OP130R[(a)]

Analysis of TCLP Semivolatiles and Pesticides in Radioactive Mixed Waste Sludges

The decision to use this method should be made during project planning (see Chapter 1). Project personnel, together with stakeholders, should determine the activities that need to be performed to qualify the method for use in the project (see Appendix B).

1.0 Scope and Application

1.1 This method is for the total analysis of the Toxicity Characteristic Leach Procedure (TCLP) semivolatile organic compounds and pesticides in radioactive mixed waste (RMW) sludges. It does not include acidic semivolatiles. The method is suitable for glovebox and hot cell operations. The specific radioactivity of the sludge or the mass that can be collected may limit the mass that can be used; this method was designed to address these limitations. The compounds determined using this method and the surrogate standards are listed in Table 1.

1.2 This method is based upon adaptation of the U.S. Environmental Protection Agency (EPA) (1992) SW-846 Methods 3550 (ultrasonic extraction), 8081 {gas chromatography (GC) of organochlorine pesticides}, 8090 (nitroaromatics by GC), and 8121 (chlorinated hydrocarbons by GC).

2.0 Summary of Method

2.1 Waste samples (1 g) are weighed out, spiked with the surrogate standards tetrachlorometaxylene (TCMX) and decachlorobiphenyl (DCBP) and matrix spikes (matrix-spiked samples only). Blanks are spiked only with surrogate standards.

After the spiked solvents evaporate, the samples are extracted three times with 5 mL of methylene chloride (a modification of EPA SW-846 Method 3550). The solvent extracts are pooled and concentrated to a 1.0-mL final volume.

2.2 The semivolatile organic compounds and pesticides are determined using capillary column GC with electron capture detection (ECD) (modified from EPA SW-846 Methods 8081, 8090, and 8121). The packed column GC-ECD SW-846 Method 8080 is also acceptable if all compounds can be resolved.

(a) This method was supplied by R. L. Schenley, P. F. Wolfe, and W. H. Griest (Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee).

Table 1. TCLP Semivolatiles and Pesticides Determined

Compound	Abbreviation	CAS No.[a]
Chlordane (technical)	CHD	57-74-9
1,4-Dichlorobenzene	DCB	106-46-7
Toxaphene	TOX	8001-35-2
Hexachloroethane	HCE	67-72-1
Nitrobenzene	NBz	98-95-3
Hexachlorobutadiene	HCB	87-68-3
2,4-Dinitrotoluene	DNT	121-14-2
Hexachlorobenzene	HCBz	118-74-1
Lindane	LIN	58-89-9
Heptachlor	HC	76-44-8
Heptachlor epoxide	HCE	1024-57-3
Endrin	END	72-20-8
Methoxychlor	MC	72-43-5
Tetrachlorometaxylene[b]	TCMX	877-09-8
Decachlorobiphenyl[b]	DCBP	2051-24-3

(a) Chemical Abstract Services Registry Number
(b) Surrogate standard

Caution: It is important that the sample extracts be analyzed for radioactivity before transport and GC analysis in non-contamination-zoned areas.

3.0 Interferences

3.1 The most common sources of interferences are co-extracted polychlorinated biphenyls (PCBs,) phthalate esters, organosulfur compounds, lipids, and waxes. The presence of high concentrations of co-eluting hydrocarbons will diminish the detector response. The high sensitivity of the ECD often allows significant masking of analytes of interest by co-eluting phthalate esters, organosulfur compounds, organophosphorus compounds, and PCBs.

3.2 Interferences by phthalate esters are often introduced due to contact of reagents or samples with flexible plastics during sample preparation. Interferences from phthalate esters can be minimized by avoiding contact with any plastic materials and by checking all solvents and reagents for contamination. Reagents and glassware may be purified by solvent extraction or heating to 400°C for 1 h and subsequent storage in covered containers.

3.3 The presence of elemental sulfur will result in large peaks that obscure a significant portion of the chromatogram. To remove sulfur, EPA SW-846 Method 3660 is recommended.

3.4 Interferences will vary significantly from waste to waste. See EPA SW-846 Method 8081 for additional guidance on interferences and cleanup procedures.

4.0 Safety

Gloves and protective clothing should be worn to protect against unnecessary exposure to organic solvents and contaminants. When handling radioactive samples, all applicable radiochemical handling procedures and health physics monitoring practices should be followed. Refer to Chapter 4 in this document for general safety information.

5.0 Apparatus and Materials

5.1 Balance: Top-loading, accurate to 0.1 g

5.2 Vials/Teflon® caps: 16 mL and/or 25 mL

5.3 Ultrasonic bath: Branson 5200 or equivalent

5.4 Centrifuge: Tabletop model

5.5 Pasteur glass pipets: Disposable, 1.0 mL

5.6 Heating block

5.7 Concentrator tube: 10 mL graduated (Organomation Associates Inc., or equivalent), volumetric calibrations verified

5.8 Autosampler vials with screw caps

5.9 **Gas Chromatograph:** Analytical system suitable for split-splitless injection and all required accessories, including syringes, analytical columns, gases, ECD, and recorder/ integrator or data system.

5.9.1 **Columns**

- Primary column: DB-5 capillary column, 30 m x 0.32 mm ID, 0.25-µm-thick film of 5% phenyl-methylpolysiloxane (or equivalent in separation performance)

- Confirmation column: DB-1701 capillary column, 30 m x 0.32 mm ID, 0.25-µm-thick film of 14% cyanopropylphenyl-methylpolysiloxane (or equivalent in separation performance)

6.0 Reagents

6.1 TCLP Pesticide Surrogate Mix in acetone, 200 µg/mL (200 ppm) of each component (from Restek, Bellefonte, Pennsylvania, or equivalent)

6.2 Toxaphene in hexane, 250 µg/mL (250 ppm) (from Environmental Resource Associates, Arvada, Colorado, or equivalent)

6.3 Chlordane in hexane, 250 µg/mL (250 ppm) (from Environmental Resource Associates, Arvada, Colorado, or equivalent)

6.4 TCLP Pesticide Mix in methanol, 2 mg/mL (2000 ppm) of each pesticide (from Restek, Bellefonte, Pennsylvania, or equivalent)

6.5 Hexachloro-1,3-butadiene, 98% pure (from CHEM Service, West Chester, Pennsylvania, or equivalent)

6.6 Hexachloroethane, 99% pure (from CHEM Service, West Chester, Pennsylvania, or equivalent)

6.7 2,4-Dinitrotoluene, 99% pure (from CHEM Service, West Chester, Pennsylvania, or equivalent)

6.8 Nitrobenzene, 99% pure (from CHEM Service, West Chester, Pennsylvania, or equivalent)

6.9 p-Dichlorobenzene, 98% pure (from Supelco, Bellefonte, Pennsylvania, or equivalent)

6.10 Hexachlorobenzene, 99% pure (from Supelco, Bellefonte, Pennsylvania, or equivalent)

6.11 Solvents: Methylene chloride and hexane (pesticide quality or equivalent)

7.0 Sample Collection, Preservation, and Handling

Sample collection, preservation, and handling should be addressed in the planning process.

The radioactivity of the samples to be analyzed by this method requires that all applicable radiochemical laboratory procedures and health physics monitoring practices be followed to

ensure that the U.S. Department of Energy (DOE) “as low as reasonably achievable” (ALARA) principle is observed.

8.0 Procedure

8.1 In a radiochemical hood, glovebox, or hot cell, 1.0 g of sludge sample should be weighed into the vial from larger samples collected from the field. If necessary, water is decanted off, and sodium sulfate (1 to 2 g) is added to dry the sample. If the sample radioactivity permits, this subsample may be removed from a glovebox or hot cell for the remaining steps. Otherwise, all operations must be carried out in the hot cell or glovebox.

8.2 All blanks, samples, and matrix-spiked samples are spiked with surrogate standards (TCMX and DCBP) at a final sample concentration of 1 µg/g. Matrix-spiked samples are spiked according to the TCLP toxicity characteristic constituents to be analyzed. For example, if analyzing CHD, the final spike concentration would be 600 ng/mL. The final spike concentration of DCB and TOX would be 10 µg/mL (10 ppm). All other TCLP analytes would be spiked at 40 ng/mL.

8.3 After evaporation of the spike solvents by open-air drying (ca. 15 min), the samples are extracted three times in 5 mL of methylene chloride (or other suitable solvent, such as methylene chloride/acetone, 1/1 vol/vol), using an ultrasonicator bath for 10 min. The water level in the ultrasonicator should be below the caps on the vials and above the sludge sample to be sonicated. Each 5-mL extract is collected by letting the sample settle and by pipetting off the organic layer. A centrifuge may be helpful in settling the sludge.

8.4 The combined methylene chloride extracts are concentrated to 0.1 mL using a heating block (40°C) and a stream of dry, clean air or nitrogen. One milliliter of hexane is added to the extract and concentrated to 0.1 mL. To minimize the loss of the more volatile constituents, these concentration steps should be conducted slowly and gently, especially in the final stages. The extract is diluted to 1.0 mL with hexane and transferred to an autosampler vial.

8.5 All extracts are analyzed on a GC equipped with an ECD, an automatic sample injector, and a data system.

8.6 Gas Chromatographic Analysis

8.6.1 GC Conditions

8.6.1.1 DB-5 (or equivalent) column, 30 m x 0.32 mm ID with a 0.25-µm film thickness in a GC with ECD, automatic sample injection system, and chromatography data system.

Carrier gas:	helium (≈2.7 mL/min);
Makeup gas :	nitrogen (≈35 mL/min)
Injector temperature:	250°C
Detector temperature:	330°C
Initial temperature:	60°C
Temperature program:	hold for 1 min at 60°C; then 60°C to 140°C at 10°C/min; then 140°C to 280°C at 14°C/min; hold 7 min at 280°C.
Total time:	26 min
Injection volume:	1.0 µL

8.6.2 **GC Analysis**

8.6.2.1 Because of mutual chromatographic interferences, calibration curves are prepared from three mixtures: CHD, TOX and DCB, and TCLP pesticides/semivolatile organic compounds. For each calibration curve, at least three concentrations of standards are injected to span the expected range of sample concentrations. The concentration of at least one standard should fall below the TCLP regulatory limit for the sample size used. In the method performance evaluation, the following concentration ranges (in µg/mL) were used: CHD (0.2 to 1), DCB and TOX (2 to 10), all other (0.03 to 0.08).

8.6.2.2 A calibration curve is prepared for each set of analytes using the primary column. Analysis of the extracts is not done unless the initial calibration curve exhibits less than 20% relative standard deviation (RSD) for each analyte, or (for following days) the continuing daily midpoint calibration is within 15% of the calculated calibration curve. If the deviation of the midpoint calibration is greater than 15% and a recheck fails to pass the 15% criterion, the calibration curve is reanalyzed after corrective actions are taken. Corrective actions include such steps as cleaning the injector, replacing the septum, and/or trimming the column at the injector, at the detector, or at both. Recalibration is not required after routine maintenance is performed, unless the midpoint calibration check fails.

8.6.2.3 The blanks and the sample extracts are injected.

8.6.2.4 The midpoint calibration check is analyzed at the beginning of a sample sequence, after every ten samples, and at the end of a sample sequence. If the midpoint calibration deviates more than 15% from the calibration curve, the samples before the midpoint standard are reanalyzed, and another calibration curve is formulated. Alternatively,

corrective actions are performed and the midpoint calibration is checked. If the midpoint calibration check passes, samples may be rerun without full recalibration.

8.6.2.5 All compounds are identified and quantitated for that particular calibration using the method of external standards. The CHD residues are quantitated by comparing the responses of three to four major peaks in each CHD standard with the peaks obtained from the sample extract. The amount of CHD is calculated using each of the major peaks, and the results of the three to four determinations are averaged. The TOX residues are quantitated by comparing the response of the "hump" of peaks in each standard with the peaks obtained from the sample extract. The amount of TOX is calculated by lumping (combining all the peak areas from all the peaks) as a single result. All other analytes are quantitated separately.

9.0 Quality Control

9.1 The use of this method should be supported by appropriate QC procedures (e.g., as outlined in Chapter 3).

9.2 A laboratory control sample, reagent blanks, and matrix spiked samples should be run with each batch of samples. They should be subjected to the same analytical procedures as those used on actual samples.

10.0 Method Performance

10.1 This method complies with requirements in Appendix A for a verified method except that no real world samples are used; surrogate samples are used in spiking experiments.

10.2 **Chromatographic Performance**. The performance of the GC method for separating and detecting the analytes is presented in Table 2. Typical retention times for the analytes on the primary and confirmation column are listed. The detection limits are calculated according to Hubaux and Vos (1970), and in units of μg of analyte per g of sludge. Chromatograms of standard compounds on the primary column are shown in Figures 1 through 3.

Table 2. Analyte Retention Times and Detection Limits on Primary and Confirmation Columns

Compound	Detection Limit on Primary Column (µg/g)	Retention Time (min) Primary Column	Retention Time (min) Confirmation Column
Chlordane (peak 1)	0.123	16.1	16.2
Chlordane (peak 2)	0.368	17.6	16.4
Chlordane (peak 3)	0.133	17.8	18.4
Chlordane (peak 4)	—	—	18.5
1,4-Dichlorobenzene	1.970	5.4	5.8
Toxaphene[a]	1.620	18.95	19.85
Hexachloroethane	0.033	6.3	6.2
Nitrobenzene	0.022	6.5	8.0
Hexachlorobutadiene	0.032	8.6	8.3
2,4-Dinitrotoluene	0.012	12.5	14.5
Hexachlorobenzene	0.028	14.4	14.6
Lindane	0.034	14.8	16.1
Heptachlor	0.030	16.1	16.4
Heptachlor epoxide	0.032	17.2	18.0
Endrin	0.028	18.5	19.3
Methoxychlor	0.018	20.1	21.2
Tetrachloro-m-xylene	—	13.5	13.6
Decachlorobiphenyl	—	24.3	24.8

(a) Retention time of central peak.

10.3 Analyte and Surrogate Standard Recoveries. Three sample matrices were spiked, extracted, and analyzed by the method, with the addition that each extract was analyzed in triplicate. The samples included a surrogate Los Alamos National Laboratory (LANL) wastewater treatment sludge, a surrogate Oak Ridge National Laboratory (ORNL) nuclear-waste-tank sludge, and sea sand. For the 13 analytes, there were three sets of extractions: CHD, DCB and TOX, and the remainder of the TCLP analytes. In all three extraction sets, the surrogates (TCMX and DCBP) were spiked into all matrices and blanks. The three extraction sets were established from the following information. Gas chromatograms of CHD and TOX showed multiple peaks in the same region of the chromatogram. Retention times of several CHD and TOX components interfere with several other TCLP constituents. To analyze DCB with the other TCLP pesticides/ semivolatiles would have resulted in a peak too small for quantitation; therefore, because of the retention time and high regulatory limit for DCB, this TCLP analyte was analyzed with toxaphene that has a “hump” of peaks between the two surrogates.

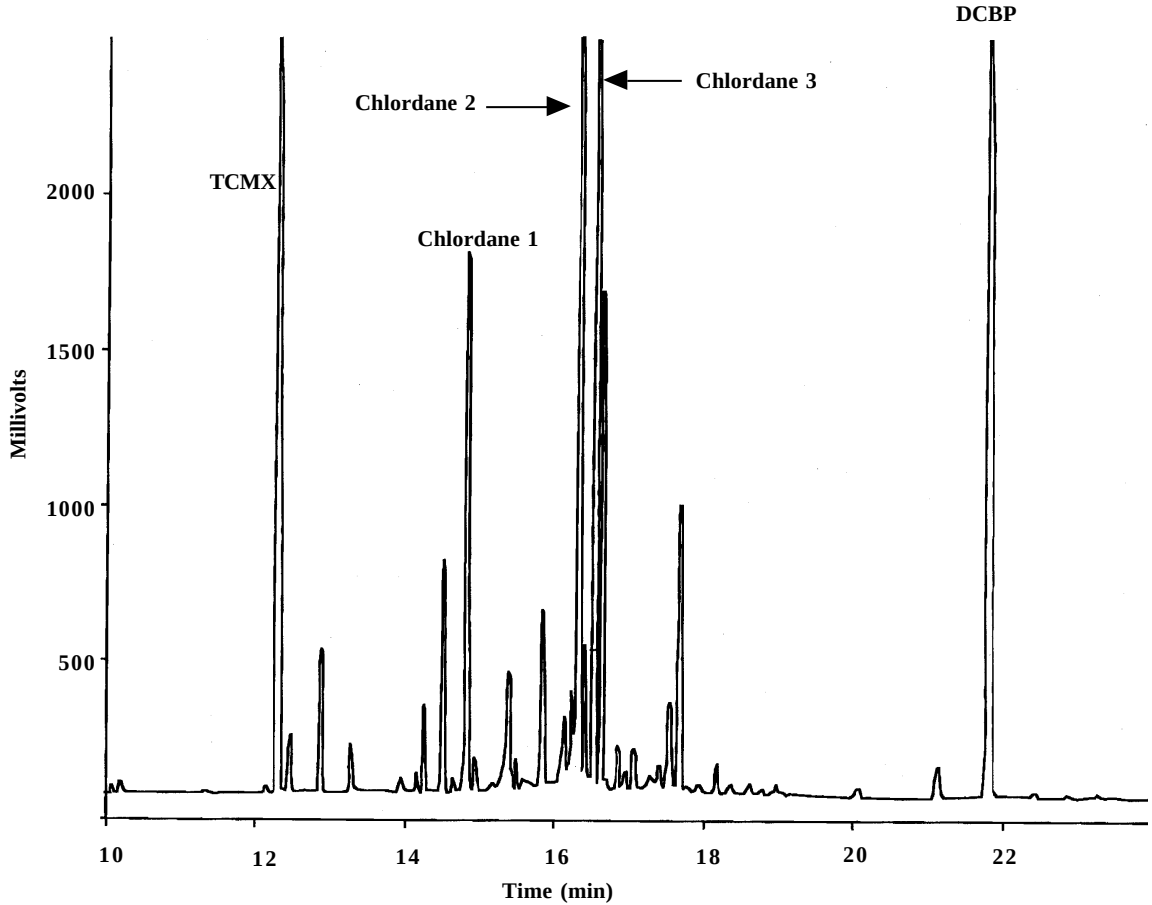

Figure 1. Chromatogram of Chlordane on Primary Column

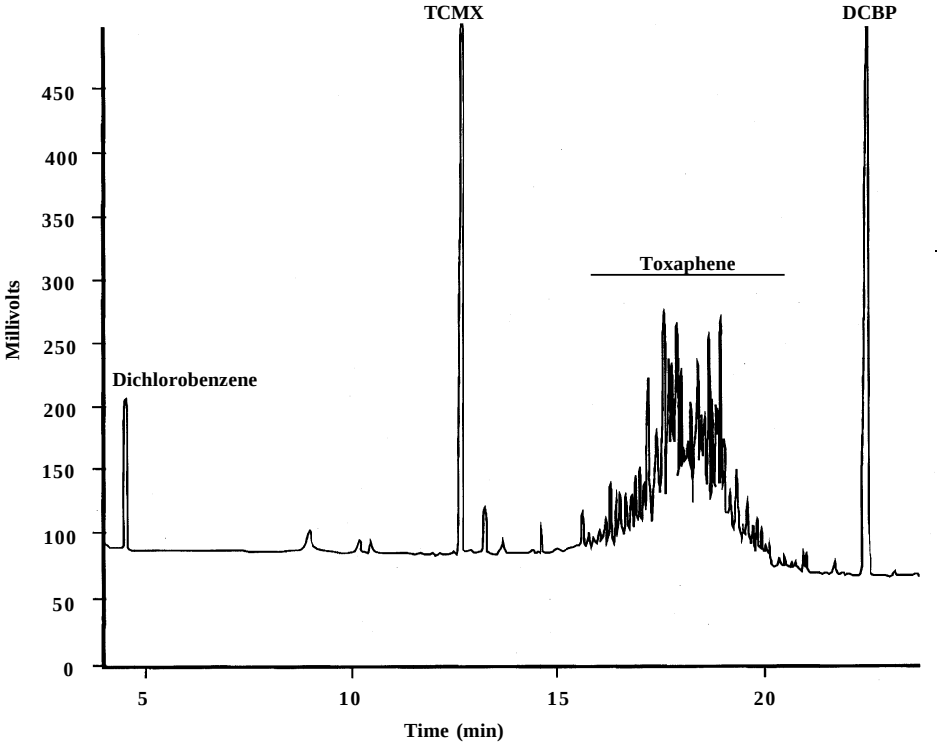

Figure 2. Chromatogram of Toxaphene and DCB on Primary Column

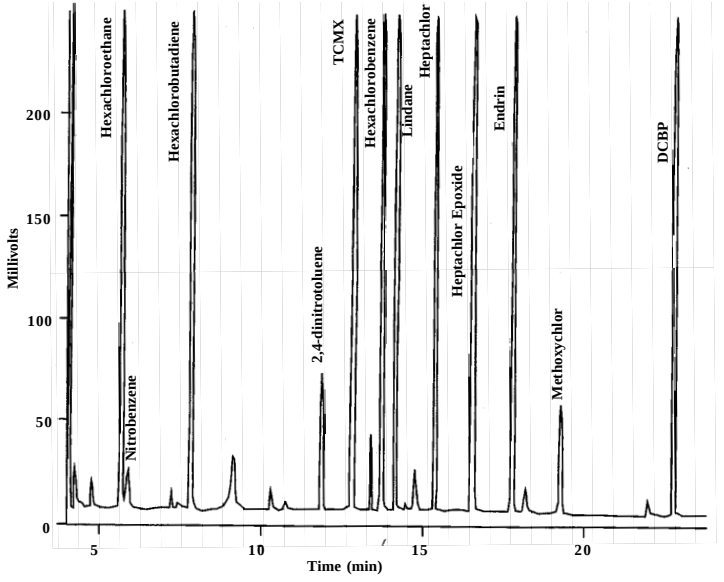

Figure 3. Chromatogram of Other Pesticides and Semivolatile Organic Compounds on Primary Column

Tables 3 through 5 list the recoveries of the TCLP semivolatiles and pesticides analyzed using this method. Recoveries are very good with the exception of NBz in the sand sample. The reason for this is not clear, but evaporative losses can be ruled out because the recovery of DCB, which has a lower boiling point, was good. Table 6 shows the very good recoveries for the surrogate standards. Surrogate and matrix spike recoveries for other matrices should be determined and control limits established per SW-846 method 8000 (i.e., average ± 3 standard deviations for surrogate standards and average ± 2 standard deviations for matrix spikes).

This method should not be used to analyze for the TCLP acidic semivolatiles. Multiple peaks were obtained for the TCLP cresols and trichlorophenols when extracts were analyzed using high-performance liquid chromatography (Method OH100R). These data indicate that these compounds will not be present in matrices of high pH that contain oxidizing agents. The multiple peaks probably are oxidation and nitration products of the cresols and trichlorophenols (see Stromatt et al. 1993; Chen et al. 1991). For the extraction of these compounds in other complex mixtures, the procedure of Stromatt et al. should be used.

10.4 **Sources of Variation**. The total variation of percent-recovery measurements is due to three experimental sources: 1) different matrix types, 2) different replicates, and 3) different injections in the GC instrument. The statistical method of variance component analysis (Searle 1971) was used to estimate the contribution to the total variation of each experimental source. Table 7 reports the standard deviations for each experimental source derived from the estimated variance components calculated by the method of maximum likelihood.

Table 3. Analyte Recoveries from LANL Surrogate Sludge

Analyte	Concentration (µg/g)	Average Recovery % (STD)[a]	Number of Replicates
Chlordane	0.6	98.2 (0.98)	6
1,4-Dichlorobenzene	10.0	89.7 (7.50)	6
Toxaphene	10.0	81.8 (1.61)	6
Hexachloroethane	0.04	68.8 (10.54)	4
Nitrobenzene	0.04	70.9 (7.12)	4
Hexachlorobutadiene	0.04	89.3 (3.43)	4
2,4-Dinitrotoluene	0.04	106 (5.02)	4
Hexachlorobenzene	0.04	117 (7.63)	4
Lindane	0.04	100 (0.82)	4
Heptachlor	0.04	123 (1.75)	4
Heptachlor epoxide	0.04	119 (2.18)	4
Endrin	0.04	131 (3.71)	4
Methoxychlor	0.04	109 (1.03)	4

(a) STD = standard deviation

Table 4. Analyte Recoveries from Sand

Analyte	Concentration (µg/g)	Average Recovery % (STD)	Number of Replicates
Chlordane	0.6	93.1 (3.78)	5
1,4-Dichlorobenzene	10.0	88.7 (7.68)	5
Toxaphene	10.0	81.5 (1.80)	5
Hexachloroethane	0.04	83.3 (6.66)	3
Nitrobenzene	0.04	39.7 (17.5)	3
Hexachlorobutadiene	0.04	84.8 (5.80)	3
2,4-Dinitrotoluene	0.04	108 (1.76)	3
Hexachlorobenzene	0.04	101 (1.15)	3
Lindane	0.04	78.8 (15.8)	3
Heptachlor	0.04	105 (5.00)	3
Heptachlor epoxide	0.04	85.0 (11.1)	3
Endrin	0.04	109 (7.21)	3
Methoxychlor	0.04	109 (7.00)	3

Table 5. Analyte Recoveries from ORNL Surrogate Sludge

Analyte	Concentration (µg/g)	Average Recovery % (STD)	Number of Replicates
Chlordane	0.6	101 (0.82)	4
1,4-Dichlorobenzene	10.0	89.0 (12.1)	4
Toxaphene	10.0	92.5 (10.4)	4
Hexachloroethane	0.04	66.8 (6.85)	4
Nitrobenzene	0.04	86.3 (1.44)	4
Hexachlorobutadiene	0.04	82.4 (2.36)	4
2,4-Dinitrotoluene	0.04	100 (3.82)	4
Hexachlorobenzene	0.04	114 (3.12)	4
Lindane	0.04	103 (0.82)	4
Heptachlor	0.04	132 (1.91)	4
Heptachlor epoxide	0.04	120 (2.19)	4
Endrin	0.04	141 (5.36)	4
Methoxychlor	0.04	117 (3.01)	4

Table 6. Surrogate Standard Recoveries

Matrix	Average Recovery TCMX %	(STD)	DCBP %	(STD)	Number of Replicates
LANL Sludge	98.7	(8.9)	82.6	(19.3)	18
Sand	107.0	(13.1)	91.4	(26.2)	24
ORNL Sludge	108.7	(14.4)	89.3	(17.8)	9
Total	104.3	(12.6)	87.9	(22.6)	51

Table 7. Standard Deviations (% Recovery) for Different Sources of Experimental Variation

	Source of Experimental Variation		
Compound	Matrix	Replicate	Injections
Chlordane	3.1	2.3	0.1
1,4-Dichlorobenzene	0.0	8.0	0.1
Toxaphene	4.3	5.4	0.4
Hexachloroethane	4.4	4.4	9.0
Nitrobenzene	18.6	9.7	2.0
Hexachlorobutadiene	2.6	2.8	3.4
2,4-Dinitrotoluene	2.3	3.5	1.9
Hexachlorobenzene	6.0	4.7	2.0
Lindane	9.7	7.9	0.3
Heptachlor	10.7	2.5	1.8
Heptachlor epoxide	16.2	5.4	2.8
Endrin	12.8	4.4	3.6
Methoxychlor	3.2	3.8	1.6
Tetrachlorometaxylene	0.0	12.3	1.8
Decachlorobiphenyl	0.0	22.1	3.6

11.0 References

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U.S. Environmental Protection Agency (EPA). 1992. *Test Methods for Evaluating Solid Waste. Volume IB, Physical/Chemical Methods,* SW-846, 3rd Edition, Final Update I, Office of Solid Waste and Emergency Response, Washington, DC. Available from the National Technical Information Service, Springfield, Virginia. Also Proposed Update II, November, 1992.

12.0 Further Reading

SAS Institute Inc. 1988. PROC VARCOMP, User's Guide, Release 6.03 Edition. Cary, North Carolina.