	63.4	2.0	9	50
carbon tetrachloride	66.4	66.4	62.8	63.0	2.0	9	50
benzene	71.7	71.3	67.3	66.9	2.5	11	60
trichloroethene	124.9	124.3	114.5	114.3	5.9	27	140
1,2-dichloropropane	74.8	72.5	66.8	67.1	4.0	18	100
bromodichloromethane	46.2	44.4	41.5	40.3	2.7	12	60
cis-1,2-dichloropropene	74.5	72.4	66.4	65.0	4.6	21	100
trans-1,2-dichloropropene	66.8	61.6	59.1	54.5	5.1	23	120
1,1,2-trichloroethane	21.3	18.3	16.8	15.2	2.6	12	60
dibromochloromethane	58.3	53.3	50.9	45.7	5.2	24	100
bromoform	70.4	62.2	58.1	52.9	7.4	34	170
4-methyl-2-pentanone	79.1	73.0	65.9	60.9	8.0	36	180
toluene	69.5	72.4	68.0	68.5	2.0	9	50
tetrachloroethene	69.1	68.3	66.1	67.6	1.3	6	50
2-hexanone	85.2	79.4	68.5	58.2	12.0	54	270
chlorobenzene	71.5	74.1	67.8	68.4	2.9	13	70
ethylbenzene	69.3	71.5	68.3	68.9	1.4	6	50
xylene (total)	196.0	200.1	197.4	200.9	2.3	10	50
styrene	71.9	72.9	67.8	69.6	2.3	10	50
bromofluorobenzene	48.2	49.0	52.6	50.8	2.0	9	50

* s = Standard Diviation, (df, n-1)

** MDL determined as described in SW-846, Third Edition, Final Update 1, July 1992, page ONE - 25 ff. The MDL is determined by multiplying the standard deviation (s) by the t-statistic for four replicates (4.54). The PQL is estimated as 5 times the MDL. These values have been rounded to the nearest 10.

Appendix A: Dry Matrix Spike Preparation:

As part of the development of this procedure, an attempt was made to spike dry concrete with known amounts of specific target analytes (matrix spike) before adding water to the sample. In this test, the concrete particles were tumbled with water (water washed) for 4 hours and then air dried for 24 hours. The contact with water and drying was to ensure that the all of the concrete had the same surface chemistry (which is primarily controlled by the degree of hydration). The concrete was then spiked at 1 part per million with the least volatile targets from SW-846 Method 8260A: tetrachlorobenzene, 1,2,3-trimethylbenzene, 1,3-dichlorobenzene, naphthalene, and hexachlorobutadiene. The test samples were equilibrated for 24 hours. The concrete was then run though the attached preparative procedure and the VOCs determined using a GC/MS method.

The spike recoveries were unacceptably low and decreased with increasing particle size (Table A-1). It is believed that the reason for the low recovery is because of problems in the concrete preparation and not because of poor VOC extraction.

It should be noted that even with spiking dry concrete, the method could qualitatively detect the compounds when present at 1 part per million. The regulatory action level for VOCs in concrete at the 300 ASE RCRA closure is 2 parts per million. Consider the following: if 1 part per million of a target was present and was extracted with 20 percent efficiency (a representative value from Table A-1), the concentration found would be 0.200 parts per million or 200 parts per billion. Because the highest method detection limit is 86 parts per billion, the target would be detectable.

Table A-1 Dry Spike Recoveries for Washed Concrete

Compound Name	Percent Recoveries			
	1/16 inch*	1/8 inch*	1/4 inch*	3/8 inch*
Tetrachlorobenzene	41	28	19	12
1,3,5-Trimethylbenzene	44	29	24	20
1,3-Dichlorobenzene	53	37	29	27
Naphthalene	57	39	35	33
Hexachlorobutadiene	12	5	12	13

* Inches refer to concrete particle size, determined by mesh size.

ANALYTICAL LABORATORIES

Issued By: K. B. Wehner
Manager,
Analytical Laboratory

S. G. Metcalf[1]

Title PREPARATION OF CONCRETE FOR VOLATILE ORGANICS ANALYSIS

Impact Level S

SUMMARY

This procedure will be used to prepare concrete samples for volatile organic analysis. This procedure describes sample preparation by ultrasonic extraction of volatile contaminates from concrete into water under zero headspace conditions.

APPLICATIONS/LIMITATIONS

This procedure applies to the preparation of concrete samples only. It is intended to be comprehensive and detailed, coupled with the realization that the problems encountered in sampling and analytical situations require a certain amount of flexibility. The solutions to these problems will depend, in part, on the skill, training, and experience of the analyst. For some situations, it will be possible to use this procedure as written. In others, it will require a combination of technical abilities, using this procedure as guidance rather than in a step-by-step, word-by-word fashion. Deviation from this procedure will be noted in the case narrative for that sample delivery group.

Contamination by carryover can occur whenever high organic concentration and low organic concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples. Whenever an unusually concentrated sample is encountered, it must be followed by the analysis of a blank to check for cross contamination.

Poor recoveries have been noted for 1,1,2,2-tetrachloroethane and 1,1,2-tricholoroethane. These compounds are believed to undergo dehydrohalogenation to form trichloloethene and 1,1-dichloroethene, respectively. The recovery for vinyl acetate is very low, however it is not listed as a target compound in the March 1990 Contract Laboratory Program Statement of Work.

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[1]Acknowledgement: This procedure was originally developed by T. L. Tung.

OFFICIALLY RELEASED

QUALITY CONTROL PROTOCOL

Matrix Spike and Matrix Spike Duplicate Analysis

1. One matrix spike and matrix spike duplicate must be prepared for each group of samples of a similar matrix, for the following, whichever is most frequent:

   a. Each batch of field samples received

   b. Every 20 field samples in a batch

   c. Each group of field samples of a similar concentration level (that is, medium- or high-level)

   d. Each 14-day calendar period during which field samples are received (receipt of the first sample starts the period).

The matrix spikes and matrix spike duplicates will follow SW-846, method 8260 as closely as possible. The same compounds will be spiked as in method 8260. The spike solution will be spike directly into the water covering the concrete sample. The syringe tip must be positioned within the layer of concrete particles if possible; if it can not be, it must be as close the concrete surface as possible.

SAFETY

Before using this procedure, the user should review the equipment and reagents lists and be familiar with each Material Safety Data Sheet (MSDS) and each applicable safety precaution. The majority of the organic compounds used in this procedure are hazardous and/or suspected to be carcinogenic (see LA-523-401 for target compound list). There may be additional hazards associated with the samples. Follow applicable radiological and industrial safety guidelines, including the *Westinghouse Hanford Company Chemical Hygiene Plan* (Moss 1991), and *Safety in the Analytical Laboratory* (Flint 1989), when handling radioactive materials, hazardous chemicals, and hazardous wastes.

REAGENTS

Organic-free Reagent Water

Reagent water is defined as water in which an interferant is not observed at or above the required quantification limit for the parameters of interest. A water purification system (for example, Millipore Super-Q[2]), or equivalent, may be used to generate reagent water.

[2]Millipore Super-Q is a trademark of Millipore Corporation.

EQUIPMENT

Analytical balance, accurate to 0.01 grams

Volatile organic analysis (VOA) vials with Teflon[3]-lined, silicone, septa lid

Sonicator

Benchtop centrifuge

Laboratory scale jaw crusher

Micro syringes (10 µL, 50 µL, 100 µL)

Micropipet, Pasteur

Safety glasses

Nitrile gloves (N-DEX)

[3]Teflon is a trademark of E.I. du Pont de Nemours and Company.

PROCEDURE STEPS

NOTE: Precleaned VOA vials are labeled and weighed, with the cap on, and the weight is recorded. They are given to the sampling team for use in sampling.

NOTE: After sampling, the sample will be in either a VOA vial or another gas tight container. Chain-of-custody documentation is required.

1. Contact the responsible scientist for directions and the number of vials to be prepared.

2. Complete and attach a label to each VOA vial.

3. Obtain tare weight of a VOA vial (with the lid on the vial).

4. Record the weight (to the nearest 0.01 grams) on the data sheet (see Appendix A).

5. Give the vials to the sampling team contact person.

NOTE: All remaining steps are performed after the samples have been received from the field.

NOTE: The vials should be approximately one-half full of concrete solid core or chips. If they are not, contact the responsible scientist for directions.

NOTE: The samples must be stored at between 2 to 6°C until they are analyzed.

NOTE: Use only refrigerators dedicated to the storage of VOA samples.

6. Allow the concrete to chill for at least one hour in a refrigerator at 2 to 6°C.

NOTE: If the sample arrives in a VOA vial no crushing is required; sample analysis can start at Step 11. If the sample pieces are too large to fit into a VOA vial, the crushing process in Steps 8 through 10 is required.

WARNING: SAFETY GLASSES SHOULD BE WORN DURING THE CRUSHING PROCESS.

7. Record in the case narrative if the concrete was used as received, or had its size reduced, the final particle size, and how size was reduced.

8. Place the concrete in a metal pan or laboratory scale-jaw crusher as directed by the responsible scientist.

9. Break the concrete into parts small enough to fit in an air-tight glass VOA vial.

PROCEDURE STEPS (Continued)

10. Quickly load a representative sample, approximately 20 g, into the vial and cap vial immediately.

11. Quickly weigh the vial (with the cap on) containing the sample.

12. Record the weight (to the nearest 0.01 grams) on the data sheet (see Appendix A).

NOTE: If the matrix spike is needed, go to Step 13. Otherwise go to Step 15 and skip Step 16.

13. Fill a microsyringe with the proper volume of spike solution or other standard as directed by the responsible scientist.

14. Dry the microsyringe tip with a facial tissue, and set it aside.

NOTE: Tap the sides of the vial gently to dislodge any air bubbles.

15. Carefully pour the reagent water slowly down the side of the vial, fill the sample vial to near the rim with reagent water (about 99% full).

NOTE: Skip Step 16 if a matrix spike is not needed.

NOTE: The syringe tip should be placed as close as possible to the concrete surface before injecting the spike solution; if possible the sample layer should be penetrated.

16. Add the matrix spike solution to the sample vial with the microsyringe prepared in Step 14.

NOTE: Fill the vial drop-by-drop from micropipet until the level is up to the rim. Avoid overfilling. There should be no head space after the cap is tightened. If any head space exists, discard the sample and prepare another sample.

NOTE: When the vial is filled a maximum of 0.3 mL of water (approximately six drops) can be allowed to overflow the vial. The vial will hold about 30 mL of water, thus a loss of 0.3 mL will cause no more than a 1% error.

17. Quickly complete filling the sample vial with water using a Pasteur micropipet and cap the vial.

18. Dry the outside of the vial if needed.

19. Weigh the vial a third time to obtain total weight.

PROCEDURE STEPS (Continued)

20. Record the total weight (to the nearest 0.01 grams) on the data sheet (see Appendix A).

21. Place the vial sideways in the ultrasonic bath.

NOTE: The sonic bath must be approximately half-full of water; water may be added if needed.

22. Sonicate the vial for 30 minutes.

23. Centrifuge the VOA vial for five minutes at approximately 1500 rpm.

NOTE: In the following step, avoid getting any particulate that may be in the water into the syringe.

24. Remove 5 mL of the water with a gas-tight syringe.

NOTE: The analysis in Step 25 must be done without delay.

25. Analyze the water extract in accordance with the volatile organic procedure (LA-523-405, or LA-523-401 as requested).

REFERENCES

Flint, S. K., 1989, *Safety in the Analytical Laboratory*, WHC-SD-CP-LB-003, Westinghouse Hanford Company, Richland, Washington.

Moss, S. S., 1991, *Westinghouse Hanford Company Chemical Hygiene Plan*, WHC-SD-CP-HSP-001, Westinghouse Hanford Company, Richland, Washington.

WHC, 1993, *Volatile Organics by Gas Chromatography/Mass Spectroscopy - Contract Laboratory Program*, LA-523-401, Westinghouse Hanford Company, Richland, Washington.

WHC, 1993, *Volatile Organics by Gas Chromatography/Mass Spectroscopy Using SW-846*, LA-523-405, Westinghouse Hanford Company, Richland, Washington.

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Sample Preparation Data Sheet

Concrete sample number . . . . . _____

Tare Weight of capped VOA vial (g) . . . . . _____

Weight of capped vial and sample (g) . . . . _____

Weight of capped vial, sample, and water (g) _____

Calculation

$$\frac{\text{ng of analyte}}{\text{mL}} \times \frac{\text{mL of water inside vial}}{\text{gram weight of sample}} = \text{ng/g of analyte} = \text{ppb}$$

Density of water will be assumed as 1, so weight of water = mL of water

$\frac{\text{ng of analyte}}{\text{mL}}$ are determined from gas chromatograph/mass (GC/MS) analysis.