Organochlorine and organophosphorous compounds, recoverable from bottom material (O-5104-83) and recoverable from suspended sediment (O-7104-83), gas chromatographic

	Codes	
Parameter	Recoverable from bottom material	Recoverable from suspended sediment
Aldrin	39333	39332
Clordane	39351	39353
DDD	39363	39362
DDE	39368	39367
DDT	39373	39372
Diazinon	39571	39573
Dieldrin	39383	39382
Endosulfan	39389	82355
Endrin	39393	39392
Ethion	39399	82347
Polychlorinated biphenals	39519	39518
Polychlorinated naphthalenes	39251	82361
Heptachlor	39413	39412
Heptachlor epoxide	39423	39422
Lindane	39343	39342
Malathion	39531	39533
Methoxychlor	39481	82351
Methyl parathion	39601	39603
Methyl trithion	39791	82345
Mirex	39758	39757
Parathion	39541	39543
Perthane8	81886	82349
Toxaphene	39403	39402
Trithion	89787	82343

1. Application

This method is suitable for the determination of recoverable organochlorine insecticides, polychlorinated biphenyls (PCB's), polychlorinated naphthalenes (PCN's), and organophosphorous insecticdes in bottom material and suspended sediment containing at least 0.1 µg/kg of the analyte.

2. Summary of method

Organochlorine and organophosphorous insecticides, PCB's, and PCN's are extracted from suspended sediment and bottom material with acetone and hexane. The organophosphorous insecticides are determined by gas chromatography using flamephotometric detectors. The extracts are then purified using adsorption chromatography on an alumina column. If PCB's, PCN's, and toxaphenes are present, the extracts are further purified using a silica gel column. The organochlorine compounds are determined by gas chromatography using electroncapture detectors.

3. Interferences

Compounds having chemical and physical properties similar to the compound of interest may cause interference. Sulfur and organosulfur compounds will interfere, but these substances can be removed by treating the final extracts with mercury; however, the mercury treatment will also remove organophosphorous compounds.

4. Apparatus

4.1 *Alumina column:* To a 130-mm x 10-mm id (inside diameter) glass tube having a coarseporosity fritted disc, add 1 cm anhydrous sodium sulfate, 10 cm alumina, and 1 cm anhydrous sodium sulfate.

4.2 *Boiling chips,* granular, micro, Hengar H-1366C, or equivalent: Rinse with hexane, air dry, and heat at 300°C overnight.

4.3 *Centrifuge tube,* 30 mL, Pyrex, graduated,

4.4 *Concentrator,* Kuderna-Danish (K-D), 500-mL flask, 5.0-mL volumetric receiver, and one-ball Snyder column.

4.5 *Gas chromatograph,* Tracor model 550, or equivalent.

4.5.1 The following conditions are recommended for organochlorine compounds:

Columns, borosilicate glass, 1.8 m x 2 mm id operated at 200°C: Column packing materials are (1) 3 percent SP 2100 on 100/120 mesh Supelcoport, or equivalent; and (2) 1.5 percent SP 2250 + 1.95 percent SP 2401 on 100/120 mesh Supelcoport, or equivalent.

Detectors, electron capture, operated at 345°C

Injection port temperature, 220°C.

Carrier gas, nitrogen or 5 percent methane in argon, flow rate 30 mL/min.

4.5.2 The following conditions are recommended for organophosphorous pesticides:

Columns, borosilicate glass, 1.8 m x 2 mm id operated at 175°C: Column packing materials are (1) 5 percent SP 2100 on 100/120 mesh Supelcoport, or equivalent; and (2) 2 percent SE-30 + 3 percent OV-210 on 100/120 mesh chromosorb HP, or equivalent.

Detectors, flame photometric, Melpar, or equivalent, operated at 210°C.

Injection port temperature, 210°C.

Carrier gas, helium or nitrogen, flow rate 30 mL/min.

4.6 *Glass filters,* 142 mm, 0.3 µm mean pore size, Gelman or equivalent: Prepare the filters by rinsing with acetone and hexane, evaporating the solvent, and heating overnight at 300°C.

4.7 *Glass wool,* fine, rinsed with hexane, air dried, and heated at 300°C overnight.

4.8 *Shaker,* wrist-action, Burrell or equivalent.

4.9 *Silica* column: To a 130-mm x 10-mm id glass tube having a coarse-porosity fritted disc, add 1 cm anhydrous sodium sulfate, 10 cm silica, and 1 cm anhydrous sodium sulfate.

5. Reagents

5.1 *Alumina adsorbent,* Woelm neutral aluminum oxide, or equivalent: Prepare deactivated adsorbent by adding 8 g deionized water to 92 g alumina and shake for at least 2 h on a wrist-action shaker. The alumina is tested for required deactivation by attempting to elute the compounds of interest from a test column according to the column fractionation scheme (table 1). If the test compounds do not elute with 20 mL hexane from the first alumina fraction, further deactivation is required.

5.2 *Mercury,* metallic, reagent grade.

5.3 *Pesticide mixed standards,* analytical reference grade, EPA analytical reference standards, or equivalent: Prepare individual stock solutions by weighing about 10 mg of each compound to at least three significant figures and quantitatively transfer each compound to a 25-mL volumetric flask. Dilute to volume with benzene and mix thoroughly. Aliquots are removed and diluted to volume with iso-octane to obtain final concentrations listed in table 2.

Table 1. Column fractionation scheme for alumina and silica columns for insecticides, PCB's, and PCN's in bottom material and suspended sediment

ALUMNA COLUMN		
Fraction 1 (20 mL hexane eluate)	Election 2 (25 mL hexane eluate)	Fraction 3 (20 mL benzene eluate)
Aldrin	Dieldrin	
Chlordane	Endrin	Diazinon
p,p-DDD	Heptachlor epoxide	Ethion
p,p-DDE	Endosulfan	Parathion
p,p-DDT		Methyl parathion
Heptachlor		Malathion
Perthane		Trithion
Lindane		Methoxychlor
Mirex		
PCB's		
PCN's		
Toxaphene		

SILICA COLUMN	
Fraction 1 (25 mL hexane eluate)	Fraction 2 (30 mL benzene eluate)
Aldrin Mirex PCB's PCN's p,p-DDE	Chlordane p,p-DDD p,p-DDE p,p-DDT Perthane Heptachlor Lindane Toxaphene

5.4 *Silica adsorbent,* Woelm silica, 70-150 mesh, or equivalent: Prepare deactivated adsorbent by adding 0.2 g deionized water to 99.8 g silica and shake for at least 2 h on a wrist-action shaker. The silica is tested for required deactivation by attempting to reproduce the elution scheme in table 1. If the test compounds do not elute with 25 mL hexane from the first silica fraction, further deactivation is required.

5.5 *Sodium sulfate,* granular, anhydrous, heat overnight at 300°C and store in a covered beaker at 130°C.

5.6 *Solvents,* acetone, benzene, hexane, and iso-octane, distilled in glass, pesticide analysis quality, Burdick and Jackson, or equivalent.

5.7 *Water,* deionized, organic-free.

6. Procedure

All glassware must be washed in warm detergent solution, rinsed with organic-free water, and heated

Table 2. Concentrations of pesticides and PCB's in mixed standard solutions used for gas chromatograph calibration of bottom material

[Picograms per microliter]

Mixture number	Compound	High Standard Concentration	Low Standard Concentration
1 -------------------	Lindane	40	20
	Heptachlor	40	20
	Aldrin	40	20
	p,p-DDE	40	20
	p,p-DDD	40	20
	Mirex	40	20
	Methoxychlor	70	35
2 -------------------	Aldrin	40	20
	Heptachlor epoxide	40	20
	Dieldrin	40	20
	Endrin	40	20
3 ------------------	Chlordane	200	100
4 ------------------	Aldrin	40	20
	Endosulfan	40	20
	Perthane	40	20
	p,p-DDT	40	20
5 -----------------	Toxaphene	600	300
6 -----------------	o,p-DDE	40	20
	o,p-DDD	40	20
	o,p-DDT	40	20
7 -------------------	Aroclor 1016 (a PCB)	300	150

8	Aroclor 1254 (a PCB)	400	200
9	Aroclor 1260 (a PCB)	300	150
10	Diazinon	100	50
	Malathion	130	65
	Ethion	100	50
11	Methyl parathion	100	50
	Parathion	100	50
	Methyl trithion	200	100
	Trithion	200	100

at 300°C overnight. Prior to use, all glassware is rinsed with the solvent. Do not use stopcock grease on any ground-glass joints. For bottom-material samples, begin at step 6.1. For suspended-sediment samples, first determine the weight of the water-suspended-sediment mixture, then filter the sample to isolate the suspended sediment. Use the filter and the retained sediment and begin at step 6.2.

6.1 Subsampling for determination of moisture:

6.1.1 Decant excess water from the bottom material. Use a spatula to thoroughly mix the moist solid. Weigh 10 g of solid into a tared weighing dish. Record the weight to three significant figures.

6.1.2 Place the tared dish containing the sample in an oven at 130°C overnight. Remove from oven, allow to cool, weigh, and record the weight to three significant figures.

6.2 Add either the filter from the suspended sediment filtration or the calculated amount of bottom material (not more than 100 g) to a 500-mL Erlenmeyer flask with a ground-glass joint. Stir the sample and slowly add deionized water until the mixture has the consistency of paste or until water begins to separate from the solid.

6.3 Add 20 mL acetone to the Erlenmeyer flask containing the sample and stopper securely. Mix the contents of the flask for 20 min using the wrist-action shaker. Add 80 mL hexane and shake again for 10 min. Decant the extract into a 1-L separatory funnel containing approximately 600 mL deionized water.

6.4 Add another 20 mL acetone to the Erlenmeyer flask and mix for 20 min. Add 80 mL hexane, mix 10 min, and decant the extract into the separatory funnel. Repeat the process as in the second extraction one more time, and collect the acetone-hexane extract in the separatory funnel containing the deionized water.

6.5 Gently mix the contents of the separatory funnel for about 1 min, and allow the layers to separate. Discard the aqueous layer and collect the extract in a 500-mL Erlenmeyer flask. Add about 1 g anhydrous sodium sulfate to the flask, cover with foil, and allow to stand for at least 2 h or store in a refrigerator until the analysis can continue.

6.6 Quantitatively transfer the extract with hexane to a K-D flask fitted with a 5-mL volumetric receiver. Add a boiling chip, attach a one-ball Snyder column, and concentrate the extract to about 5 mL on a water bath at about 90°C. Remove the K-D apparatus from the water bath, allow to cool, dry the joints with a towel, and rinse the joints into the receiver with hexane. Disconnect the receiver and concentrate on an evaporative concentrator to 2-4 mL, rinsing down the sides of the receiver during concentration with small amounts of hexane. Adjust the volume of extract in the receiver to 5.0 mL with hexane.

6.7 Prepare an alumina column for adsorption chromatography cleanup, referring to table 1 for the fractionation scheme. Elute the column with 30 mL hexane to remove contaminants. Discard the eluate. Quantitatively transfer the extract obtained in step 6.6 to the top of the column and elute using 45 mL hexane (the column void volume is about 5 mL). Collect the first 20 mL (fraction 1) and the second 20 mL (fraction 2) in graduated centrifuge tubes. Change the elution solvent to benzene and collect 30 mL of eluate (fraction 3). Reduce the second and third fractions to 1.0 mL each on an evaporative concentrator and analyze by gas chromatography. Treat the first fraction as described in step 6.8.

6.8 Prepare a silica column. Elute the column with 30 mL hexane and discard the eluate. Reduce the volume of the first alumina fraction on an evaporative concentrator to about 0.5 mL and quantitatively transfer it to the top of the silica column. Add hexane to the top of the column and collect 25 mL of eluate (fraction 1) in a graduated centrifuge tube. As the last of the hexane enters the top sodium sulfate layer, add benzene to the top of the column and collect 30 mL of eluate (fraction 2) in a graduated centrifuge tube. Reduce the volume of each of these fractions to 1.0 mL on an evaporative concentrator and analyze each by gas chromatography. Sulfur can be removed from the first alumina or first silica fraction by adding several drops of mercury and shaking for at least 1 min. The addition of mercury is continued until no further reaction occurs, as evidenced by blackening of the mercury.

6.9 Prepare gas chromatograph calibration curves daily with the mixed standards listed in table 2. Operating conditions must be identical to those used for sample analysis. Calibrate both analytical columns. Record the volume of the standard injected and the retention time and integrated peak area of each component in the standard.

6.10 Inject an aliquot of sample extract into the gas chromatograph. Record the volume injected. Identify peaks by retention time. The identification must be made on both analytical columns. Record the retention time and integrated area of any identified peak. Dilute any extract containing an identifiable component above the highest standard (see table 2).

7. Calculations

7.1 Calculate the wet weight required for a dry weight equivalent of 50 g:

$$\text{Wet weight (in g)} = \frac{W_1}{W_2} \times 50 \text{ g},$$

where

wet weight = weight of sample used for extraction, in g,
W_1= wet weight of sample, in g, and
W_2 = dry weight of sample, in g.

7.2 Calculate the response factor of each identified component in the calibration standard:

$$RF = \frac{A_1}{C_S \times V_1}$$

where

RF = response factor of identified component in calibration standard, in area/pg,
C_S = concentration of standard, in pg/µL,
V_1 = volume of standard injected, in µL, and
A_1 = integrated peak area of identified component in calibration standard.

7.3 Calculate the concentration of each identified component in the original bottom-material sample from the equation

$$\text{Concentration } (\mu g/kg) = \frac{A_2 \times V_2}{V_3 \times W \times RF}$$

where

RF = response factor of identified calibration standard component, in area/pg,
A_2 = integrated peak area of identified sample component,
V_2 = final volume of sample extract, in mL,
V_3 = volume of sample extract injected, in µL, and
W = dry weight equivalent of sample, in g.

7.4 Calculate the concentration of each identified component in the original suspended sediment from the following equation:

$$\text{Concentration } (\mu g/Kg) = \frac{A_2 \times V_2}{V_3 \times V_4 \times RF}$$

where

RF = response factor of identified calibration standard component, in area/pg,
A_2 = integrated peak area of identified sample component,
V_2 = final volume of sample extract, in mL,
V_3 = volume of sample extract injected, in µL, and
V_4 = weight of sample in g expressed in mL (1.000 mL=1.000g).

8. Report

8.1 Bottom material

8.1.1 Report concentrations of organochlorine compounds (except chlordane, perthane, toxaphene, PCB's, and PCN's) and organophosphorous insecticides in bottom material as follows: less than 0.1 µg/kg, as "less than 0.1 µg/kg" 0.1 to 1.0 µg/kg, one significant figure; 1.0 µg/kg and above, two significant figures.

8.1.2 Report concentrations of chlordane, perthane, PCB's, and PCN's in bottom materials as follows: less than 1.0 µg/kg, as "less than 1.0 µg/kg"; 1.0 µg/kg and above, two significant figures.

8.1.3 Report concentrations of toxaphene in bottom materials as follows: less than 10 µg/kg, as "less than 10 µg/kg"; 10 µg/kg and above, two significant figures.

8.2 Suspended sediment

8.2.1 Report concentrations of organochlorine compounds (except chlordane, perthane, toxaphene, PCB's, and PCN's) and organophosphorous insecticides in suspended sediment as follows: less than 0.01 µg/Kg as "less than 0.01 µg/Kg"; 0.01 to 0.10 µg/Kg, one significant figure; 0.1 µg/Kg and above, two significant figures.

8.2.2 Report concentrations of chlordane, perthane, PCB's, and PCN's in suspended sediment as follows: less than 0.1 µg/Kg, as "less than 0.1 µg/Kg"; 0.1 µg/Kg and above, two significant figures.

8.2.3 Report concentrations of toxaphene in suspended sediment as follows: less than 1.0 µg/Kg, as "less than 1.0 µg/Kg"; 1.0 µg/Kg and above, two significant figures.

9. Precision

It is estimated that the percent relative standard deviation for recoverable insecticides and PCB's from bottom material and suspended sediment will be greater than that reported for dissolved insecticides and PCB's (method O-1104-83).

Selected references

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