

Base/neutral extractable compounds, total
recoverable, gas chromatographic/mass
spectrometric (O-3118-83)

<i>Parameter</i>	<i>Code</i>
Acenaphthene-----	34205
Acenaphthylene-----	34200
Anthracene-----	34220
Benzidine-----	39120
Benzo(a)anthracene-----	34526
Benzo(b)fluoranthene-----	34230
Benzo(k)fluoranthene-----	34242
Benzo(g,h,i)perylene-----	34521
Benzo(a)pyrene-----	34247
4-Bromophenyl phenyl ether-----	34636
Butyl benzyl phthalate-----	34292
bis(2-Chloroethoxy)methane-----	34278
bis(2-Chloromethyl)ether-----	34273
bis(2-Chloroisopropyl)ether-----	34283
2-Chloronaphthalene-----	34581
4-Chlorophenyl phenyl ether-----	34641
Dibenz(a,h)anthracene-----	34556
1,2-Dichlorobenzene-----	34536
1,3-Dichlorobenzene-----	34566
1,4-Dichlorobenzene-----	34571
3,3'-Dichlorobenzidine-----	34631
Diethyl phthalate-----	34336
Dimethyl phthalate-----	34341
Di-n-butyl phthalate-----	39110
2,4-Dinitrotoluene-----	34611
2,6-Dinitrotoluene-----	34626
Di-n-octylphthalate-----	34596
bis(2-Ethylhexyl)phthalate-----	39100
Fluoranthene-----	34376
Hexachlorobenzene-----	39700
Hexachlorobutadiene-----	39702
Hexachlorocyclopentadiene-----	34386
Hexachloroethane-----	34396
Indeno(1,2,3-ed)pyrene-----	34403
Naphthalene-----	34696
Nitrobenzene-----	34447
N-Nitrosodimethylamine-----	34438
N-Nitrosodiphenylamine-----	34433
N-Nitrosodi-n-propylamine-----	34428
Phenanthrene-----	34461
2,3,7,8-Tetrachlorodibenzo-p-dioxin-----	34675
1,2,4-Trichlorobenzene-----	34551

1. Application

This method is suitable for the determination of methylene chloride extractable base/neutral compounds in water and water-suspended-sediment mixtures containing at least 5 µg/L of the analyte.

2. Summary of method

Organic base/neutral compounds are extracted from water and water-suspended-sediment mixtures

with methylene chloride. The extract is concentrated and analyzed by gas chromatography (GC) using a flame-ionization detector (FID) or a mass spectrometric (MS) detector.

3. Interferences

Any compound having chemical and physical properties similar to an analyte of interest may interfere.

4. Apparatus

4.1 *Boiling chips*, micro, carbon chips: Rinse with hexane, air dry, and heat at 300° C overnight.

4.2 *Concentrator*, *Kuderna-Danish (K-D)*, 500 mL, all glass, with ground-glass joints, a 10.0 mL receiver, and a one-ball Snyder column.

4.3 *Evaporative concentrator*, Organomation N-Evap, or equivalent: Water bath must be maintained at 50° to 55°C.

4.4 *Gas chromatograph/mass spectrometer/data system*, (GC/MS) Hewlett-Packard 5985 B GC/MS, or equivalent: The gas chromatograph is used with one of the following options:

4.4.1 *Columns*, fused silica capillary column, 25 m x 0.20 mm id (inside diameter), SE-54 bonded column, 0.33-µm film thickness.

Detector, mass spectrometer (MS).

Injection temperature, 260°C.

Carrier gas, 1mL/min, helium.

Transfer line temperature, 285°C.

Mode, splitless injection.

Program rate, 45° to 300°C, 2.5-min initial hold, 6°C/min, 15-min final hold.

4.4.2 *Columns*, two fused silica capillary columns, 25 m x 0.20 mm id, SE-54 bonded column, 0.33-µm film thickness.

Detectors, mass spectrometer, FID 285°C.

Injection temperature, 260°C.

Mode, splitless injection.

Carrier gas, 1 mL/min, helium.

Transfer line, 285°C.

Program rate, 45° to 300°C, 2.5-min initial hold, 6°C/min, 15-min final hold.

5. Reagents

5.1 *Base/neutral standards*, EPA analytical reference grade or highest purity available: Weigh 20 mg of the compound to three significant figures, quantitatively transfer to a 100-mL volumetric flask, and dilute to volume with methylene chloride. Prepare dilutions in methylene chloride to obtain solutions containing 2, 10, and 20

5.2 *DFTPP (Decafluorotriphenylphosphine) solution*, 50 ng/μL: Dilute 20 μL DFTPP (Supelco, or equivalent, 25-mg/mL solution) to 10 mL in a volumetric flask with methylene chloride.

5.3 *Internal standards*, perdeuteronaphthalene (naphthalene-d₈), Aldrich Chemical Co., or equivalent; perdeuterophenanthrene (phenanthrene-d₁₀), Kor Isotopes, Division of Kor, Inc., or equivalent; and perdeuterochrysene (chrysene-d₁₂), Kor Isotopes, Division of Kor, Inc., or equivalent. Weigh about 20 mg of perdeuteronaphthalene, perdeuterophenanthrene, and perdeuterochrysene to three significant figures, quantitatively transfer to a 100mL volumetric flask, and dilute to volume with methylene chloride.

5.4 *Sodium chloride*, reagent grade: Heat at 300°C overnight and store in a closed glass container.

5.5 *Sodium hydroxide*, 37 percent (weight/ volume): Dissolve 185 g sodium hydroxide pellets in 500 mL organic-free water and reflux 8 hr. Cool and store at 4°C.

5.6 *Sodium sulfate*, granular, anhydrous, reagent grade: Heat at 300°C overnight and store in a glass-stoppered Erlenmeyer flask at 130°C.

5.7 *Solvents*, hexane, isopropanol, and methylene chloride, glass distilled, pesticide analysis quality, Burdick and Jackson, or equivalent.

5.8 *Surrogate standards*, 1-fluoronaphthalene, Aldrich Chemical Co., or equivalent; 2,2'difluorobiphenyl, Pfaltz and Bauer Co., or equivalent; and p-dibromobenzene, FDA, or equivalent. Weigh 4 mg of each of the three compounds to three significant figures, quantitatively transfer to a 100mL volumetric flask, and dilute to volume with isopropanol.

5.9 *Water*, organic-free.

6. Procedure

All glassware must be washed in a warm detergent solution, rinsed with organic-free water, and heated at 300°C overnight. Immediately before use, it must be rinsed with methylene chloride. Stopcock grease should not be used on ground-glass joints.

6.1 Immediately upon receipt of the sample, store at 4°C. Extraction must begin within 48 h following receipt of the sample.

6.2 A blank must accompany each group of samples. For each sample and blank, rinse a 2-L separatory funnel and a 500-mL Erlenmeyer flask with methylene chloride.

6.3 Weigh the capped sample bottle to three significant figures and record the weight for subsequent calculations.

6.4 Adjust the sample to pH 11, as indicated by pH paper, by the addition of sodium hydroxide solution.

6.5 Pour the sample into a separatory funnel containing 100 g sodium chloride. Allow the sample bottle to drain into the separatory funnel for several minutes. Stopper and shake until the salt is dissolved.

6.6 Weigh the empty, capped sample bottle to three significant figures, calculate and record the net sample weight.

6.7 Add 1 mL of the surrogate standard (step 5.8) to the sample in the separatory funnel.

6.8 Add 100 mL methylene chloride to the empty sample bottle and swirl to wash the sides of the container with the solvent. The Teflon liner is not rinsed because of the potential of contamination from solvent that has contacted the cap threads and the surface beneath the liner. Pour the contents of the bottle into the separatory funnel.

6.9 Stopper the separatory funnel and shake for at least 1 min, venting often to relieve pressure.

6.10 Drain the organic layer into a 500-mL Erlenmeyer flask containing approximately 30 g sodium sulfate.

6.11 Extract the sample two more times with 50 mL methylene chloride by repeating steps 6.8 through 6.10, collecting the two organic extracts in the Erlenmeyer flask containing the sodium sulfate.

NOTE: The aqueous phase may be retained and extracted for the acidic extractable organic compounds after adjusting the pH to 2 (method O-3117).

6.12 Cover the Erlenmeyer flask with aluminum foil and allow to stand at room temperature for approximately 4 h.

6.13 Quantitatively transfer the dried extract into a K-D apparatus, add a boiling chip, and attach a Snyder column.

6.14 Concentrate the extract to about 5 mL by heating the apparatus on a 80°C water bath in a fume hood.

6.15 Allow the K-D apparatus to cool. Dry the apparatus with a towel, especially around the ground-glass joint of the receiver.

6.16 Separate the Snyder column from the KD flask and rinse the walls of the K-D flask with approximately 2 mL methylene chloride. Separate the receiver from the K-D flask and rinse the ground-glass

joint of the K-D flask into the receiver with methylene chloride.

6.17 Reduce the volume of the methylene chloride in the receiver to less than 0.9 mL on the evaporative concentrator. During the concentration, rinse the receiver walls two or three times with small portions of methylene chloride.

6.18 Stopper the receiver with a ground-glass stopper and store the extract at 4°C until analysis can proceed.

NOTE: The extract can be combined with the extract from the acidic extractable organic compounds (method O-3117) immediately before injection into the GC/MS.

6.19 Immediately before analysis, add 0.05 mL of internal standard. Adjust the final volume of the sample extract in the receiver to 1.0 mL.

6.20 Mass spectrometer tuning:

6.20.1 Use perfluorotributylamine to tune the mass spectrometer in a manner that results in satisfactory calibration of mass assignments as well as agreement with the criteria listed in step 6.20.2.

6.20.2 Set the MS to scan the mass range 40-450 amu (atomic mass units). Temperature program the GC from 45° to 275°C at 20°C/min with an initial hold of 1.5 min. Inject 50 ng (1 µL of solution, step 5.2). Obtain a background corrected mass spectrum of DFTPP and verify that all of the following criteria are met:

Ion abundance criteria

51	-----30-60 percent of mass 198
68	-----<2 percent of mass 69
70	-----<2 percent of mass 69
127	-----40-60 percent of mass 198
197	-----<1 percent of mass 198
198	-----Base peak, 100 percent relative abundance
199	-----5-9 percent of mass 198
275	-----10-30 percent of mass 198
365	----->1 percent of mass 198
441	-----<mass 443
442	----->40 percent of mass 198
443	-----17-23 percent of mass 442

6.21 Analyze the extract by injection of an aliquot into the GC/MS system optimized as follows:

6.21.1 For systems configured with option A, analyze the mass range 40 to 450 amu at a scan rate sufficient to obtain a minimum of 5 scans per chromatographic peak. Record the total ion current chromatogram and the mass spectrum of each peak.

6.21.2 For systems configured with option B, analyze the mass range 40 to 450 amu at a scan rate

rate sufficient to obtain a minimum of 5 scans per chromatographic peak. Record the total ion current

sufficient to obtain a minimum of 5 scans per chromatographic peak. Record the total ion current chromatogram and the mass spectrum of each peak as well as the retention time and integrated area of each peak from the FID.

6.22 Process the data to determine the identity of the extractable base/neutral compounds including the priority pollutants in the following manner:

6.22.1 Identification of the target compounds is accomplished by a computerized reverse search procedure employing a 25-scan retention time window.

6.22.2 Identification of the extractable base/neutral compounds that are not target compounds is accomplished by a computerized library search versus the National Bureau of Standards library reference spectra on each peak.

6.23 Determine the largest characteristic ion and quantitate the area on this ion for any identified peak, including the internal standard peak and the surrogate standards peaks. Alternatively, if the system is configured with option B, the quantitation can be carried out on the FID response rather than on the mass spectrometer response. The integrated area of an identified peak from the FID is recorded for subsequent calculations. The better chromatogram (FID or MS) is used for quantitation.

6.24 Confirm the surrogate compounds found in the sample by injecting an aliquot of the corresponding surrogate standards (step 5.8) into the gas chromatograph and analyze according to steps 6.21 through 6.23. Record the integrated area obtained.

6.25 Confirm any identified extractable base/neutral compounds found in the sample by injecting an aliquot of the corresponding base/neutral standard into the gas chromatograph and analyze according to steps 6.21 through 6.23. Record the integrated area obtained. If a base/neutral standard is not available, quantitate relative to the internal standard (see step 7.6).

7. Calculations

7.1 Calculations of response factors and relative response factors:

7.1.1 Calculate the response factor for each compound in the base/neutral standard or surrogate standard (step 6.23) using the following equation:

$$RF_i = \frac{A_{Si}}{C_{Si}}$$

where

RF_i = response factor of compound i in standard, in area/ng,

C_{si} = amount of compound i injected, in ng/ μ L, and

A_{si} = area of compound i peak in the standard.

7.1.2 Calculate the response factor of the internal standard using the following equation:

$$RFI = \frac{AI_i}{CI_i}$$

where

RFI = response factor of internal standard, in area/ng,

CI_i = amount of internal standard in base/neutral standard, in ng injected, and

AI_i = area of internal standard peak.

7.1.3 Calculate a relative response factor by the following equation:

$$RRF_i = \frac{RF_i}{RFI}$$

where

RRF_i = relative response factor, compound i ,

RF_i = response factor of compound i , and

RFI = response factor of internal standard.

7.2 Calculations of recoveries of surrogates: Calculate the percent recovery of each surrogate standard recovered from the original Water-suspended-sediment mixture using the following equation:

$$\text{Percent recovery} = \frac{A \times CI_2 \times V_3 \times 100}{RRF_i \times AI_2 \times C_S \times V_4}$$

where

A = area of identified surrogate peak in sample extract,

CI_2 = amount of internal standard injected, in ng,

RRF_i = relative response factor of compound i ,

AI_2 = area of internal standard peak in sample extract,

C_S = concentration of standard, in ng/ μ L,

V_3 = final volume of extract, in mL, and

V_4 = volume injected, in μ L.

7.3 Calculation of concentrations of analytes: Calculate the concentration of each identified extractable base/neutral priority pollutant in the original water-suspended-sediment mixture using the following equation:

$$\text{Concentration } (\mu\text{g/L}) = \frac{A \times CI \times V_3 \times 1,000}{RRF_i \times AI_2 \times W \times V_4}$$

where

A = area of identified peak in sample extract,

CI_2 = amount of internal standard injected, in ng,

RRF = relative response factor of compound i ,

AI_2 = area of internal standard peak in sample extract,

W = weight of sample extracted, expressed in mL (1.000 g = 1.000 mL),

V_3 = final volume of extract, in mL, and

V_4 = volume injected, in μ L.

7.4 Calculations of concentrations of other compounds: The

concentrations of all other identified extractable base/neutral compounds in the original water sample for which there are no standards, are calculated relative to the concentration of the internal standard, and are semiquantitative for the purposes of a general organic scan. The response factor of the compound is assumed to be exactly equal to that of the internal standard. Calculate the concentration using the following equation:

$$\text{Concentration } (\mu\text{g/L}) = \frac{A \times V_3 \times 1,000}{RFI \times W \times V_4}$$

where

RFI = response factor of internal standard, in area/ng,

A = area of identified peak in sample,

W = weight of sample extracted, expressed in mL (1.000 g = 1.000 mL),

V_3 = final volume of extract, in mL, and

V_4 = volume injected, in μ L.

8. Report

8.1 Report concentrations of extractable base/neutral organic compounds (except chrysene, benzo(a) anthracene, dioctyl phthalate, benzo(b) fluoranthene, benzo(k) fluoranthene, benzo(a) pyrene, indeno(1,2,3-cd) pyrene, dibenz(a,h) anthracene, and benzo(g,h,i) perylene) in water and water-suspended-sediment mixtures as follows: less than 5.0 μ g/L, as "less than 5.0 μ g/L"; 5.0 μ g/L and above, two significant figures.

8.2 Report concentrations of chrysene, benzo(a) anthracene, dioctyl phthalate, benzo(b) fluoranthene, benzo(k) fluoranthene, benzo(a) pyrene, indeno(1,2,3-cd) pyrene, dibenz(a,h) anthracene, and benzo(g,h,i) perylene as follows: less than 10 μ g/L, as "less than 10 μ g/L"; 10 μ g/L and above, two significant figures.

9. Precision

9.1 Surrogate recoveries must be from 40 percent to 130 percent unless a matrix effect can be demonstrated. Water and water-suspended-sediment samples were spiked with surrogate standards and recoveries were determined by two operators in a single laboratory over an 8-mo period. Results are as follows:

Compound	Ion used for quantitation	Concentration (ng/ μ L)	Number of samples analyzed	Average recovery (percent)	Relative standard deviation (percent)
1-Fluoronaphthalene	146	48-104	45	65	29
p-Dibromobenzene	236	51-107	46	67	26
2,2'-Difluorobiphenyl	190	43-79	46	68	20

9.2 Deionized water samples were spiked with base/neutral extractable compounds and recoveries were determined by two operators in a single laboratory over a 1-yr period. Results are as follows:

Compound	Ion used for quantitation	Concentration (ng/ μ L)	Number of samples analyzed	Average recovery (percent)	Relative standard deviation (percent)
Acenaphthylene	152	190	2	105	--
Anthracene	178	100-177	5	66	45
Benzo(a)anthracene	228	69	5	79	23
Benzo(k)fluoranthene	262	50-71	2	98	--
Benzo(a)pyrene	252	50-100	5	115	22
bis(2-chloroethoxy)methane	93	50-100	3	64	--
4-Bromophenylphenylether	248	100	5	48	6

Compound	Ion used for quantitation	Concentration (ng/ μ L)	Number of samples analyzed	Average recovery (percent)	Relative standard deviation (percent)
4-Chlorophenylphenylether	204	50	1	111	---
Chrysene	228	50-113	6	42	46
Dibenz(a,h)anthracene	278	69	1	71	---
Di-n-butylphthalate	149	100	5	53	19
1,2-Dichlorobenzene	146	50-100	5	56	43
1,3-Dichlorobenzene	146	100-201	6	97	30
1,4-Dichlorobenzene	146	102	1	51	---
Diethyl phthalate	149	50-100	14	69	37
Dimethylphthalate	163	199	1	19	---
2,4-Dinitrotoluene	165	50-106	6	63	19
Dimethylphthalate	149	100	15	69	42
bis(2-ethylhexyl) phthalate	149	100	2	42	---
Fluorene	166	50-197	5	99	11
Fluoranthene	202	224	1	98	---
Hexachlorobenzene	284	50-76	3	91	---
Hexachlorobutadine	225	50-74	3	94	---
Indeno(1,2,3-cd)pyrene	276	50	1	104	---
Naphthalene	128	50-130	6	81	17
Nitrobenzene	77	219	1	50	---
N-Nitrosodimethylamine	74	50	1	68	---
N-Nitrosodiphenylamine	169	50	1	48	---
Phenanthrene	178	218	1	94	---
Pyrene	202	50-334	16	94	16
1,2,4-Trichlorobenzene	180	100	5	78	24

Selected references

- Glaser, J.A., Foerst, D.L., McKee, G.D., Quave, S.A., and Budde, W.L., 1981 Trace analysis for wastewaters: Environmental Science and Technology, v. 15, p. 1426-1435.
- Sauter, A.D., Betowski, L.D., Smith, T.R., Strickler, V.A., Beimer, R.G., Colby, B.M., and Wilkison, J.E., 1981, Fuser silica capillary column GC/MS for the analysis of priority pollutants: Journal of High Resolution Chromatography and Chemical Communications, v. 4, p. 366-384.
- U.S. Environmental Protection Agency, 1979, Base/neutral acids, and pesticides-Method 625: Federal Register, v. 44, no. 233, p. 69,540.

