METHOD 8060

PHTHALATE ESTERS

1.0 SCOPE AND APPLICATION

1.1 Method 8060 is used to determine the concentration of various phthalate esters. Table 1 indicates compounds that may be determined by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8060 provides gas chromatographic conditions for the detection of ppb levels of phthalate esters. 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 an electron capture detector (ECD) or a flame ionization detector (FID). Ground water samples should be determined by ECD.

2.2 The method provides a second gas chromatographic column that may be helpful in resolving the analytes from interferences that may occur and for analyte confirmation.

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 Phthalate esters contaminate many types of products commonly found in the laboratory. The analyst must demonstrate that no phthalate residues contaminate the sample or solvent extract under the conditions of analysis. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced.

3.3 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All 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.

3.4 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.

TABLE 1. RETENTION TIME AND DETECTION LIMIT INFORMATION FOR PHTHALATE ESTERS

Compound	Retention time (min) Col. 1[a]	Retention time (min) Col. 2[b]	Method detection limit (ug/L) ECD	Method detection limit (ug/L) FID
Benzyl butyl phthalate	*6.94	**5.11	0.34	15
Bis(2-ethylhexyl)phthalate	*8.92	**10.5	2.0	20
Di-n-butyl phthalate	8.65	3.50	0.36	14
Diethyl phthalate	2.82	1.27	0.49	31
Dimethyl phthalate	2.03	0.95	0.29	19
Di-n-octyl phthalate	*16.2	**8.0	3.0	31

[a]Column 1: Supelcoport 100/120 mesh coated with 1.5% SP-2250/1.95% SP-2401 packed in a 180-cm x 4-mm I.D. glass column with carrier gas at 60 mL/min flow rate. Column temperature is 180°C, except where * indicates 220°C. Under these conditions the retention time of Aldrin is 5.49 min at 180°C and 1.84 min at 220°C.

[b]Column 2: Supelcoport 100/120 mesh with 3% OV-1 in a 180-cm x 4-mm I.D. glass column with carrier gas at 60 mL/min flow rate. Column temperature is 200°C, except where ** indicates 220°C. Under these conditions the retention time of Aldrin is 3.18 min at 200°C and 1.46 min at 220°C.

TABLE 2. DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-level soil by sonication with GPC cleanup	670
High-level soil and sludges by sonication	10,000
Non-water miscible waste	100,000

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

[b]PQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

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 4-mm I.D. glass column packed with 1.5% SP-2250/1.95% SP-2401 on Supelcoport 100/120 mesh or equivalent.

4.1.2.2 Column 2: 1.8-m x 4-mm I.D. glass column packed with 3% OV-1 on Supelcoport 100/120 mesh or equivalent.

4.1.3 **Detectors:** Flame ionization (FID) or electron capture (ECD).

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

4.3 Kuderna-Danish (K-D) apparatus:

4.3.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts

4.3.2 **Evaporation flask:** 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.3.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 **Snyder column:** Two-ball micro (Kontes K-569001-0219 or equivalent).

4.4 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.5 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.6 Microsyringe: 10-uL.

4.7 Syringe: 5-mL.

4.8 Vials: Glass, 2- and 20-mL capacity with Teflon-lined screw cap.

5.0 REAGENTS

5.1 Solvents: Hexane, acetone, 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 check standards 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 effec-

tiveness 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., phthalates that are not expected to be in the sample) 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 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, or as is, pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550.

7.1.2 Prior to gas chromatographic analysis, the extraction solvent must be exchanged to hexane. The exchange is performed during the K-D procedures listed in all of the extraction methods. The exchange is performed as follows.

7.1.2.1 Following K-D of the methylene chloride extract to 1 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 min.

7.1.2.2 Momentarily remove the Snyder column, add 50 mL of hexane, a new boiling chip, and reattach the macro-Snyder column. Concentrate the extract using 1 mL of hexane to prewet the Snyder column. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min. The extract will be handled differently at this point, depending on whether or not cleanup is needed. If cleanup is not required, proceed to Paragraph 7.1.2.3. If cleanup is needed, proceed to Paragraph 7.1.2.4.

7.1.2.3 If cleanup of the extract is not required, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of hexane. A 5-mL syringe is

recommended for this operation. Adjust the extract volume to 10.0 mL. Stopper the concentrator tube and store refrigerated at 4°C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. Proceed with gas chromatographic analysis.

7.1.2.4 If cleanup of the extract is required, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with a minimum amount of hexane. A 5-mL syringe is recommended for this operation. Add a clean boiling chip to the concentrator tube and attach a two-ball micro-Snyder column. Prewet the column by adding about 0.5 mL of hexane to the top. Place the micro-K-D apparatus on the water bath (80°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.1.2.5 Remove the micro-Snyder column and rinse the flask and its lower joint into the concentrator tube with 0.2 mL of hexane. Adjust the extract volume to 2.0 mL and proceed with either Method 3610 or 3620.

7.2 Gas chromatography conditions (Recommended): The analysis for phthalate esters may be conducted using either a flame ionization or an electron capture detector. The ECD may, however, provide substantially better sensitivity.

7.2.1 **Column 1:** Set 5% methane/95% argon carrier gas flow at 60 mL/min flow rate. Set column temperature at 180°C isothermal.

7.2.2 **Column 2:** Set 5% methane/95% argon carrier gas flow at 60 mL/min flow rate. Set column temperature at 200°C isothermal.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 The procedure for internal or external 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 confirm 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 Examples of GC/ECD chromatograms for phthalate esters are shown in Figures 1 and 2.

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

7.4.5 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each analyte peak in the sample chromatogram. See Section 7.8 of Method 8000 for calculation equations.

7.4.6 If peak detection and identification are prevented due to interferences, the hexane extract may undergo cleanup using either Method 3610 or 3620.

7.5 Cleanup:

7.5.1 Proceed with either Method 3610 or 3620, using the 2-mL hexane extracts obtained from Paragraph 7.1.2.5.

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 of interest at the following concentrations in acetone: butyl benzyl phthalate, 10 ug/mL; bis(2-ethylhexyl) phthalate, 50 ug/mL; di-n-octyl phthalate, 50 ug/mL; and any other phthalate, 25 ug/mL.

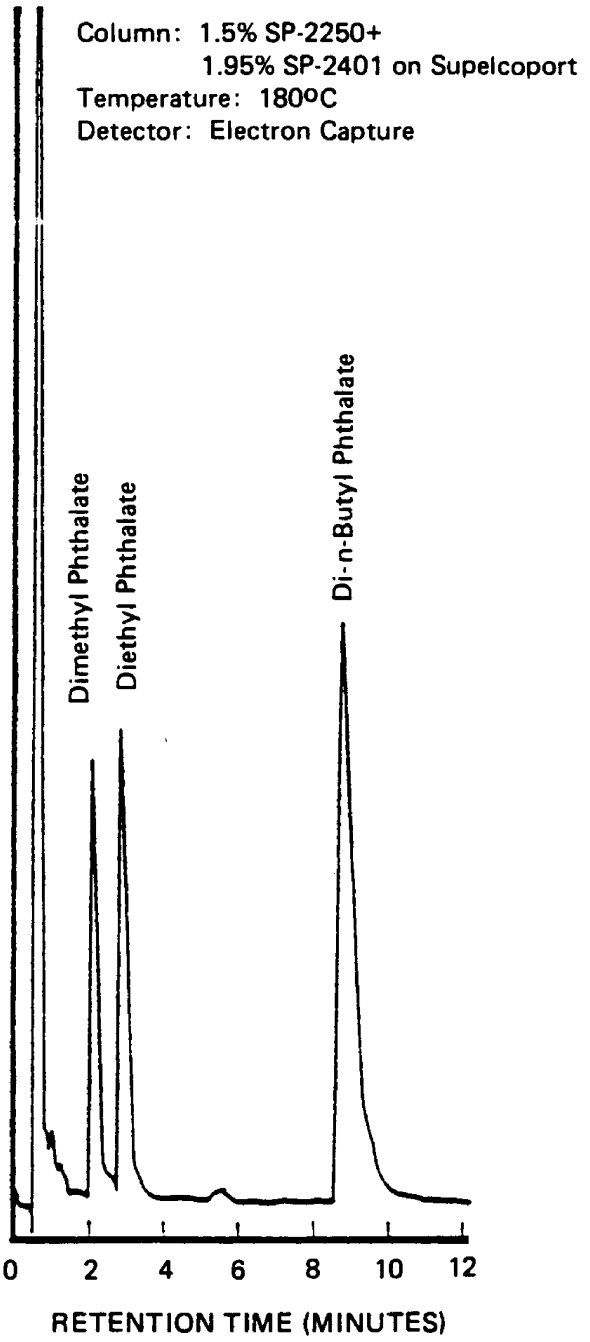


Figure 1. Gas chromatogram of phthalates (example 1).

Column: 1.5% SP-2250+
1.95% SP-2401 on Supelcoport
Temperature: 180°C
Detector: Electron Capture

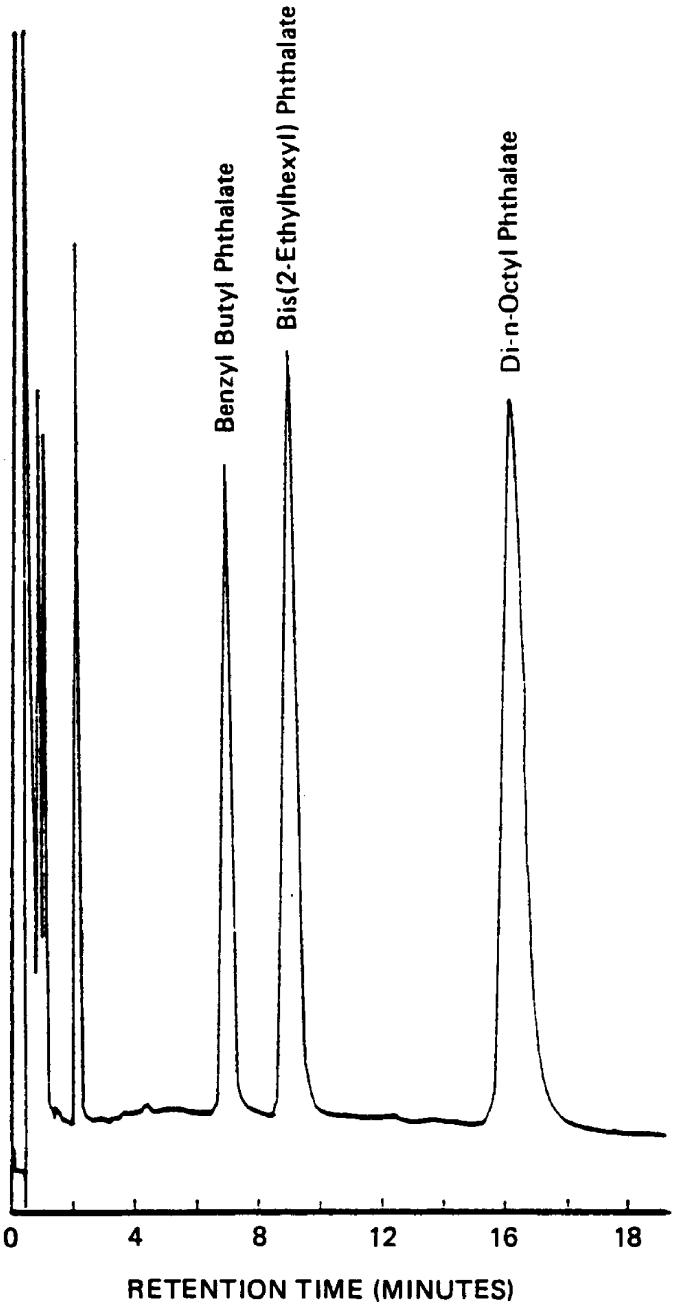


Figure 2. Gas chromatogram of phthalates (example 2).

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 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 is 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 0.7 to 106 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 4.

9.2 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 1 - Phthalates. Report for EPA Contract 68-03-2606 (in preparation).

2. "Determination of Phthalates in Industrial and Municipal Wastewaters," EPA-600/4-81-063, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, October 1981.

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

4. "EPA Method Validation Study 16, Method 606 (Phthalate Esters)," Report for EPA Contract 68-03-2606 (in preparation).

5. 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.

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

TABLE 3. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{x}$ (ug/L)	Range P, P_s (%)
Bis(2-ethylhexyl)phthalate	50	38.4	1.2-55.9	D-158
Butyl benzyl phthalate	10	4.2	5.7-11.0	30-136
Di-n-butyl phthalate	25	8.9	10.3-29.6	23-136
Diethyl phthalate	25	9.0	1.9-33.4	D-149
Dimethyl phthalate	25	9.5	1.3-35.5	D-156
Di-n-octyl phthalate	50	13.4	D-50.0	D-114

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

$\bar{x}$ = 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 606. These criteria are based directly upon the method performance data in Table 4. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 4.

TABLE 4. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Bis(2-ethylhexyl) phthalate	0.53C+2.02	0.80$\bar{x}$-2.56	0.73$\bar{x}$-0.17
Butyl benzyl phthalate	0.82C+0.13	0.26$\bar{x}$+0.04	0.25$\bar{x}$+0.07
Di-n-butyl phthalate	0.79C+0.17	0.23$\bar{x}$+0.20	0.29$\bar{x}$+0.06
Diethyl phthalate	0.70C+0.13	0.27$\bar{x}$+0.05	0.45$\bar{x}$+0.11
Dimethyl phthalate	0.73C+0.17	0.26$\bar{x}$+0.14	0.44$\bar{x}$+0.31
Di-n-octyl phthalate	0.35C-0.71	0.38$\bar{x}$+0.71	0.62$\bar{x}$+0.34

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

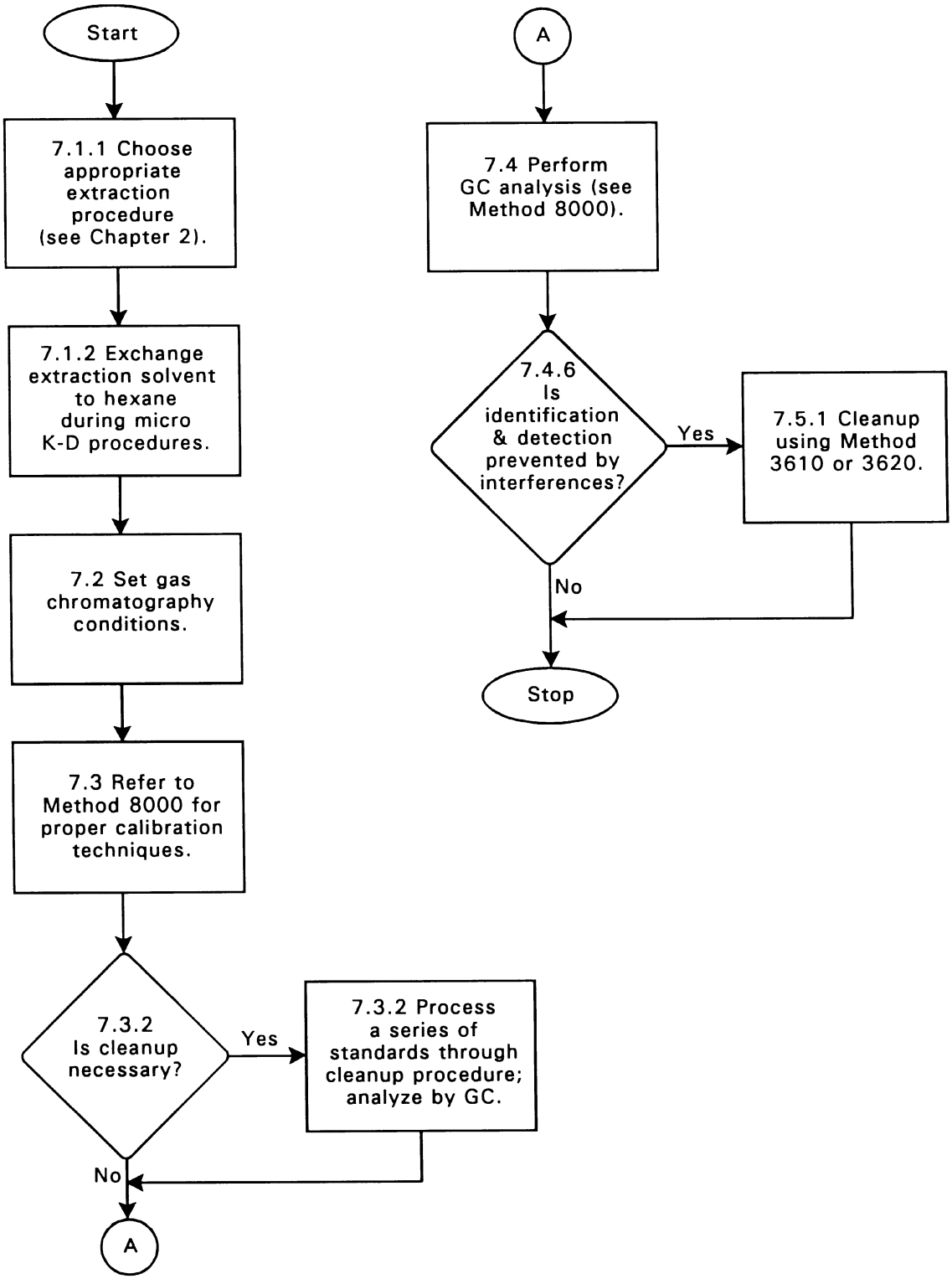
s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{x}$, in ug/L.

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.

[a]Criteria from 40 CFR Part 136 for Method 606.


Start
7.1.1 Choose appropriate extraction procedure (see Chapter 2).
7.1.2 Exchange extraction solvent to hexane during micro K-D procedures.
7.2 Set gas chromatography conditions.
7.3 Refer to Method 8000 for proper calibration techniques.
7.3.2 Is cleanup necessary?
Yes
7.3.2 Process a series of standards through cleanup procedure; analyze by GC.
No
A
A
7.4 Perform GC analysis (see Method 8000).
7.4.6 Is identification & detection prevented by interferences?
Yes
7.5.1 Cleanup using Method 3610 or 3620.
No
Stop