

STANDARD OPERATING PROCEDURE
For
USEPA METHOD 525.2, Rev. 2.0
Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry

SOP #: EPA 525.2

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Page 1 of 33

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TABLE OF CONTENTS

	Page
LIST OF REVISIONS.....	3
LIST OF TABLES.....	5
1.0 SCOPE AND APPLICATION	6
2.0 SUMMARY OF METHOD.....	7
3.0 DEFINITIONS.....	7
4.0 INTERFERENCES	9
5.0 SAFETY	9
6.0 EQUIPMENT AND SUPPLIES	9
7.0 REAGENTS AND STANDARDS.....	10
8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE.....	12
9.0 QUALITY CONTROL	12
10.0 CALIBRATION AND STANDARDIZATION	16
11.0 PROCEDURE.....	19
12.0 DATA ANALYSIS AND CALCULATIONS	22
13.0 METHOD PERFORMANCE	22
14.0 POLLUTION PREVENTION.....	23
15.0 WASTE MANAGEMENT.....	23
16.0 REFERENCES.....	24
17.0 TABLES AND VALIDATION DATA	25
APPENDIX: OPERATION OF THE THERMO ITQ 900 GC/MS FOR THE ANALYSIS OF ENVIRONMENTAL SAMPLES BY USEPA METHOD 525.2	31



LIST OF REVISIONS

Rev. #	Date	Description of Revision	Page #
0	March 1999	None	
1.0	March 2000	Section 6.1 changed	8
		Section 6.10.5 added	9
		Section 8.4.1 - In first sentence, "when available" deleted, and new sentence added to end of paragraph: "Samples that come to the lab without a FRB. "	11
		Section 9.7 - In first sentence, "replicates of" deleted and "at a frequency of 5% or one per batch, whichever is more frequent" added to end of first sentence. New sentence added: "The LFM solution is the same used as a quality control sample (Section 9.9)"	12
		Section 9.9 - Second sentence: Twice changed to Once .	13
		Section 10.2.2 - Second sentence: may be changed to are , and "or in a separate injection" deleted.	13
		Section 10.2.3 - "for example" deleted and "that contains all the analytes of interest" added. "0.5-2 µg/L" changed to "at 2 ng/µL"	14
		Section 10.2.5 - 0.1, 0.5, 1.0, 2.0, 10 ng/µL added	14
		Section 10.2.5.1 – deleted	15
		Section 10.3.2 - "0.5 ng calibration" changed to "0.5 ng/µL"	17
		Section 11.1.6 - the word "tube" replaced by "funnel"	18
		Section 11.5 – Added	19
		Section 13.1 - Added "2.0 µg/L after the word "adipate"	20
		Section 13.2.2, 13.2.3, 13.2.5, 13.2.6, & 13.2.7 - Deleted.	
		Section 13.2.4 renumbered to Section 13.2.2 . Section 13.2.8 renumbered to Section 13.2.3	
1.1	July 2001	Section 8.2.1 – Added	11
		Section 9.6 changed	12
		Section 9.9 changed	12 - 13
		Section 9.10 Added	13
		Table 4 – New Precision, Accuracy and MDL determined	25
1.2	October 2001	Section 8.3 – within 14 days changed to within 14 days of collection; sample collection changed to sample extraction	12 – 13
		Section 9.8, 9.9, and 9.10 renumbered to 9.9, 9.10, 9.11; New Section 9.8 added	
		Section 11.5.5, through 11.5.8 changed to 11.5.6 through 11.5.9, new section 11.5.5 added.	19
		Table 1 replaced with new table	22
1.3	September 2002	Section 2.1 added	



Rev. #	Date	Description of Revision	Page #
		Additions to Section 8.2	11
		Additions to Section 8.3	11
		Added Table 1: Sample Storage and Sample Extract Storage	24
1.4	November 2003	Table 4 Updated	26
1.5	December 2003	Table 4 Updated – New MDLs	26
1.6	February 2004	Section 10.3.6.6 was updated Section 13.1 was updated	17 20
1.7	December 2006	Replaced old DEP Logo with state seal + MassDEP Minor revisions throughout document Updated analyte retention times (Table 3) Updated analyte MDLs (Table 4)	Title page & header 25 26
1.8	February 2007	Revised Section 12.1.3 – Added procedure for documenting peak manual integration. Added Appendix – Instrument Operation	20 28-31
1.9	February 2010	Minor revisions Section 16.0 – Reference #6 added	throughout document 23
2.0	February 2011	Revisions to reflect new instrument Table 3 – Updated analyte retention times Table 4 – Updated analyte MDLs	Throughout document 25 26
2.1	December 2012	Updated entire document to reflect the addition of chlordane components, simazine, and toxaphene as method target analytes. New Section 9.11 added – References Table 1. New Section 10.2.2 added – Describes GC program conditions for running DFTPP. New Section 10.2.4 added – Describes GC program conditions for running samples. Table 4 – Added IDC and MDL data for chlordane components, simazine, and toxaphene. Editorial revisions throughout document.	
2.2	January 2013	Table 4 – Updated analyte MDLs	



LIST OF TABLES

	Page
TABLE 1. QUALITY CONTROL ELEMENTS AND ACCEPTANCE LIMITS FOR THE ANALYSIS OF ORGANIC COMPOUNDS IN DRINKING WATER BY LIQUID-SOLID EXTRACTION AND CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY BY EPA METHOD 525.2.....	25
TABLE 2. ION ABUNDANCE CRITERIA FOR BIS(PERFLUOROPHENYL)PHENYL PHOSPHINE (DECAFLUOROTRIPHENYLPHOSPHINE, DFTPP).....	26
TABLE 3. RETENTION TIME DATA, QUANTITATION IONS, AND INTERNAL STANDARD REFERENCES FOR METHOD ANALYTES.....	27
TABLE 4. PRECISION, ACCURACY, AND MDL IN REAGENT WATER USING LIQUID-SOLID C18 DISK EXTRACTION AND THE ION TRAP MASS SPECTROMETER.....	29



1.0 SCOPE AND APPLICATION

- 1.1 This is a general-purpose method for the determination of semivolatile organic compounds in finished drinking water, source water, or drinking water in any treatment stage. The method is applicable to a wide range of organic compounds that are efficiently partitioned from the water sample onto a C18 organic phase chemically bonded to a solid matrix in a disk or cartridge and sufficiently volatile and thermally stable for gas chromatography. The following analytes are determined by this method in our laboratory:

<u>ANALYTE</u>	<u>MW¹</u>	<u>CAS #</u>
Acenaphthylene	152	208-96-8
Alachlor	269	15972-60-8
Aldrin	362	309-00-2
Anthracene	178	120-12-7
Atrazine	215	1912-24-9
Benz[a]anthracene	228	56-55-3
Benzo[b]fluoranthene	252	205-82-3
Benzo[k]fluoranthene	252	207-08-9
Benzo[a]pyrene ²	252	50-32-8
Benzo[g,h,i]perylene	276	191-24-2
Butylbenzyl Phthalate	312	85-68-7
Cis-Chlordane	406	5103-71-9
Trans-Chlordane	406	5103-74-2
Chlordane components:		
Alpha-Chlordane	406	5103-71-9
Gamma-Chlordane	406	5103-74-2
Trans-Nonachlor	440	39765-80-5
Chrysene	228	218-01-9
Dibenz[a,h]anthracene	278	53-70-3
Di-n-butyl Phthalate	278	84-74-2
Diethylphthalate	222	84-66-2
Di(2-ethylhexyl)adipate ²	370	103-23-1
Di(2-ethylhexyl)phthalate ²	390	117-81-7
Dimethyl Phthalate	194	131-11-3
Endrin	378	72-20-8
Fluorene	166	86-73-7
Heptachlor	370	76-44-8
Heptachlor Epoxide	386	1024-57-3
Hexachlorobenzene	282	118-74-1
Hexachlorocyclopentadiene	270	77-47-4
Indeno[1,2,3,c,d]pyrene	276	193-39-5
Lindane	288	58-89-9
Methoxychlor	344	72-43-5
Pentachlorophenol	264	87-86-5
Phenanthrene	178	85-01-8
Pyrene	202	129-00-0
Simazine	201	122-34-9



<u>ANALYTE</u>	<u>MW</u> ¹	<u>CAS #</u>
Toxaphene		8001-35-2

¹ Monoisotopic molecular weight calculated from the atomic masses of the isotopes with the smallest masses.

² Regulated compounds for which WES currently holds EPA certification.

- 1.2 Method detection limit (MDL) is defined as the statistically calculated minimum amount that can be measured with 99% confidence that the reported value is greater than zero (1). The MDL is compound dependent and is particularly dependent on extraction efficiency and sample matrix. The MDLs for the analytes determined by this method are listed in Table 4. The concentration calibration range demonstrated in this method is 0.1 µg/L and 10 µg/L for most analytes.

2.0 SUMMARY OF METHOD

Organic compound analytes, internal standards, and surrogates are extracted from a water sample by passing 1 L of water sample through a disk containing a solid matrix with a chemically bonded C18 organic phase (liquid-solid extraction, LSE). The organic compounds are eluted from the disk with small quantities of ethyl acetate followed by methylene chloride, and this extract is concentrated further by evaporation of some of the solvent. The sample components are separated, identified, and measured by injecting an aliquot of the concentrated extract into a high-resolution fused silica capillary column of a gas chromatography/mass spectrometry (GC/MS) system. Compounds eluting from the GC column are identified by comparing their measured mass spectra and retention times to reference spectra and retention times in a database. Reference spectra and retention times for analytes are obtained by the measurement of calibration standards under the same conditions used for samples. The concentration of each identified component is measured by relating the MS response of the quantitation ion produced by that compound to the MS response of the quantitation ion produced by a compound that is used as an internal standard. Surrogate analytes, whose concentrations are known in every sample, are measured with the same internal standard calibration procedure.

- 2.1 The analyst using this method has more than 22 years of experience in GC/MS analysis and is skilled in the interpretation of chromatograms and mass spectra. Each new analyst is restricted to work under the supervision of an experienced analyst until fully trained. Each new analyst must demonstrate the ability to generate acceptable results by doing an initial demonstration of capability and by analyzing a known quality control sample.

3.0 DEFINITIONS

- 3.1 Internal Standard (IS): A pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same solution. The internal standard must be an analyte that is not a sample component.
- 3.2 Surrogate Analyte (SA): A pure analyte(s), that is extremely unlikely to be found in any sample that is added to a sample aliquot in known amount(s) before extraction or other processing, and is measured with the same procedures used to measure other sample components. The purpose of a SA is to monitor method performance with each sample.
- 3.3 Laboratory Duplicates (LD1 and LD2): Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate precision



associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

- 3.4 Field Duplicates (FD1 and FD2): Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.
- 3.5 Laboratory Reagent Blank (LRB): An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interference are present in the laboratory environment, the reagents, or the apparatus.
- 3.6 Field Reagent Blank (FRB): An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.
- 3.7 Instrument Performance Check Solution (IPC): A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of method criteria.
- 3.8 Laboratory Fortified Blank (LFB): An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample. Its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.
- 3.9 Laboratory Fortified Sample Matrix (LFM): An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample. Its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.
- 3.10 Stock Standard Solution (SSS): A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.
- 3.11 Primary Dilution Standard Solution (PDS): A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.
- 3.12 Calibration Standard (CAL): A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.
- 3.13 Quality Control Sample (QCS): A solution of method analytes of known concentrations that is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.



4.0 INTERFERENCES

- 4.1 During analysis, major contaminant sources are glassware, reagents, and liquid-solid extraction devices. Analyses of field and laboratory reagent blanks provide information about the presence of contaminants.
- 4.2 Interfering contamination may occur when a sample containing low concentrations of compounds is analyzed immediately after a sample containing relatively high concentrations of compounds. Syringes and splitless injection port liners must be cleaned carefully or replaced as needed and the column may have to be cut. After analysis of a sample containing high concentrations of compounds, a laboratory reagent blank should be analyzed to ensure that accurate values are obtained for the next sample.

5.0 SAFETY

- 5.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method.
- 5.2 Some method analytes have been tentatively classified as known or suspected human or mammalian carcinogens. Pure standard materials and stock standard solutions of these compounds should be handled with suitable protection for skin, eyes, etc.

6.0 EQUIPMENT AND SUPPLIES

- 6.1 All glassware is meticulously cleaned. This is accomplished by washing in a Lancer laboratory washer (or by hand) with detergent and water, rinsing fifteen times with hot tap water, rinsing with ASTM Type I reagent water, and then rinsing with acetone followed by a rinse with methylene chloride. The glassware is air-dried after washing.
- 6.2 Sample containers: New 1-L amber glass bottles fitted with Teflon-lined screw cap are used and discarded after analysis.
- 6.3 Volumetric flasks: Various sizes.
- 6.4 Laboratory vacuum system: Sufficient capacity to maintain a minimum vacuum of approximately 66 cm (26 inches of mercury).
- 6.5 TurboVap Concentrator II, Zymark Corporation. Nitrogen is used to concentrate extracts in the TurboVap.
- 6.6 Micro syringes: Various sizes.
- 6.7 Vials: Various sizes, amber with Teflon-lined screw caps.
- 6.8 Drying funnel containing about 5 to 7 grams of anhydrous sodium sulfate, held by glass wool, to avoid residual water from contaminating the extract.
- 6.9 Analytical balance: Mettler Toledo, AB 204.



- 6.10 Fused silica capillary gas chromatography column: 30-m x 0.25-mm ID coated with a 0.25- μ m bonded film of polyphenylmethylsilicone (Thermo Scientific, TG-SQC).
- 6.11 Gas chromatograph/tandem mass spectrometer/data system (GC/MS/MS/DS): ITQ-900, Thermo Scientific.
- 6.11.1 Thermo Trace Ultra GC capable of temperature programming and equipped for splitless/split injection. The injection tube liner is a multiple baffle liner made by Restek and is about 2 mm in diameter. The injection system does not allow the analytes to contact hot stainless steel or other metal surfaces that promote decomposition.
- 6.11.2 The GC/MS interface allows the capillary column or transfer line exit to be placed within a few mm of the ion source.
- 6.11.3 A Thermo Scientific ITQ 900 Tandem MS, is used. This mass spectrometer is capable of electron ionization at a nominal electron energy of 70 eV to produce positive ions and is capable of scanning from 45 to 450 amu with a complete scan cycle time (including scan overhead) of 1.0 sec or less (Scan cycle time = total MS data acquisition time in sec divided by number of scans in the chromatogram). This spectrometer produces a mass spectrum that meets all criteria in Table 2 when 5 ng of Decafluorotriphenylphosphine (DFTPP) is introduced into the GC.
- 6.11.4 An interfaced data system is used to acquire, store, reduce, and output mass spectral data. The computer software has the capability of processing stored GC/MS data by recognizing a GC peak within any given retention time window, comparing the mass spectra from the GC peak with spectral data in a user-created database, and generating a list of tentatively identified compounds with their retention times and scan numbers. The software also allows integration of the ion abundance of any specific ion between specified time or scan number limits, calculation of response factors as defined in Section 10.2.6 (or construction of a linear regression calibration curve), calculation of response factor statistics (mean and standard deviation), and calculation of concentrations of analytes using either the calibration curve or the equation in Section 12.
- 6.11.5 A Thermo Scientific AS 3000 automatic sampler is used to inject the blanks, standards, and samples into the GC.

7.0 REAGENTS AND STANDARDS

- 7.1 Helium carrier gas: Ultra high purity grade
- 7.2 Empore extraction disks: They contain octadecyl-bonded silica uniformly enmeshed in an inert matrix. Disks are 47 mm in diameter and 0.5 mm in thickness. One liter of reagent water passes through the disks in 5-20 min using a vacuum of about 66 cm (26 in.) of mercury.
- 7.3 Solvents
- 7.3.1 Methylene chloride, ethyl acetate, acetone, toluene, and methanol – High purity pesticide quality.
- 7.3.2 Reagent water: ASTM Type I reagent-grade water is used and produced by an in-house Millipore Milli-Q water purification system specific for organic chemical analysis.



- 7.4 Hydrochloric acid: 6 N
- 7.5 Sodium sulfate: Anhydrous, heated to 400°C for 4 hours in a muffle furnace.
- 7.6 Stock standard solutions: Individual solutions of analytes, surrogates, and internal standards are purchased from commercial suppliers.
- 7.7 Mixtures that contain the analytes of interest dissolved in methanol, ethyl acetate or acetone are used as primary dilution standards and are purchased from commercial suppliers. From this primary dilution standard, the calibration standards are prepared. Chlordane, simazine, and toxaphene are prepared separately. Ethyl acetate is used for all further dilutions. The primary dilution standard solution is stored in an amber vial in a freezer @ -20°C, and checked frequently for signs of degradation or evaporation, especially just before preparing calibration solutions.
- 7.8 Fortification solution of internal standards and surrogates: An internal standard solution of acenaphthene-D₁₀, phenanthrene-D₁₀, and chrysene-D₁₂, in methanol, ethyl acetate, or acetone at a concentration of 500 µg/mL of each is purchased from commercial suppliers and used in the preparation of the calibration solutions and to fortify the actual water samples. Similarly, a surrogate compound solution that contains 1,3-dimethyl-2-nitrobenzene, perylene-D₁₂, and triphenylphosphate at a concentration of 500 µg/mL in acetone is used to fortify the calibration standard and the actual water samples. A 10-µL solution added to 1 L of water gives a concentration of 5 µg/L of each internal standard or surrogate. These fortification solutions are stored in an amber vial in a freezer at -20°C.
- 7.9 GC/MS performance check solution: A solution in methylene chloride of the following compounds at 5-ng/µL each: DFTPP, endrin, and 4,4'-DDT. This solution is stored in an amber vial in a freezer at -20°C. DFTPP is less stable in acetone or ethyl acetate than it is in methylene chloride.
- 7.10 Calibration solutions (CAL1 through CAL6): A series of six concentration calibration solutions in at least 80% ethyl acetate, which contain target analytes (except pentachlorophenol) are prepared at 10, 5, 2, 1, 0.5, and 0.2 ng/µL, or other suitable concentrations, from the mixtures purchased from commercial suppliers, with a constant concentration of 5 ng/µL of each internal standard and surrogate in each CAL solution. CAL1 through CAL6 are prepared by combining appropriate aliquots of the primary dilution standard solution (Section 7.7) and the fortification solution (500 µg/mL) of internal standards and surrogates (Section 7.8). Pentachlorophenol is included in this solution at a concentration four times the other analytes. Chlordane and toxaphene are prepared individually at different concentrations: chlordane at 0.5, 1.0, 2.0, 5.0, 10, 20, and 40 ng/µL; and toxaphene at 10, 25, 50, 75, 100, 125, and 150 ng/µL. These solutions are stored in culture tubes or 2-mL amber vials at -20°C in a freezer and they are checked regularly for signs of degradation; for example, the appearance of anthraquinone from the oxidation of anthracene. The preparation of the dilutions from the primary standards is documented in the laboratory book of standards. Aliquots of the calibration solutions are transferred to 1.5-mL amber vials and placed in the auto-sampler tray to be run in the GC/MS.
- 7.11 Reducing agent: Sodium sulfite, anhydrous. Sodium thiosulfate is not recommended as it may produce a residue of elemental sulfur that can interfere with some analytes.
- 7.12 Fortification solution for recovery standard: A solution of terphenyl-D₁₄ at a concentration of 2500 µg/mL in methylene chloride or ethyl acetate is obtained from a supplier and a 2.5-µL aliquot of this solution is added to each field sample extract to check for the recovery of the internal standards in the extraction process.



8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample collection: When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 2 min). Adjust the flow to about 500 mL/min and collect samples from the flowing stream. Keep samples sealed from collection time until analysis. When sampling from an open body of water, fill the sample container with water from a representative area. Sampling equipment, including automatic samplers, must be free of plastic tubing, gaskets, and other parts that may leach interfering analytes into the water sample. Automatic samplers that composite samples over time should use refrigerated glass sample containers if possible.

8.2 Sample dechlorination and preservation: All samples are iced or refrigerated at 4°C and kept in the dark from the time of collection until extraction. Residual chlorine should be reduced at the sampling site by the addition of 40-50 mg of sodium sulfite (this may be added as a solid with stirring or shaking until dissolved) to each water sample. It is very important that the sample be dechlorinated prior to adding acid to lower the pH of the sample. Adding sodium sulfite and HCl to the sample bottles prior to shipping to the sampling site is not permitted. Hydrochloric acid should be used at the sampling site to retard the microbiological degradation of some analytes in water. The sample pH is adjusted to < 2 with 6N hydrochloric acid. This is the same pH used in the extraction and is required to support the recovery of acidic compounds like pentachlorophenol.

Samples are stored in a refrigerator in the dark at 4°C until extracted. The refrigerator's temperature is monitored and recorded daily.

8.3 Holding time: Samples are extracted within 14 days of collection and the extracts are stored in a freezer at -25 to -10°C. Extracts are analyzed within 30 days of sample extraction.

8.4 Field Blanks

8.4.1 Field reagent blanks (FRB) are processed along with each sample set, which is composed of the samples collected from the same general sample site at approximately the same time. This FRB is prepared in the laboratory by filling a sample container with reagent water and adjusting the pH to less than 2 with 6N hydrochloric acid. The container is sealed and shipped to the sampling site along with the empty sample container. The FRB is returned to the laboratory together with filled sample bottles. Samples that come to the lab without a FRB will be analyzed, but the collector will be notified that if any compound is found in them, the results are qualified since there is no way of determining that there was no contamination during the sampling trip.

8.4.2 When sodium sulfite and hydrochloric acid are added to samples, the same amounts are added to the FRB.

9.0 QUALITY CONTROL

9.1 Initial demonstration of low disk system background: Before any samples are analyzed, or any time a new supply of disks is received from a supplier, a laboratory reagent blank is analyzed to demonstrate that the laboratory reagent blank (LRB) is reasonably free of contamination that would prevent the determination of any analyte of concern. In this same experiment, it is demonstrated that the preparation of the disks is acceptable. Consistent flow rate with all samples is an indication of proper preparation.



- 9.1.1 A source of potential contamination is the liquid-solid extraction (LSE) disk which could contain phthalate esters, silicon compounds, and other contaminants that could prevent the determination of method analytes (Ref. 5). Although disks are generally made of an inert matrix, they may still contain phthalate material. Generally, phthalate esters can be leached from the disks into ethyl acetate and methylene chloride, and produce a variable background in the water sample. If the background contamination is sufficient to prevent accurate and precise measurements, the condition is corrected before proceeding with the initial demonstration. The disks are rinsed three times with 1:1 ethyl acetate:methylene chloride mix before extraction.
- 9.1.2 Other sources of background contamination are solvents, reagents, and glassware. Background contamination must be reduced to an acceptable level before proceeding with the next section. In general, background from method analytes should be below the method detection limit. Glassware is cleaned according to Section 6.1.
- 9.1.3 Approximately 5-20 min will normally be required to pass one liter of drinking water through a disk. The extraction time should not vary unreasonably among disks.
- 9.2 Initial demonstration of laboratory accuracy and precision: A minimum of four replicates of a laboratory-fortified blank containing each analyte of concern at a concentration of 2.0 µg/L or some other concentrations (e.g., 8.0 µg/L for pentachlorophenol) is analyzed. Chlordane (20 µg/L) and toxaphene (50 µg/L) are extracted separately.
- 9.2.1 Each replicate is prepared by adding sodium sulfite or HCl according to Section 8.2, then adding an appropriate aliquot of the primary dilution standard solution to reagent water. This information is entered in the extractions lab book. Each replicate is analyzed according to the procedures described in Section 11.
- 9.2.2 Calculate the measured concentration of each analyte in each replicate, the mean concentration of each analyte in all replicates, and mean accuracy (as mean percentage of true value) for each analyte, and the precision (as relative standard deviation, RSD) of the measurements for each analyte.
- 9.2.3 For each analyte and surrogate, the mean accuracy, expressed as a percentage of the true value, should be 70-130% and the RSD should be < 30%. If these criteria are not met, the accuracy and precision study is repeated.
- 9.2.4 For MDL calculation, seven replicate laboratory-fortified blanks which have been fortified with all analytes of interest at 0.5 µg/L (2.0 µg/L for pentachlorophenol) or other concentration are analyzed. Chlordane (5 µg/L) and toxaphene (10 µg/L) are extracted and analyzed separately. The MDL of each analyte is calculated using the procedure described in Section 13.1.2 (Ref. 1). These analyses are performed over a period of three or four days to produce more realistic method detection limits.
- 9.2.5 A summary of the initial demonstration of precision and accuracy, and the MDL determination is given in Table 4.
- 9.2.6 A system of control charts to monitor the surrogate standard recovery is maintained in the WES LIMS.
- 9.3 The integrated areas of the quantitation ions of the internal standards are monitored. The area of quantitation of each IS is divided by the area of the quantitation ion of the recovery standard, Terphenyl-D14.



- 9.4 With each batch of samples processed as a group within a 12-hour work shift, a laboratory reagent blank is analyzed to determine the background system contamination. Any time a new batch of LSE disks is received, or new supplies of other reagents are used, the demonstration of low background, described in Section 9.1 is repeated.
- 9.5 With each batch of samples processed as a group within a work shift, a single laboratory-fortified blank (LFB) containing each analyte listed in Section 1.1, at a concentration of 0.5 µg/L or some other concentration is analyzed. The spiking solution for the LFB is prepared from a stock solution from a source different from the source for the calibration standards. If more than 20 samples are included in a batch, analyze a LFB for every 20 samples. The accuracy of the measurements is evaluated. If it is not within $\pm 30\%$, the problem is located and corrected before additional samples are analyzed.
- 9.6 To determine that the sample matrix does not contain materials that adversely affect method performance, laboratory-fortified matrix samples (LFM) are analyzed at a frequency of 5% or one per batch whichever is more frequent. The precision, accuracy, and method detection limits of analytes should be in the same range as obtained with laboratory-fortified blanks. The LFM solution is the same used as a laboratory-fortified blank (Section 9.5)
- 9.7 The spiking solution for the LFB and the LFM is prepared as follows:

Into a 10-mL volumetric flask containing about 5 mL of ethyl acetate, the following is added:

- 1 mL of a solution from a manufacturer containing the insecticides included in the list in Section 1.1, at a concentration of 100 µg/mL in acetone.
- 200 µL of a solution from a manufacturer containing the PAHs included in the list in Section 1.1, at a concentration of 500 µg/mL in acetone.
- 1 mL of a solution from a manufacturer containing the phthalates and adipate included in the list in Section 1.1, plus hexachlorobenzene and hexachlorocyclopentadiene at a concentration of 100 µg/mL in acetone. This solution also contains pentachlorophenol at a concentration of 400 µg/mL
- When requested for analysis, chlordane and toxaphene are prepared individually.

The volume in the volumetric flask is made up to 10 mL with ethyl acetate, the flask is inverted several times for thorough mixing and the resulting solution of the compounds described above at a concentration of 10 ng/µL (pentachlorophenol is at 40 ng/µL) is used as the spiking solution; 50 µL of this spiking solution are added to 1 L of reagent water and to 1 L of the sample to be spiked.

- 9.8 With each set of samples, a field reagent blank (FRB) is analyzed. The results of this analysis will help define contamination resulting from field sampling and transportation activities.
- 9.9 Quarterly, a quality control sample from an external source is analyzed. Once a year, a Proficiency Test sample is analyzed and three times a year, a sample from another source is analyzed. If measured analyte concentrations are not of acceptable accuracy (Section 9.2.3), the entire analytical procedure must be checked to locate and correct the problem source. Every time the system is calibrated, a standard from an external source is analyzed.



- 9.10 The quality control sample used is a blind sample purchased from a recognized supplier that contains at a minimum the following compounds:

Acenaphthylene
Alachlor
Aldrin
Anthracene
Atrazine
Benz[a]anthracene
Benzo[b]fluoranthene
Benzo[k]fluoranthene
Benzo[a]pyrene
Benzo[g,h,i,l]perylene
Butylbenzyl phthalate
Cis-chlordane
Trans-chlordane
Chlordane components:
 Alpha-chlordane
 Gamma-chlordane
 Trans-nonachlor
Chrysene
Dibenz[a,h]anthracene
Di-n-butyl phthalate
Diethylphthalate
Di(2-ethylhexyl)adipate
Di(2-ethylhexyl)phthalate
Dimethyl phthalate
Endrin
Fluorene
Heptachlor
Heptachlor epoxide
Hexachlorobenzene
Hexachlorocyclopentadiene
Indeno[1,2,3,c,d]pyrene
Lindane
Methoxychlor



Pentachlorophenol

Phenanthrene

Pyrene

Simazine

Toxaphene

- 9.11 A summary of quality control elements and acceptance limits for this method is contained in Table 1.

10.0 CALIBRATION AND STANDARDIZATION

- 10.1 Acceptable initial calibration is documented before any samples are analyzed and repeated intermittently throughout sample analysis as dictated by results of continuing calibration checks. After initial calibration is successful, a continuing calibration check is analyzed each day or at the beginning of each period in which analyses are performed not to exceed 12 h.

10.2 Initial calibration

- 10.2.1 Calibrate the mass and abundance scales of the MS with perfluorotributylamine to meet the requirements in Section 10.2.3.

- 10.2.2 GC program conditions for the analysis of DFTPP: Helium carrier gas flow rate 33 cm/sec. Initial temperature 90°C held in splitless mode for 0.5 min. Heat to 310°C at 40 °C/min; hold at 310°C for 1 min. Total run time 7 min. Data acquisition starts at 4.5 min.

- 10.2.3 Inject into the GC/MS system a 1-μL aliquot of the 5 ng/μL solution of DFTPP, endrin, and 4,4'-DDT. The endrin and DDT degradation checks are performed simultaneously with the DFTPP check. Acquire a mass spectrum that includes data for m/z 45-450. Use GC conditions that produce a narrow (at least five scans per peak) symmetrical peak for each compound (Section 10.2.3.1). If the DFTPP mass spectrum does not meet all criteria in Table 2, the MS is retuned and adjusted to meet all criteria before proceeding with calibration. A single spectrum or an average spectrum across the GC peak may be used to evaluate the performance of the system. Locate any degradation products of endrin (i.e., endrin ketone [EK] and endrin aldehyde [EA]) and 4,4'-DDT (i.e., 4,4'-DDT, 4,4'-DDE, and 4,4'-DDD) at their appropriate retention times and m/z ratios. Endrin ketone peak is located at approximately 1.1 to 1.2 times the endrin retention with prominent m/z 67 and 137 ions in the mass spectrum. If degradation of either endrin or DDT exceeds 20%, maintenance is performed on the GC injection port and/or other areas of the system before proceeding with the calibration. The percent breakdown using peak areas based on total ion current (TIC) is calculated as follows:

$$\% \text{ endrin breakdown} = \frac{\sum \text{TIC area of endrin degradation peaks (EA + EK)}}{\sum \text{TIC area of total endrin peaks (endrin + EA + EK)}}$$

Where Σ = the mathematical summation symbol, sigma.



$$\% \text{ 4,4' - DDT breakdown} = \frac{\sum \text{TIC area of DDT degradation peaks (DDE + DDD)}}{\sum \text{TIC area of total DDT peaks (DDT + DDE + DDD)}}$$

Where Σ = the mathematical summation symbol, sigma.

- 10.2.4 GC program conditions for the analysis of samples: Helium carrier gas flow rate 33 cm/sec. Initial temp 40°C held in splitless mode for 0.5 min. Heat to 230°C at 40°C/min; heat to 310°C at 5°C/min; hold at 310°C for 1 min. Total run time 24 min. Data acquisition starts at 4 min.
- 10.2.4.1 A 1- μ L aliquot of a medium concentration calibration solution that contains all the analytes of interest at 2 ng/ μ L or some other concentration is injected. Chlordane and toxaphene are analyzed separately. Acquire and store data from m/z 45-450 with a total cycle time (including scan overhead time) of 1.0 sec or less. Cycle time is adjusted to measure at least five or more spectra during the elution of each GC peak.
- 10.2.5 Performance criteria for the medium calibration; examine the stored GC/MS data with the data system software.
- 10.2.5.1 GC performance: Anthracene and phenanthrene should be separated by baseline. Benz[a]anthracene and chrysene should be separated by a valley whose height is less than 25% of the average peak height of these two compounds. If the valley between benz[a]anthracene and chrysene exceeds 25%, the GC column requires maintenance (See Section 10.3.6).
- 10.2.5.2 MS sensitivity: The GC/MS/DS peak identification software should be able to recognize a GC peak in the appropriate retention time window for each of the compounds in calibration solution, and make correct identifications. If fewer than 99% of the compounds are recognized, system maintenance is required (See Section 10.3.6).
- 10.2.6 If all performance criteria are met, inject a 1- μ L aliquot of each of the other CAL solutions using the same GC/MS conditions: 0.2, 0.5, 1.0, 5.0, and 10 ng/ μ L or other suitable concentrations.
- 10.2.7 Response factors (RF) are calculated with the equation below or by the system software for each analyte of interest and surrogate for each CAL solution using the internal standard whose retention time is nearest the retention time of the analyte or surrogate. Table 3 contains the internal standards for each analyte and surrogate, and quantitation ions for all compounds. The RF is a unit-less number, but units used to express quantities of analyte and internal standard must be equivalent. Chlordane and toxaphene are calculated with the average response factor equation using the combined areas of three to five of the most intense and reproducible peaks in each of the calibration standard chromatograms.



$$RF = \frac{(A(x))(Q(is))}{(A(is))(Q(x))}$$

where:

A(x) = Integrated abundance of the quantitation ion of the analyte.

A(is) = Integrated abundance of the quantitation ion internal standard.

Q(x) = Quantity of analyte injected in ng or concentration units.

Q(is) = Quantity of internal standard injected in ng or concentration units

- 10.2.7.1 For each analyte and surrogate, calculate the mean RF from the analyses of the six CAL solutions. Calculate the standard deviations (SD) and the relative standard deviation (RSD) from each mean:

$$RSD = 100 (SD/M).$$

If the RSD of any analyte or surrogate mean RF exceeds 30%, either analyze additional aliquots of appropriate CAL solutions to obtain an acceptable RSD of RFs over the entire concentration range or take action to improve GC/MS performance (See Section 10.3.6).

- 10.3 Continuing calibration check: The MS tune and initial calibration at the beginning of each 12-hour work shift during which analyses are performed are verified using the following procedure.

10.3.1 Inject a 1-μL aliquot of the 5 ng/μL DFTPP, endrin, and 4,4'-DDT. Acquire a mass spectrum for DFTPP that includes data for m/z 45-450. Ensure that all criteria in Section 10.2.2 are met.

10.3.2 Inject a 1-μL aliquot of a 0.5 ng/μL or other concentration solution and analyze with the same conditions used during the initial calibration.

10.3.3 Demonstrate acceptable performance for the criteria shown in Section 10.2.4

10.3.4 Determine that the absolute areas of the quantitation ions of the internal standards and surrogate(s) have not decreased by more than 30% from the areas measured in the most recent continuing calibration check, or by more than 50% from the areas measured during initial calibration. If these areas have decreased by more than these amounts, adjustments must be made to restore system sensitivity. These adjustments may require cleaning of the MS ion source, or other maintenance as indicated in Section 10.3.6, and recalibration.

10.3.5 The RF for each analyte and surrogate must be within 30% of the mean value measured in the initial calibration. If these conditions do not exist, remedial action must be taken which may require recalibration.



- 10.3.5.1 Because of the large number of compounds on the analyte list, it is possible for a few analytes of interest to be outside the continuing calibration criteria. If analytes that missed the calibration check are detected in samples, they may be quantified using a single-point calibration. The single-point standards should be prepared at concentrations that produce responses close ($\pm 20\%$) to those of the unknowns. If the same analyte misses the continuing calibration check on three consecutive work shifts, remedial action is taken. If more than 10% of the analytes of interest miss the continuing calibration check on a single day, remedial action is taken.
- 10.3.6 Some possible remedial actions: Major maintenance such as cleaning the ion source, replacing filament assemblies, etc., requires returning to the initial calibration step.
- 10.3.6.1 Check and adjust GC and/or MS operating conditions; check the MS resolution, and calibrate the mass scale.
- 10.3.6.2 Clean or replace the splitless injection liner.
- 10.3.6.3 Flush the GC column with solvent according to manufacturer's instructions.
- 10.3.6.4 Break off a short portion (about 1 meter) of the column from the end near the injector or replace GC column. This action will cause a change in retention times.
- 10.3.6.5 Prepare fresh CAL solutions, and repeat the initial calibration step.
- 10.3.6.6 Clean the MS ion source.
- 10.3.6.7 Replace any components that allow analytes to come into contact with hot metal surfaces.
- 10.3.6.8 Replace the MS electron multiplier, or any other faulty components.

11.0PROCEDURE

11.1 Disk Extraction

- 11.1.1 Standard 47-mm diameter disks are used. Larger disks (90-mm diameter) may be used if sample compositing is being done or special matrix problems are encountered. If larger disks are used, the washing solvent volume is 15 mL, the conditioning solvent volume is 15 mL, and the elution solvent volume is two 15 mL aliquots.
- 11.1.2 To 1 L of sample, add 5 mL of MeOH. Mix well. Add 10 μL of 500 ng/ μL internal and surrogate standards solution and mix well. The resulting concentration of these compounds in the sample is 5 $\mu\text{g/L}$.
- 11.1.3 Insert the disk into the filter apparatus (Figure 1). The disk is washed 3 times with 5 mL of a 1:1 mixture of ethyl acetate (EtAc) and methylene chloride (MeCl_2) by adding the solvent to the disk, drawing about half through the disk, allowing it to soak the disk for about a minute, then drawing the remaining solvent through the disk. (NOTE: Soaking the disk may not be desirable when disks other than Teflon are used. Instead, apply a constant, low vacuum to ensure adequate contact time between solvent and disk.)



- 11.1.4 Pre-wet the disk with 5 mL of methanol (MeOH) by adding the MeOH to the disk and allowing it to soak for about a minute, then drawing most of the remaining MeOH through the disk. A layer of MeOH is left on the surface of the disk, which should not be allowed to go dry from this point until the end of the sample extraction. This is a critical step for a uniform flow and good recovery.

Rinse the disk with 5 mL of reagent water by adding the water to the disk and draining most through, again leaving a layer on the surface of the disk. Add the water sample to the reservoir and apply full vacuum to begin the extraction. Particulate-free water may pass through the disk in as little as 5 min without reducing analyte recoveries. Extract the entire sample, draining as much water from the sample container as possible. Dry the disk by maintaining vacuum for about 10 min.

- 11.1.5 Remove the filtration top, but do not disassemble the reservoir and fritted base. Insert a 60-mL vial to contain the eluant. The only constraint on the vial is that it fit around the drip tip of the fritted base. Reassemble the apparatus.

Add 5 mL of ethyl acetate to the sample bottle, and rinse the inside walls thoroughly. Allow the solvent to settle to the bottom of the bottle and then transfer it to the disk (a disposable pipet is used to do this) rinsing the sides of the glass filtration solvent through the disk. Draw about half of the solvent through the disk, release the vacuum, and allow the disk to soak for a minute. Draw the remaining solvent through the disk. (NOTE: Soaking the disk may not be desirable if disks other than Teflon are used. Instead, apply a constant, low vacuum in this Section to ensure adequate contact time between solvent and disk.)

Repeat the above step with methylene chloride.

Using a disposable pipette, rinse the filtration reservoir with two 3-mL portions of 1:1 EtAC:MeCl₂. Draw the solvent through the disk and into the collector vial.

- 11.1.6 Pour the combined eluates through a drying funnel containing about 5 to 7 grams of anhydrous sodium sulfate which is held in place by a small amount of glass wool. Rinse the vial, funnel, and sodium sulfate with two 3-mL portions of 1:1 EtAC:MeCl₂ mixture. Collect all the extract and washings into the concentrator tube of the Turbo Vap Concentrator.

Concentrate to between 0.5 and 1 mL under a gentle stream of nitrogen. Do not concentrate the extract to less than 0.5 mL since this will result in losses of analytes. Rinse the wall of the Turbo Vap tube about 15 times and make any volume adjustments with ethyl acetate. An aliquot of the recovery standard is added to the concentrated extract to check the recovery of the internal standards and the extract is placed in a 1.5-mL amber vial.

- 11.2 Before any samples are analyzed, the DFTPP and the CCC check must be done and their criteria met (Section 10.3). Place the extract vial in the tray of the automatic sampler and analyze a 1 μ L aliquot with the GC/MS system under the same conditions used for the initial and continuing calibrations (Section 10.2.3).
- 11.3 At the conclusion of data acquisition, use the same software that was used in the calibration procedure to tentatively identify peaks in predetermined retention time windows of interest. Use the data system software to examine the ion abundances of components of the chromatogram.



- 11.4 Identification of Analytes: Identify a sample component by comparison of its mass spectrum (after background subtraction) to a reference spectrum in the user-created database. The GC retention time of the sample component should be within 5 sec of the retention time observed for that same compound in the most recently analyzed continuing calibration check standard.
- 11.4.1 In general, all ions that are present above 10% relative abundance in the mass spectrum of the standard should be present in the mass spectrum of the sample component and should agree within absolute 20%. For example, if an ion has a relative abundance of 30% in the standard spectrum, its abundance in the sample spectrum should be in the range of 10 to 50%. Some ions, particularly the molecular ion, are of special importance, and should be evaluated even if they are below 10% relative abundance.
- 11.4.2 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When GC peaks obviously represent more than one sample component [i.e., broadened peak with shoulder(s) or valley between two or more maxima], appropriate analyte spectra and background spectra can be selected by examining plots of characteristic ions for tentatively identified components. When analytes co-elute (i.e., only one GC peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the co-eluting compound.
- 11.4.3 Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different GC retention times (See Section 10.2.4.1). Acceptable resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the average height of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. Benzo[b] and Benzo[k] Fluoranthene have sufficiently different retention times to permit the identification of the two isomers.
- 11.5 The sequence of analysis is as follows:
- 11.5.1 DFTPP, Endrin, and 4,4'-DDT solution
- 11.5.2 2 ng of calibration standard followed by all other calibration standards and an external source standard (if instrument calibration has to be done) or 0.5 ng or other concentration of check standard (daily check of initial calibration).
- 11.5.3 Laboratory Reagent Blank
- 11.5.4 Laboratory-Fortified Blank
- 11.5.5 Quality Control Sample from an external source (quarterly)
- 11.5.6 Samples
- 11.5.7 Field Reagent Blank
- 11.5.8 Laboratory-Fortified Matrix
- 11.5.9 Check Standard – 0.5 ng or other concentration



12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Concentrations are calculated by measuring the characteristic ions listed in Table 3.

12.1.1 Calculate analyte and surrogate concentrations as follows:

$$C(x) = \frac{(A(x))(Q(is))}{(A(is)) RF V}$$

Where:

- C (x) = Concentration (µg/L) of analyte or surrogate in the water sample
- A (x) = Integrated abundance of the quantitation ion of the analyte in the sample.
- A(is) = Integrated abundance of the quantitation ion of the internal standard in the sample.
- Q (is) = Total quantity (in micrograms) of internal standard added to the water sample.
- V = Original water sample volume in liters.
- RF = Mean response factor of analyte from the initial calibration.

12.1.2 Calculations utilize all available digits of precision, but final reported concentrations are rounded to an appropriate number of significant figures (one digit of uncertainty).

12.1.3 Calculations described in 12.1.1 are performed by the system's software. When manual integration of chromatographic peak(s) is necessary, the laboratory maintains copies of data print-outs from before and after manual integration. Electronic copies of the modified data file(s) are saved in a shared W drive. The laboratory follows the procedure for manual integration of GC peaks developed by the lab and the instructions given by the instrument tutorials. The tutorials can be accessed from the icon on the computer desktop.

13.0 METHOD PERFORMANCE

13.1 Accuracy and precision data (Table 4) for each listed analyte were obtained at a concentration of 2.0 µg/L (with the exception of pentachlorophenol which was at 8.0 µg/L, chlordane at 5 µg/L, and toxaphene at 10 µg/L) in reagent water utilizing the disk technology and an ion trap detector. The average recoveries in the tables represent seven replicate analyses done over a period of several months.

13.1.2 With these data, method detection limits (MDL) in the table were calculated using the system software based on the formula:

$$MDL = S t(n-1, 1-\alpha = 0.99)$$



Where:

$t(n-1, 1-\alpha = 0.99)$ = Student's t value for the 99% confidence level with n-1 degrees of freedom

n = Number of replicates

S = Standard deviation of replicate analyses.

13.2 Problem compounds

13.2.1 Some polycyclic aromatic hydrocarbons (PAH), including the labeled PAHs used in this method as internal standards, are rapidly oxidized and/or chlorinated in water containing residual chlorine. Therefore, residual chlorine must be reduced at the time of sampling. These same types of compounds, especially anthracene, benzo[a]anthracene, and benzo[a]pyrene, are susceptible to photodegradation; therefore, care should be taken to avoid exposing standards, samples, and extracts to direct light. Low recoveries of some PAH compounds have been observed when the cartridge or disk was air dried longer than 10 min (Section 11.1.4). Drying times longer than 10 min should be avoided, or nitrogen may be used to dry the cartridge or disk to minimize the possible oxidation of these analytes during the drying step.

13.2.2 Phthalate esters and other background components appear in variable quantities in laboratory and field reagent blanks, and generally cannot be accurately measured at levels below about 2 µg/L. Subtraction of the concentration in the blank from the concentration in the sample at or below the 2 µg/L level is not allowed because the concentration of the background in the blank is highly variable. If any contamination is found in the blanks, it is reported and the data are flagged

13.2.3 If cyanazine is to be determined, a separate sample must be collected. Cyanazine degrades in the sample when it is stored under acidic conditions or when sodium sulfite is present in the stored sample. Samples collected for cyanazine determination MUST NOT be dechlorinated or acidified when collected. They should be iced or refrigerated and analyzed within 14 days. However, these samples MUST be dechlorinated and acidified immediately prior to fortification with internal standards and extraction using the same quantities of acid and sodium sulfite described in Section 8.

14.0 POLLUTION PREVENTION

14.1 Refer to the WES Environmental Management System (EMS) policy and SOPs regarding pollution prevention.

14.2 The quantity of chemicals purchased should be based on expected usage during its shelf life. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

15.0 WASTE MANAGEMENT

15.1 WES laboratories fully comply with all applicable federal, state, and local environmental regulations. WES is also committed to protecting the air, water, and land by minimizing and controlling all chemical releases from fume hoods, biological safety cabinets, and bench operations. Refer to the WES EMS policy and SOPs regarding waste management.



- 15.2 This method utilizes the new liquid-solid (LSE) extraction technology to remove the analytes from water. It requires the use of very small volumes of organic solvent and very small quantities of pure analytes, thereby eliminating the potential hazards to both the analyst and the environment involved with the use of large volumes of organic solvents in conventional liquid-liquid extractions.
- 15.3 All waste solvents are collected in sealed waste containers. Once the waste containers reach capacity, they are transferred to the WES hazardous waste storage room where they are emptied into a waste solvent drum. Within 180-days of waste accumulation, the waste solvent drum is transported off the premises by a licensed hazardous waste management contractor. Under the WES EMS, a chemical inventory database has been developed to track purchases and use of solvents and other hazardous materials, and the waste generated by the use of these chemicals.

16.0 REFERENCES

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17.0 TABLES AND VALIDATION DATA

TABLE 1. Quality Control Elements and Acceptance Limits for the Analysis of Organic Compounds In Drinking Water By Liquid-Solid Extraction And Capillary Column Gas Chromatography/Mass Spectrometry by EPA Method 525.2

QC Elements	Frequency	Acceptance Criteria	Corrective Action
Sample Extract Storage	Every extract	Extracts are stored in freezer at -25 to -10°C and analyzed within 30 days of sample extraction.	Qualify data (H) as suspect (holding time exceeded). Contact sample collector to collect new sample
MS Calibration	Beginning of every twelve hours of analysis	EPA DFTPP specifications	MS retuned
Degradation Products	Beginning of every twelve hours of analysis	Degradation < 20%	Maintenance of the GC system
Laboratory Reagent Blank	With each batch of samples processed as a group in a work shift	Contamination of method analytes < MDL	Identify source of contamination and reduce it to acceptable levels
Initial Calibration (IC)	Every time the calibration verification does not meet criteria	* RSD within 30% of the mean RF for each compound on each cal level	Necessary adjustments to the system and recalibration
Internal Standards	Added to all blanks, standards and samples	Area of quant ion \geq 30% area in CCC or \geq 50% area in IC	Identify source of error and recalibrate if necessary
Surrogate Standards	Added to all blanks, standards, and samples	Value within 30% of true value. Area of quant ion \geq 30% area in CCC or \geq 50% area in IC	Identify source of error and recalibrate if necessary
Recovery Standard (Terphenyl D14)	Added to extracts of all blanks, samples and LFM	Internal standard recovery \geq 70%	Identify source of error and recalibrate if necessary
Calibration Verification (CCC)	Beginning of twelve hours of analysis	For each compound RF must be within 30% of mean RF in IC	Identify source of error and recalibrate if necessary
Field Reagent Blank	With each set of samples from the same site	Method Analytes < MDL	Determine if the contamination is from the lab
Field Duplicates	10%	RPD: 0 - 20%	Review all analyses done in the day to determine that it is not a lab error
Laboratory-Fortified Blank	With each batch of samples as a group in 12 hours or every 20 samples	Value for each analyte, 70 – 130% of true value	Identify source of error and repeat extraction if necessary
Laboratory-Fortified Sample Matrix	Every 20 samples processed in the same batch	Value for each analyte, 70 – 130% of true value	Identify source of error and repeat extraction if necessary
Proficiency Test	Once a year	EPA specifications	Participate in another



TABLE 1. Quality Control Elements and Acceptance Limits for the Analysis of Organic Compounds In Drinking Water By Liquid-Solid Extraction And Capillary Column Gas Chromatography/Mass Spectrometry by EPA Method 525.2

QC Elements	Frequency	Acceptance Criteria	Corrective Action
Study			study for compounds that failed
QC Sample from an External Source	Three times a year	EPA specifications	Determine source of error and repeat analysis
MDL determination (USEPA, 1997)	When significant changes are made to the instrument or in the laboratory	Target analyte concentration spiked into the blank matrix must not exceed 10 times (approximately) the experimentally determined MDL	Repeat MDL study spiking the blank matrix with lower concentration of the target analyte
<p>* Resolution: Anthracene and Phenanthrene separated by baseline, valley between Benzo(a)anthracene and crysene < 25% of the average peak height of these two compounds.</p> <p>Sensitivity: No less than 99% of the compounds should be recognized by the system. Regulated compounds should always pass.</p>			

TABLE 2. Ion Abundance Criteria For Bis(Perfluorophenyl)Phenyl Phosphine (Decafluorotriphenylphosphine, DFTPP)

Mass (M/z)	Relative Abundance Criteria	Purpose of Checkpoint (1)
51	10-80% of the base peak	Low mass sensitivity
68	<2% of mass 69	Low mass resolution
70	<2% of mass 69	Low mass resolution
127	10-80% of the base peak	Low-mid mass sensitivity
197	<2% of mass 198	Mid-mass resolution
198	Base peak or >50% of 442	Mid-mass resolution and sensitivity
199	5-9% of mass 198	Mid-mass resolution and isotope ratio
275	10-60% of the base peak	Mid-high mass sensitivity
365	>1% of the base peak	Baseline threshold
441	Present and < mass 443	High mass resolution
442	Base peak or >50% of 198	High mass resolution and sensitivity
443	15-24% of mass 442	High mass resolution and isotope ratio



TABLE 3. Retention Time Data, Quantitation Ions, And Internal Standard References For Method Analytes.

Compound	Retention Time (min:sec)	Quantitation Ion	IS Reference
Internal Standards			
acenaphthene-d10	5:48	164	
chrysene-d12	11:42	240	
phenanthrene-d10	6:67	188	
Surrogates			
1,3-dimethyl-2-nitrobenzene	4:35	134	1
perylene-d12	15:88	264	3
Triphenylphosphate	10:58	326/325	3
Target Analytes			
Acenaphthylene	5:38	152	1
Alachlor	7:13	160	2
Aldrin	7:65	66	2
Anthracene	6:74	178	2
Atrazine	6:36	200/215	1
benzo(a)anthracene	11:37	228	3
benzo(b)fluoranthene	14:66	252	3
benzo(k)fluoranthene	14:74	252	3
1,12-benzoperylene	19:99	276	3
benzo(a)pyrene	15:68	252	3
butyl benzophthalate	10:06	149	3
cis-chlordane	8:65	375/373	2
trans-chlordane	8:44	409	2
Chrysene	11:49	228	3
dibenzo(a,h)anthracene	19:33	278	3
di-n-butylphthalate	7:29	149	2
di-2-ethylhexyl)adipate	10:24	129	3
di(2-ethylhexyl)phthalate	11:76	149	3
Diethylphthalate	5:76	149	1
Dimethylphthalate	5:29	163	1
Endrin	9:41	67/81	2
Fluorene	5:86	166	1
HCH, gamma (Lindane)	6:57	181	1
Heptachlor	7:25	100	2
heptachlor epoxide	8:12	353	2
Hexachlorobenzene	6:38	284	1
hexachlorocyclopentadiene	4:94	237	1
indeno(1,2,3,c,d)pyrene	19:23	276	3
Methoxychlor	11:38	227	3
Pentachlorophenol	6:54	226	2
Phenanthrene	6:69	178	2
Pyrene	8:63	202	2
Alpha-Chlordane	8:33	375	2
Gamma-Chlordane	8:39	375	2
Trans-Nonachlor	8:60	409	2
Simazine	6:28	201/186	2



TABLE 3. Retention Time Data, Quantitation Ions, And Internal Standard References For Method Analytes.

Compound	Retention Time (min:sec)	Quantitation Ion	IS Reference
Toxaphene	8:93	159	2
Toxaphene2	9:35	159	2
Toxaphene3	9:74	173	2
Toxaphene4	10:4	159	2
Toxaphene5	10:77	159	2
Multi-ramp linear temperature program conditions (Section 10.2.3.1).			



TABLE 4. Precision, Accuracy, and MDL in Reagent Water Using Liquid-Solid C18 Disk Extraction and the Ion Trap Mass Spectrometer

Target Analytes	IDC ^A Spike (µg/L)	Mean Accuracy (% of True Value)	Rel. Std. Dev. (%)	MDL ^B Spike (µg/L)	Method Detection Limit (µg/L)
Hexachlorocyclopentadiene	2.0	85	10.1	0.5	0.14
Dimethyl phthalate	2.0	114	8.80	0.5	0.14
Acenaphthylene	2.0	101	8.35	0.5	0.13
Diethylphthalate	2.0	111	3.09	0.5	0.078
Fluorene	2.0	102	9.58	0.5	0.086
Hexachlorobenzene	2.0	85	3.00	0.5	0.13
Atrazine	2.0	111	10.5	0.5	0.092
Lindane	2.0	99	10.8	0.5	0.039
Pentachlorophenol	8.0	120	8.04	2.0	0.56
Phenanthrene	2.0	91	5.62	0.5	0.057
Anthracene	2.0	91	9.41	0.5	0.058
Alachlor	2.0	112	11.3	0.5	0.15
Heptachlor	2.0	81	11.1	0.5	0.14
Aldrin	2.0	105	5.38	0.5	0.11
Di-n-butyl phthalate	2.0	119	7.98	0.5	0.18
Heptachlor epoxide	2.0	101	18.4	0.5	0.16
Cis-chlordane	2.0	88	10.9	0.5	0.21
Trans-chlordane	2.0	82	9.03	0.5	0.16
Pyrene	2.0	92	8.62	0.5	0.064
Endrin	2.0	127	7.08	0.5	0.21
Butylbenzylphthalate	2.0	109	8.85	0.5	0.21
Bis (2EH) adipate	2.0	104	7.86	0.5	0.21
Methoxychlor	2.0	96	7.97	0.5	0.092
Benzo(a)anthracene	2.0	95	6.11	0.5	0.073
Chrysene	2.0	97	6.36	0.5	0.072
Bis (2EH) phthalate	2.0	111	7.96	0.5	0.056
Benzo(b)fluoranthene	2.0	106	7.07	0.5	0.092
Benzo(k)fluoranthene	2.0	100	7.49	0.5	0.063
Benzo(a)pyrene	2.0	106	8.21	0.5	0.059
Indeno-1,2,3-cd-pyrene	2.0	119	6.97	0.5	0.14
Dibenzo-a,h-anthracene	2.0	109	6.13	0.5	0.23
1,12-benzoperylene	2.0	109	6.73	0.5	0.11
Chlordane components	20	79	12.0	5	1.5
Simazine	2.0	78	16.3	0.5	0.28
Toxaphene	50	83	8.7	10	1.9

^A Initial Demonstration of Capability (IDC) data were generated from runs on October 5, 6 & 7, 2010, except for chlordane components and toxaphene, which were determined from runs on November 27, 28 & 29, 2012, and simazine, which was determined on September 7, 2012.

^B Method Detection Limit (MDL) data were generated from runs on December 27, 2012 through January 2, 2013.

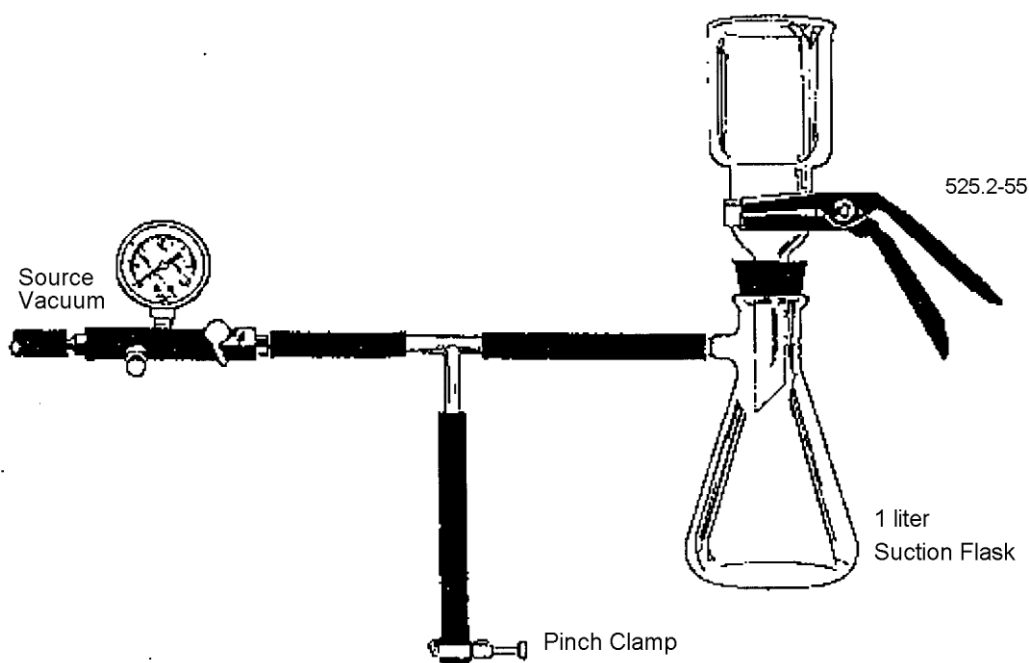


FIGURE 1. Disk Extraction Apparatus



APPENDIX: OPERATION OF THE THERMO ITQ 900 GC/MS FOR THE ANALYSIS OF ENVIRONMENTAL SAMPLES BY USEPA METHOD 525.2

A1.0 BEFORE RUNNING SAMPLES

Step	Action
	GC/MS TUNING AND LEAK CHECKS
1	On desktop, click Start. Double click on Tune icon.
2	Click Automatic Tune tab
3	Click on Check for Air/Water
4	Click ON
5	The instrument will produce a report after a few minutes. Make sure that there are no air leaks. Print report. Otherwise, troubleshoot instrument following instructions in the User Manual located in the Thermo Fisher Scientific folder. If there are no leaks and tuning is fine, PRESS OFF. Close Tune section.

A2.0 SETTING UP FOR DFTPP AND DEGRADATION PRODUCTS

Step	Action
1	DFTPP, Endrin, and 4,4'-DDT solution is kept in Freezer # 4 located in the Organic Chemistry Equipment Room.
2	Allow vial to reach room temperature. Place vial with the GC/MS performance solution in auto-sampler tray.
3	On the desktop screen, click Envirolab Forms 3.0 and press Production Mode. Click new batch and name batch. Enter master method. Enter data file number.
4	Enter Sample Name. Enter sample type by clicking down arrow and select Tune/Breakdown.
5	Enter Operator's name
6	Enter any comments.
7	Enter vial position.
8	Right click mouse and press Submit Batch.



A3.0DFTPP DATA ANALYSIS

Step	Action
1	AFTER RUN IS FINISHED: For Manual Report (Ad-Hoc Report) Click Method Development in Production Mode. Click Method View.
2	Select QA/QC tab. Click Tune.
3	Select File and Mass Spectrum.
4	Select data file to be used.
5	Activate Spectrum window and select the DFTPP peak.
6	Select scan to be processed and obtain spectrum.
7	Right click on spectrum window.
8	Click Export.
9	Click Clipboard Nominal Mass.
10	Go back to Thermo EnviroLab screen.
11	Click Create Tune Report as PDF file.
12	Report will be created. Print report if DFTPP is within criteria.
13	For the % Breakdown report, see the User's Manual located in the Thermo Fisher Scientific folder.

A4.0SETTING INSTRUMENT FOR RUNNING STANDARDS AND SAMPLES

Step	Action
1	Place vial(s) in auto-sampler tray.
2	From desktop, click EnviroLab Forms 3.0
3	Press Production Mode. Press New Batch.
4	On File Name, enter the data file number that follows the last number used.
5	Enter all other pertinent information related to the sample(s).
6	On Method, enter the method to be used to run the samples.



A5.0 ANALYSIS OF GC/MS DATA

Instructions on how to analyze GC/MS data are found in User's Manual located in the Thermo Fisher Scientific folder on the desktop.

Step	Action
1	CALIBRATION INSTRUCTIONS See Thermo User's Manual found on the desktop.
2	QUALITATIVE ANALYSIS INSTRUCTIONS See Qualitative Analysis of GC/MS Data in the Thermo User's Manual
3	QUANTITATIVE ANALYSIS INSTRUCTIONS See Quantitative Analysis of GC/MS Data in the Thermo User's Manual.