METHOD 8020A

AROMATIC VOLATILE ORGANICS BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8020 is used to determine the concentration of various aromatic volatile organic compounds. The following compounds can be determined by this method:

Compound Name	CAS No.[a]	Appropriate Technique	
		Purge-and-Trap	Direct Injection
Benzene	71-43-2	b	b
Chlorobenzene	108-90-7	b	b
1,2-Dichlorobenzene	95-50-1	b	b
1,3-Dichlorobenzene	541-73-1	b	b
1,4-Dichlorobenzene	106-46-7	b	b
Ethylbenzene	100-41-4	b	b
Toluene	108-88-3	b	b
Xylenes		b	b

a Chemical Abstract Services Registry Number.
b adequate response by this technique.

1.2 Table 1 lists the method detection limit for each target analyte in organic-free reagent water. Table 2 lists the estimated quantitation limit (EQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8020 provides chromatographic conditions for the detection of aromatic volatile compounds. Samples can be introduced into the GC using direct injection or purge-and-trap (Method 5030). Ground water samples must be determined using Method 5030. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a photo-ionization detector (PID).

2.2 If interferences are encountered, the method provides an optional gas chromatographic column that may be helpful in resolving the analytes from the interferences and for analyte confirmation.

3.0 INTERFERENCES

3.1 Refer to Method 5030 and 8000.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A field sample blank prepared from organic-free reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

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 or purge-and-trap sample introduction and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.2 Columns

4.1.2.1 Column 1: 6 ft x 0.082 in ID #304 stainless steel or glass column packed with 5% SP-1200 and 1.75% Bentone-34 on 100/120 mesh Supelcoport, or equivalent.

4.1.2.2 Column 2: 8 ft x 0.1 in ID stainless steel or glass column packed with 5% 1,2,3-Tris(2-cyanoethoxy)propane on 60/80 mesh Chromosorb W-AW, or equivalent.

4.1.3 Detector - Photoionization (PID) (h-Nu Systems, Inc. Model PI-51-02 or equivalent).

4.2 Sample introduction apparatus - Refer to Method 5030 for the appropriate equipment for sample introduction purposes.

4.3 Syringes - A 5 mL Luerlok glass hypodermic and a 5 mL, gas-tight with shutoff valve.

4.4 Volumetric flask, Class A - Appropriate sizes with ground glass stoppers.

4.5 Microsyringe - 10 and 25 µL with a 0.006 in ID needle (Hamilton 702N or equivalent) and a 100 µL.

4.6 Analytical balance - 0.0001 g.

5.0 REAGENTS

5.1 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2 Methanol (CH_3OH) - pesticide quality or equivalent. Store away from other solvents.

5.3 Stock standards - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standards in methanol using assayed liquids. Because of the toxicity of benzene and 1,4-dichlorobenzene, primary dilutions of these materials should be prepared in a hood.

5.3.1 Place about 9.8 mL of methanol in a 10 mL tared ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.0001 g.

5.3.2 Using a 100 µL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.3.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.3.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store, with minimal headspace, at 4°C and protect from light.

5.3.5 All standards must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

5.4 Secondary dilution standards: Using stock standard solutions, prepare in methanol secondary dilution standards, as needed, that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Section 5.5 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace for volatiles and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.5 Calibration standards: Calibration standards at a minimum of five concentrations are prepared in organic-free reagent water from the secondary dilution of the stock standards. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Each standard should contain each analyte for detection by this method (e.g., some or all of the compounds listed in the target analyte list may be included). In order to prepare accurate aqueous standard solutions, the following precautions must be observed.

5.5.1 Do not inject more than 20 µL of alcoholic standards into

100 mL of organic-free reagent water.

5.5.2 Use a 25 µL Hamilton 702N microsyringe or equivalent (variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water).

5.5.3 Rapidly inject the alcoholic standard into the filled volumetric flask. Remove the needle as fast as possible after injection.

5.5.4 Mix aqueous standards by inverting the flask three times only.

5.5.5 Fill the sample syringe from the standard solution contained in the expanded area of the flask (do not use any solution contained in the neck of the flask).

5.5.6 Never use pipets to dilute or transfer samples or aqueous standards.

5.5.7 Aqueous standards are not stable and should be discarded after 1 hr, unless properly sealed and stored. The aqueous standards can be stored up to 24 hr, if held in sealed vials with zero headspace.

5.6 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. Alpha,alpha,alpha-trifluorotoluene has been used successfully as an internal standard.

5.6.1 Prepare calibration standards at a minimum of five concentrations for each parameter of interest as described in Section 5.5.

5.6.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 5.3 and 5.4. It is recommended that the secondary dilution standard be prepared at a concentration of 15 mg/L of each internal standard compound. The addition of 10 µL of this standard to 5.0 mL of sample or calibration standard would be equivalent to 30 µg/L.

5.6.3 Analyze each calibration standard according to Section 7.0, adding 10 µL of internal standard spiking solution directly to the syringe.

5.7 Surrogate standards: The analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and organic-free reagent water blank with surrogate compounds (bromochlorobenzene, bromofluorobenzene, 1,1,1-trifluorotoluene, fluorobenzene, and difluorobenzene are recommended) which encompass the range of the temperature program used in this method. From stock standard solutions prepared as in Section 5.3, add a volume to give 750 µg of

each surrogate to 45 mL of organic-free reagent water contained in a 50 mL volumetric flask, mix, and dilute to volume for a concentration of 15 ng/µL. Add 10 µL of this surrogate spiking solution directly into the 5 mL syringe with every sample and reference standard analyzed. If the internal standard calibration procedure is used, the surrogate compounds may be added directly to the internal standard spiking solution (Section 5.6.2).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Volatile compounds are introduced into the gas chromatograph either by direct injection or purge-and-trap (Method 5030). Method 5030 may be used directly on ground water samples or low-concentration contaminated soils and sediments. For medium-concentration soils or sediments, methanolic extraction, as described in Method 5030, may be necessary prior to purge-and-trap analysis. Method 5030 also provides guidance on the analysis of aqueous miscible and non-aqueous miscible liquid wastes (see Section 7.4.1.1 below).

7.2 Gas chromatography conditions (Recommended):

7.2.1 Column 1:

Carrier gas (He) flow rate:	36 mL/min
For lower boiling compounds:	
Initial temperature:	50°C, hold for 2 min;
Temperature program:	50°C to 90°C at 6 °C/min, hold until all compounds have eluted.
For higher boiling range of compounds:	
Initial temperature:	50°C, hold for 2 min;
Temperature program:	50°C to 110 °C at 3 °C/min, hold until all compounds have eluted.

Column 1 provides outstanding separations for a wide variety of aromatic hydrocarbons. Column 1 should be used as the primary analytical column because of its unique ability to resolve para-, meta-, and ortho-aromatic isomers.

7.2.2 Column 2:

Carrier gas (He) flow rate:	30 mL/min
Initial temperature:	40°C, hold for 2 min;
Temperature program:	40°C to 100 °C at 2 °C/min, hold until all compounds have eluted.

Column 2, an extremely high polarity column, has been used for a number of years to resolve aromatic hydrocarbons from alkanes in complex

samples. However, because resolution between some of the aromatics is not as efficient as with Column 1, Column 2 should be used as a confirmatory column.

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 Calibration must take place using the same sample introduction method that will be used to analyze actual samples (see Section 7.4.1).

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

7.4 Gas chromatographic analysis:

7.4.1 Introduce volatile compounds into the gas chromatograph using either Method 5030 (purge-and-trap method) or the direct injection method. If the internal standard calibration technique is used, add 10 µL of internal standard to the sample prior to purging.

7.4.1.1 Direct injection: In very limited applications (e.g., aqueous process wastes), direct injection of the sample into the GC system with a 10 µL syringe may be appropriate. The detection limit is very high (approximately 10,000 µg/L); therefore, it is only permitted when concentrations in excess of 10,000 µg/L are expected or for water soluble compounds that do not purge. The system must be calibrated by direct injection (bypassing the purge-and-trap device).

Non-aqueous miscible wastes may also be analyzed by direct injection if the concentration of target analytes in the sample falls within the calibration range. If dilution of the sample is necessary, follow the guidance for High Concentration samples in Method 5030, Section 7.3.3.2.

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

7.4.3 Table 1 summarizes the estimated retention times and detection limits for a number of organic compounds analyzable using this method. An example of the separation achieved by Column 1 is shown in Figure 1. Figure 2 shows an example of the separation achieved using Column 2.

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

7.4.5 Calculation of concentration is covered in Method 8000.

7.4.6 If analytical interferences are suspected, or for the purpose of confirmation, analysis using the second GC column is recommended.

7.4.7 If the response for a peak is off scale, i.e., beyond the calibration range of the standards, prepare a dilution of the sample with organic-free reagent water. The dilution must be performed on a second aliquot of the sample which has been properly sealed and stored prior to use.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 8000 for gas chromatographic procedures. Quality control to ensure the proper operation of the purge-and-trap device is covered in Method 5030.

8.2 Quality control required to validate the GC system operation is found in Method 8000.

8.2.1 The quality control check sample concentrate (Method 8000) should contain each parameter of interest at a concentration of 10 mg/L in methanol.

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 recovery is within limits (limits established by performing QC procedure outlined in Method 8000).

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

- Check to be sure that 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 This method was tested by 20 laboratories using organic-free reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 2.1 - 500 µg/L. Single operator precision,

overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 4.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample introduction technique, and by the calibration procedure used.

9.3 The method detection limits reported in Table 1 were generated under optimum analytical conditions by an Agency contractor (Ref. 7) as guidance, and may not be readily achievable by all laboratories at all times.

10.0 REFERENCES

1. Bellar, T.A., and J.J. Lichtenberg, J. Amer. Water Works Assoc., 66(12), pp. 739-744, 1974.

2. Bellar, T.A., and J.J. Lichtenberg, "Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds", in Van Hall (ed.), Measurement of Organic Pollutants in Water and Wastewater, ASTM STP 686, pp. 108-129, 1979.

3. Dowty, B.J., S.R. Antoine, and J.L. Laseter, "Quantitative and Qualitative Analysis of Purgeable Organics by High Resolution Gas Chromatography and Flame Ionization Detection", in Van Hall, ed., Measurement of Organic Pollutants in Water and Wastewater. ASTM STP 686, pp. 24-35, 1979.

4. Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 11 - Purgeables and Category 12 - Acrolein, Acrylonitrile, and Dichlorodifluoromethane. Report for EPA Contract 68-03-2635.

5. "EPA Method Validation Study 24, Method 602 (Purgeable Aromatics)", report for EPA Contract 68-03-2856.

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. Gebhart, J.E., S.V. Lucas, S.J. Naber, A.M. Berry, T.H. Danison and H.M. Burkholder, "Validation of SW-846 Methods 8010, 8015, and 8020"; Report for EPA Contract 68-03-1760, Work Assignment 2-15; US EPA, EMSL-Cincinnati, 1987."

TABLE 1.
CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS
FOR AROMATIC VOLATILE ORGANICS

Compound	Retention time (min) Col. 1	Retention time (min) Col. 2	Method detection limit[a] (µg/L)
Benzene	3.33	2.75	0.2
Chlorobenzene[b]	9.17	8.02	0.2
1,4-Dichlorobenzene	16.8	16.2	0.3
1,3-Dichlorobenzene	18.2	15.0	0.4
1,2-Dichlorobenzene	25.9	19.4	0.4
Ethyl Benzene	8.25	6.25	0.2
Toluene	5.75	4.25	0.2
Xylenes			

a Using purge-and-trap method (Method 5030). See Sec. 9.3.
b Chlorobenzene and m-xylene may co-elute on some columns.

TABLE 2.
DETERMINATION OF ESTIMATED QUANTITATION LIMITS (EQLs)
FOR VARIOUS MATRICES[a]

Matrix	Factor
Ground water	10
Low-concentration soil	10
Water miscible liquid waste	500
High-concentration soil and sludge	1250
Non-water miscible waste	1250

a EQL = [Method detection limit (see Table 1)] X [Factor found in this table]. For non-aqueous samples, the factor is on a wet-weight basis. Sample EQLs are highly matrix-dependent. The EQLs determined herein are provided for guidance and may not always be achievable.

TABLE 3.
QC ACCEPTANCE CRITERIA[a]

Parameter	Range for Q (µg/L)	Limit for s (µg/L)	Range for $\bar{x}$ (µg/L)	Range P, P_s (%)
Benzene	15.4-24.6	4.1	10.0-27.9	39-150
Chlorobenzene	16.1-23.9	3.5	12.7-25.4	55-135
1,2-Dichlorobenzene	13.6-26.4	5.8	10.6-27.6	37-154
1,3-Dichlorobenzene	14.5-25.5	5.0	12.8-25.5	50-141
1,4-Dichlorobenzene	13.9-26.1	5.5	11.6-25.5	42-143
Ethylbenzene	12.6-27.4	6.7	10.0-28.2	32-160
Toluene	15.5-24.5	4.0	11.2-27.7	46-148

Q = Concentration measured in QC check sample, in µg/L.

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

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

P, P_s = Percent recovery measured.

a Criteria from 40 CFR Part 136 for Method 602, using packed columns, and were calculated assuming a check sample concentration of 20 µg/L. 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 1. When capillary columns are used, see Method 8021 for performance data.

TABLE 4.
METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION

Parameter	Accuracy, as recovery, x' (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S' (µg/L)
Benzene	0.92C+0.57	$0.09\bar{x}+0.59$	$0.21\bar{x}+0.56$
Chlorobenzene	0.95C+0.02	$0.09\bar{x}+0.23$	$0.17\bar{x}+0.10$
1,2-Dichlorobenzene	0.93C+0.52	$0.17\bar{x}-0.04$	$0.22\bar{x}+0.53$
1,3-Dichlorobenzene	0.96C-0.04	$0.15\bar{x}-0.10$	$0.19\bar{x}+0.09$
1,4-Dichlorobenzene	0.93C-0.09	$0.15\bar{x}+0.28$	$0.20\bar{x}+0.41$
Ethylbenzene	0.94C+0.31	$0.17\bar{x}+0.46$	$0.26\bar{x}+0.23$
Toluene	0.94C+0.65	0.09x+0.48	0.18x+0.71

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

s_r' = Expected single analyst standard deviation of measurements at an average concentration of x, in µg/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of x, in µg/L.

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

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

Figure 1 Chromatogram of Aromatic Volatile Organics
(column 1 conditions)

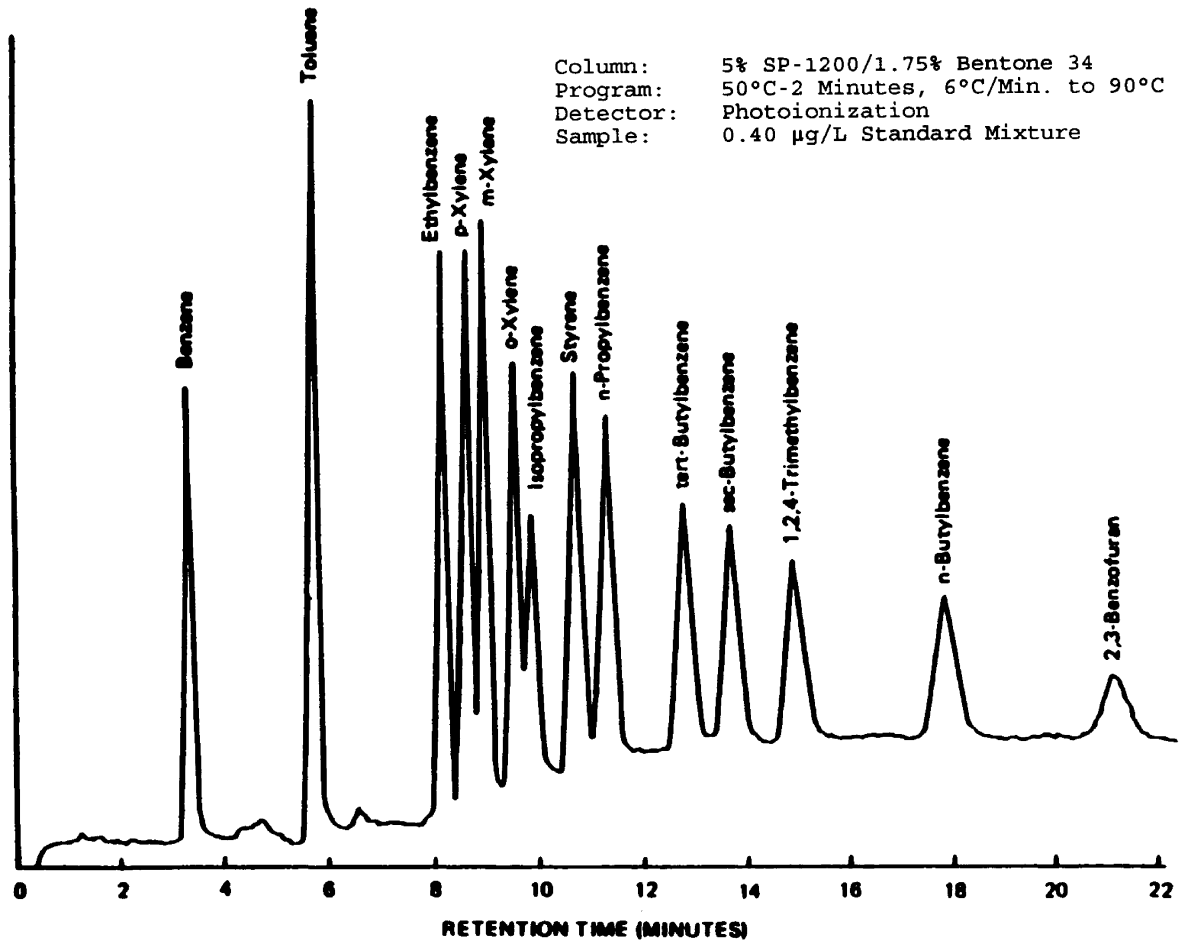
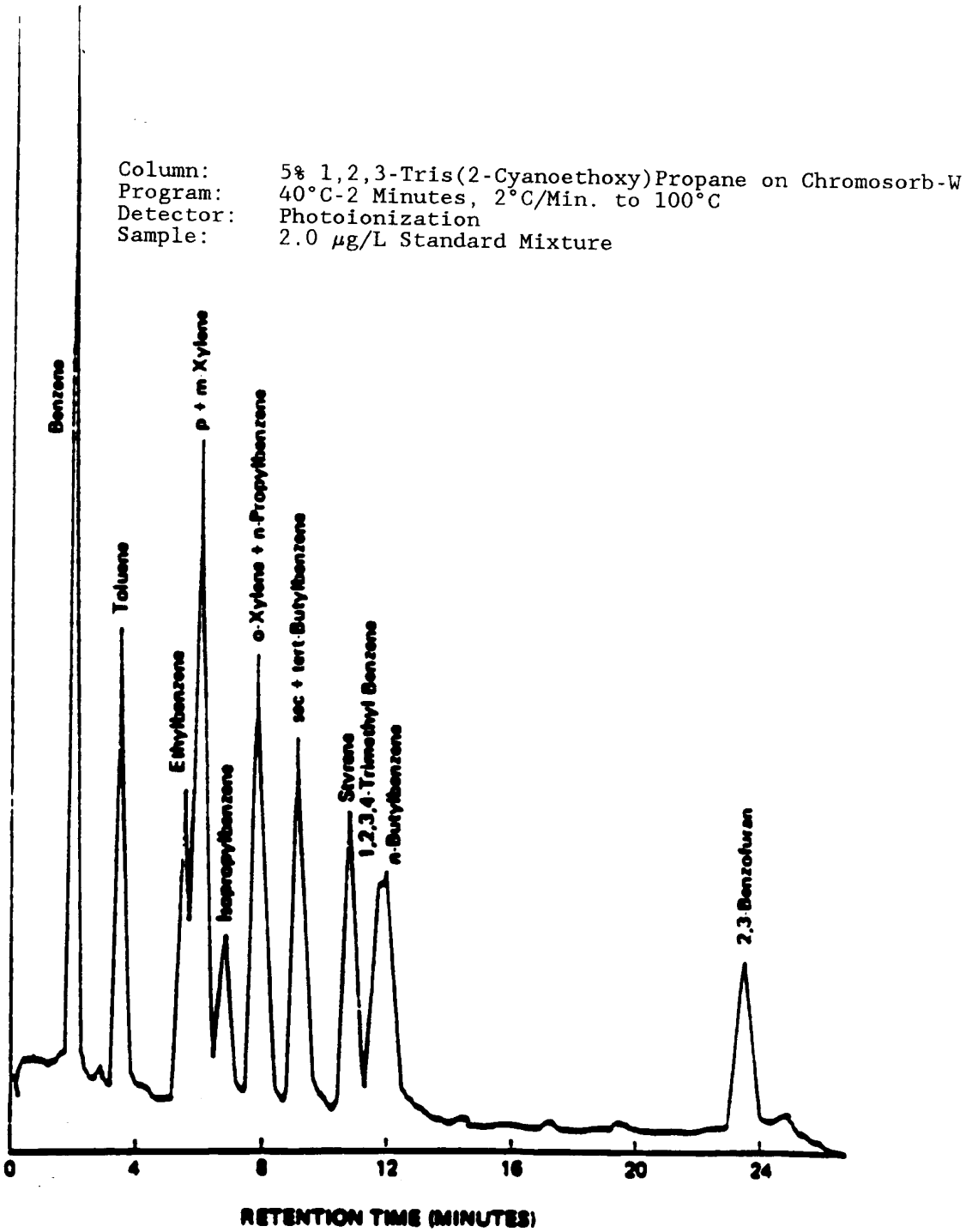
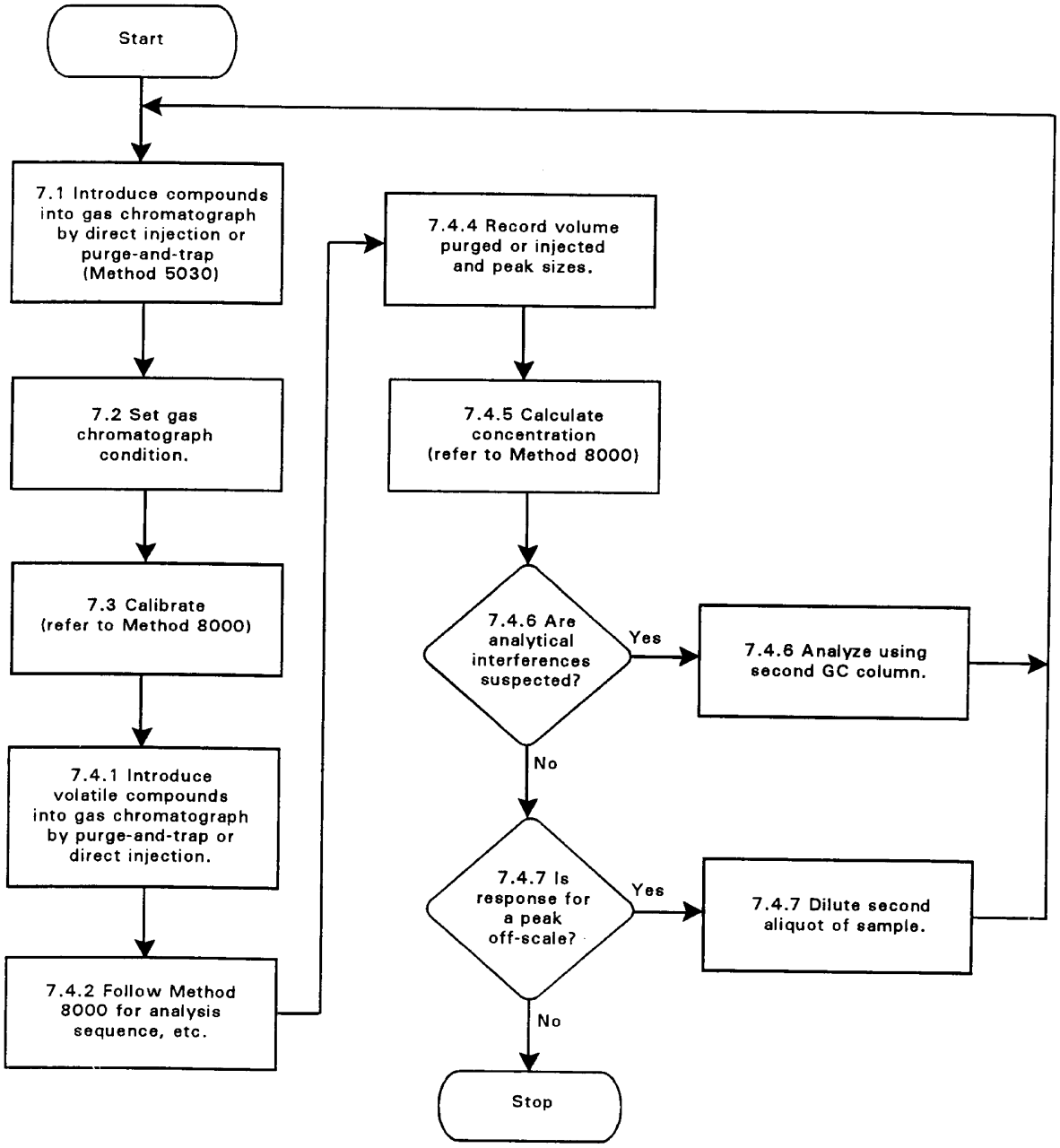


Figure 2
Chromatogram of Aromatic Volatile Organics
(column 2 conditions)




Start
7.1 Introduce compounds into gas chromatograph by direct injection or purge-and-trap (Method 5030)
7.2 Set gas chromatograph condition.
7.3 Calibrate (refer to Method 8000)
7.4.1 Introduce volatile compounds into gas chromatograph by purge-and-trap or direct injection.
7.4.2 Follow Method 8000 for analysis sequence, etc.
7.4.4 Record volume purged or injected and peak sizes.
7.4.5 Calculate concentration (refer to Method 8000)
7.4.6 Are analytical interferences suspected?
Yes
7.4.6 Analyze using second GC column.
No
7.4.7 Is response for a peak off-scale?
Yes
7.4.7 Dilute second aliquot of sample.
No
Stop