METHOD 8100

POLYNUCLEAR AROMATIC HYDROCARBONS

1.0 SCOPE AND APPLICATION

1.1 Method 8100 is used to determine the concentration of certain polynuclear aromatic hydrocarbons (PAH). Table 1 indicates compounds that may be determined by this method.

1.2 The packed column gas chromatographic method described here cannot adequately resolve the following four pairs of compounds: anthracene and phenanthrene; chrysene and benzo(a)anthracene; benzo(b)fluoranthene and benzo(k)fluoranthene; and dibenzo(a,h)anthracene and indeno(1,2,3-cd)pyrene. The use of a capillary column instead of the packed column, also described in this method, may adequately resolve these PAHs. However, unless the purpose of the analysis can be served by reporting a quantitative sum for an unresolved PAH pair, either liquid chromatography (Method 8310) or gas chroma-tography/mass spectroscopy (Method 8270) should be used for these compounds.

2.0 SUMMARY OF METHOD

2.1 Method 8100 provides gas chromatographic conditions for the detection of ppb levels of certain polynuclear aromatic hydrocarbons. Prior to use of this method, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2- to 5-uL aliquot of the extract is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by a flame ionization detector (FID).

2.2 If interferences prevent proper detection of the analytes of interest, the method may also be performed on extracts that have undergone cleanup using silica gel column cleanup (Method 3630).

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences, under the conditions of the analysis, by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.3 Interferences coextracted from samples will vary considerably from source to source, depending upon the waste being sampled. Although general cleanup techniques are recommended as part of this method, unique samples may require additional cleanup.

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TABLE 1. GAS CHROMATOGRAPHY OF POLYNUCLEAR AROMATIC HYDROCARBONS[a]

Compound	Retention time (min)
Acenaphthene	10.8
Acenaphthylene	10.4
Anthracene	15.9
Benzo(a)anthracene	20.6
Benzo(a)pyrene	29.4
Benzo(b)fluoranthene	28.0
Benzo(j)fluoranthene	
Benzo(k)fluoranthene	28.0
Benzo(ghi)perylene	38.6
Chrysene	24.7
Dibenz(a,h)acridine	
Dibenz(a,j)acridine	
Dibenzo(a,h)anthracene	36.2
7H-Dibenzo(c,g)carbazole	
Dibenzo(a,e)pyrene	
Dibenzo(a,h)pyrene	
Dibenzo(a,i)pyrene	
Fluoranthene	19.8
Fluorene	12.6
Indeno(1,2,3-cd)pyrene	36.2
3-Methylcholanthrene	
Naphthalene	4.5
Phenanthrene	15.9
Pyrene	20.6

[a]Results obtained using Column 1.

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4.0 APPARATUS AND MATERIALS

    4.1 Gas chromatograph:

        4.1.1 **Gas chromatograph:** Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak areas and/or peak heights is recommended.

        4.1.2 **Columns:**

            4.1.2.1 Column 1: 1.8-m x 2-mm I.D. glass column packed with 3% OV-17 on Chromosorb W-AW-DCMS (100/120 mesh) or equivalent.

            4.1.2.2 Column 2: 30-m x 0.25-mm I.D. SE-54 fused silica capillary column.

            4.1.2.3 Column 3: 30-m x 0.32-mm I.D. SE-54 fused silica capillary column.

        4.1.3 **Detector:** Flame ionization (FID).

    4.2 Volumetric flask: 10-, 50-, and 100-mL, ground-glass stopper.

    4.3 Microsyringe: 10-uL.

5.0 REAGENTS

    5.1 Solvents: Hexane, isooctane (2,2,4-trimethylpentane) (pesticide quality or equivalent).

    5.2 Stock standard solutions:

        5.2.1 Prepare stock standard solutions at a concentration of 1.00 ug/uL by dissolving 0.0100 g of assayed reference material in isooctane and diluting to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

        5.2.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

        5.2.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.3 Calibration standards: Calibration standards at a minimum of five concentration levels should be prepared through dilution of the stock standards with isooctane. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with a check standard indicates a problem.

5.4 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.4.1 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest as described in Paragraph 5.3.

5.4.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane.

5.4.3 Analyze each calibration standard according to Section 7.0.

5.5 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with one or two surrogates (e.g., 2-fluorobiphenyl and 1-fluoronaphthalene) recommended to encompass the range of the temperature program used in this method. Method 3500, Section 5.3.1.1, details instructions on the preparation of base/neutral surrogates. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1. Extracts must be stored under refrigeration and must be analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction:

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550. To achieve maximum sensitivity with this method, the extract must be concentrated to 1 mL.

7.2 Gas chromatography conditions (Recommended):

7.2.1 **Column 1:** Set nitrogen carrier gas flow at 40-mL/min flow rate. Set column temperature at 100°C for 4 min; then program at 8°C/min to a final hold at 280°C.

7.2.2 **Column 2:** Set helium carrier gas at 20-cm/sec flow rate. Set column temperature at 35°C for 2 min; then program at 10°C/min to 265°C and hold for 12 min.

7.2.3 **Column 3:** Set helium carrier gas at 60 cm/sec flow rate. Set column temperature at 35°C for 2 min; then program at 10°C/min to 265°C and hold for 3 min.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques.

7.3.1 The procedure for internal or external standard calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.3.2 If cleanup is performed on the samples, the analyst should process a series of standards through the cleanup procedure and then analyze the samples by GC. This will validate elution patterns and the absence of interferents from the reagents.

7.4 Gas chromatographic analysis:

7.4.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 uL of internal standard to the sample prior to injection.

7.4.2 Follow Section 7.6 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence.

7.4.3 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.4 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes. See Section 7.8 of Method 8000 for calculation equations.

7.4.5 If peak detection and identification are prevented due to interferences, the extract may undergo cleanup using Method 3630.

7.5 Cleanup:

7.5.1 Proceed with Method 3630. Instructions are given in this method for exchanging the solvent of the extract to hexane.

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7.5.2 Following cleanup, the extracts should be analyzed by GC, as described in the previous paragraphs and in Method 8000.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000, Section 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each analyte at the following concentrations in acetonitrile: naphthalene, 100 ug/mL; acenaphthylene, 100 ug/mL; acenaphthene, 100 ug/mL; fluorene, 100 ug/mL; phenanthrene, 100 ug/mL; anthracene, 100 ug/mL; benzo(k)fluoranthene, 5 ug/mL; and any other PAH at 10 ug/mL.

8.2.2 Table 2 indicates the calibration and QC acceptance criteria for this method. Table 3 gives method accuracy and precision as functions of concentration for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Section 8.10).

8.3.1 If recovery is not within limits, the following procedures are required.

· Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.

· Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

· Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

9.0 METHOD PERFORMANCE

9.1 The method was tested by 16 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 0.1 to 425 ug/L. Single operator precision,

overall precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships for a flame ionization detector are presented in Table 3.

9.2 This method has been tested for linearity of spike recovery from reagent water and has been demonstrated to be applicable over the concentration range from 8 x MDL to 800 x MDL with the following exception: benzo(ghi)perylene recovery at 80 x and 800 x MDL were low (35% and 45%, respectively).

9.3 The accuracy and precision obtained will be determined by the sample matrix, sample-preparation technique, and calibration procedures used.

10.0 REFERENCES

1. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 9 - PAHs," Report for EPA Contract 68-03-2624 (in preparation).

2. Sauter, A.D., L.D. Betowski, T.R. Smith, V.A. Strickler, R.G. Beimer, B.N. Colby, and J.E. Wilkinson, "Fused Silica Capillary Column GC/MS for the Analysis of Priority Pollutants," Journal of HRC&CC 4, 366-384, 1981.

3. "Determination of Polynuclear Aromatic Hydrocarbons in Industrial and Municipal Wastewaters," EPA-600/4-82-025, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, September 1982.

4. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

5. "EPA Method Validation Study 20, Method 610 (Polynuclear Aromatic Hydrocarbons)," Report for EPA Contract 68-03-2624 (in preparation).

6. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

7. Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, pp. 58-63, 1983.

TABLE 2. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\overline{x}$ (ug/L)	Range P, P_s (%)
Acenaphthene	100	40.3	D-105.7	D-124
Acenaphthylene	100	45.1	22.1-112.1	D-139
Anthracene	100	28.7	11.2-112.3	D-126
Benzo(a)anthracene	10	4.0	3.1-11.6	12-135
Benzo(a)pyrene	10	4.0	0.2-11.0	D-128
Benzo(b)fluoranthene	10	3.1	1.8-13.8	6-150
Benzo(ghi)perylene	10	2.3	D-10.7	D-116
Benzo(k)fluoranthene	5	2.5	D-7.0	D-159
Chrysene	10	4.2	D-17.5	D-199
Dibenzo(a,h)anthracene	10	2.0	0.3-10.0	D-110
Fluoranthene	10	3.0	2.7-11.1	14-123
Fluorene	100	43.0	D-119	D-142
Indeno(1,2,3-cd)pyrene	10	3.0	1.2-10.0	D-116
Naphthalene	100	40.7	21.5-100.0	D-122
Phenanthrene	100	37.7	8.4-133.7	D-155
Pyrene	10	3.4	1.4-12.1	D-140

s = Standard deviation of four recovery measurements, in ug/L.

$\overline{x}$ = Average recovery for four recovery measurements, in ug/L.

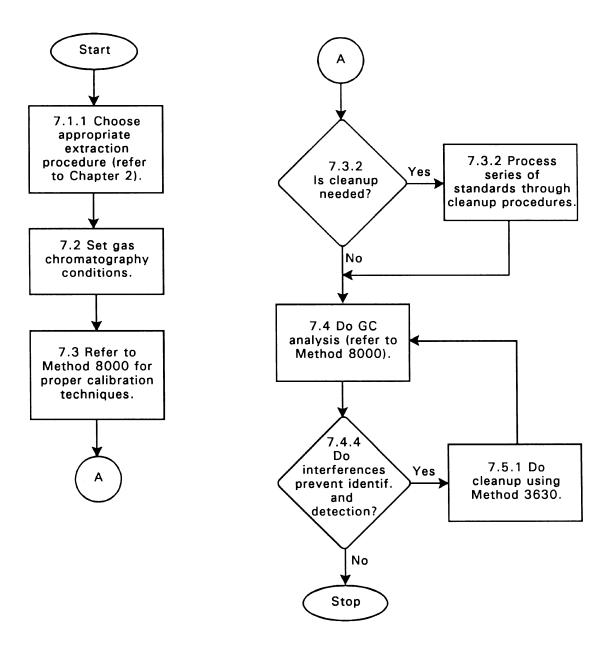P, P_s = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 610. These criteria are based directly upon the method performance data in Table 3. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 3.

TABLE 3. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Acenaphthene	0.52C+0.54	$0.39\bar{x}+0.76$	$0.53\bar{x}+1.32$
Acenaphthylene	0.69C-1.89	$0.36\bar{x}+0.29$	$0.42\bar{x}+0.52$
Anthracene	0.63C-1.26	$0.23\bar{x}+1.16$	$0.41\bar{x}+0.45$
Benzo(a)anthracene	0.73C+0.05	$0.28\bar{x}+0.04$	$0.34\bar{x}+0.02$
Benzo(a)pyrene	0.56C+0.01	$0.38\bar{x}-0.01$	$0.53\bar{x}-0.01$
Benzo(b)fluoranthene	0.78C+0.01	$0.21\bar{x}+0.01$	$0.38\bar{x}-0.00$
Benzo(ghi)perylene	0.44C+0.30	$0.25\bar{x}+0.04$	$0.58\bar{x}+0.10$
Benzo(k)fluoranthene	0.59C+0.00	$0.44\bar{x}-0.00$	$0.69\bar{x}+0.10$
Chrysene	0.77C-0.18	$0.32\bar{x}-0.18$	$0.66\bar{x}-0.22$
Dibenzo(a,h)anthracene	0.41C-0.11	$0.24\bar{x}+0.02$	$0.45\bar{x}+0.03$
Fluoranthene	0.68C+0.07	$0.22\bar{x}+0.06$	$0.32\bar{x}+0.03$
Fluorene	0.56C-0.52	$0.44\bar{x}-1.12$	$0.63\bar{x}-0.65$
Ideno(1,2,3-cd)pyrene	0.54C+0.06	$0.29\bar{x}+0.02$	$0.42\bar{x}+0.01$
Naphthalene	0.57C-0.70	$0.39\bar{x}-0.18$	$0.41\bar{x}+0.74$
Phenanthrene	0.72C-0.95	$0.29\bar{x}+0.05$	$0.47\bar{x}-0.25$
Pyrene	0.69C-0.12	$0.25\bar{x}+0.14$	$0.42\bar{x}-0.00$

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{x}$, in ug/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{x}$, in ug/L.

C   = True value for the concentration, in ug/L.

$\bar{x}$ = Average recovery found for measurements of samples containing a concentration of C, in ug/L.

METHOD 8100
POLYNUCLEAR AROMATIC HYDROCARBONS

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        ( Start )
            │
            ▼
┌──────────────────────┐
│ 7.1.1 Choose         │
│ appropriate          │
│ extraction           │
│ procedure (refer     │
│ to Chapter 2).       │
└──────────────────────┘
            │
            ▼
┌──────────────────────┐
│ 7.2 Set gas          │
│ chromatography       │
│ conditions.          │
└──────────────────────┘
            │
            ▼
┌──────────────────────┐
│ 7.3 Refer to         │
│ Method 8000 for      │
│ proper calibration   │
│ techniques.          │
└──────────────────────┘
            │
            ▼
          ( A )
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              ( A )
                │
                ▼
            7.3.2                       ┌─────────────────────┐
            Is cleanup    ── Yes ──▶    │ 7.3.2 Process       │
            needed?                     │ series of           │
                │                       │ standards through   │
               No                       │ cleanup procedures. │
                │                       └─────────────────────┘
                ▼◀───────────────────────────────┘
┌──────────────────────┐
│ 7.4 Do GC            │◀──────────────┐
│ analysis (refer to   │               │
│ Method 8000).        │               │
└──────────────────────┘               │
                │                       │
                ▼                       │
            7.4.4                   ┌─────────────────────┐
            Do                      │ 7.5.1 Do            │
            interferences ── Yes ──▶│ cleanup using       │
            prevent identif.        │ Method 3630.        │
            and                     └─────────────────────┘
            detection?
                │
               No
                │
                ▼
            ( Stop )
```