

METHOD 8030A

ACROLEIN AND ACRYLONITRILE BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8030 is used to determine the concentration of the following volatile organic compounds:

Compound Name	CAS No. ^a
Acrolein (Propenal)	107-02-8
Acrylonitrile	107-13-1

^a Chemical Abstract Services Registry Number.

1.2 Table 1 lists chromatographic conditions and method detection limits for acrolein and acrylonitrile in organic-free reagent water. Table 2 lists the estimated quantitation limit (EQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8030 provides gas chromatographic conditions for the detection of the target analytes. Samples can be analyzed using direct injection or purge-and-trap (Method 5030). Tenax should be used as the trap packing material. Ground water samples must be analyzed using Method 5030. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a flame ionization detector (FID).

2.2 The method provides an optional gas chromatographic column that may be helpful in resolving the analytes from co-eluting non-target compounds and for analyte confirmation.

3.0 INTERFERENCES

3.1 Refer to Methods 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 trip 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 height and/or peak area is recommended.

4.1.2 Columns

4.1.2.1 Column 1 - 10 ft x 2 mm ID stainless steel or glass packed with Porapak-QS (80/100 mesh) or equivalent.

4.1.2.2 Column 2 - 6 ft x 0.1 in. ID stainless steel or glass packed with Chromosorb 101 (60/80 mesh) or equivalent.

4.1.3 Detector - Flame ionization (FID).

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

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

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

4.5 Microsyringes - 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 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

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

5.3 Hydrochloric acid, HCl - 1:1 (v/v).

5.4 Sodium hydroxide, NaOH - 10N solution. Dissolve 40 g NaOH in organic-free reagent water and dilute to 100 mL.

5.5 Stock standards - Stock solutions may be prepared from pure standard

materials or purchased as certified solutions. Prepare stock standards in organic-free reagent water using assayed liquids. Because acrolein and acrylonitrile are lachrymators, primary dilutions of these compounds should be prepared in a hood.

5.5.1 Place about 9.8 mL of organic-free reagent water in a 10 mL tared ground-glass stoppered volumetric flask. For acrolein standards the water must be adjusted to pH 4-5 using hydrochloric acid (1:1 v/v) or sodium hydroxide (10N), if necessary. Weigh the flask to the nearest 0.0001 g.

5.5.2 Using a 100 μ L syringe, immediately add two or more drops of assayed reference material to the flask, then reweigh. The liquid must fall directly into the water without contacting the neck of the flask.

5.5.3 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.

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

5.5.5 Prepare fresh standards daily.

5.6 Secondary dilution standards - Prepare secondary dilution standards as needed, in organic-free reagent water, from the stock standard solutions. The secondary dilution standards must 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 5.7 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace, and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.7 Calibration standards - Prepare calibration standards in organic-free reagent water from the secondary dilution standards at a minimum of five concentrations. 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. In order to prepare accurate aqueous standard solutions, the following precautions must be observed.

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

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

5.7.3 Standards must be prepared daily.

5.8 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.

5.8.1 Prepare calibration standards at a minimum of five concentrations for each parameter of interest, as described in Section 5.7.

5.8.2 Prepare a spiking solution containing each of the internal standards, using the procedures described in Sections 5.5 and 5.6. 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 μ L of this standard to 5.0 mL of sample or calibration standard would be equivalent to 30 μ g/L.

5.8.3 Analyze each calibration standard according to Section 7.0, adding 10 μ L of internal standard spiking solution directly to the syringe.

5.9 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 one or two surrogate compounds (e.g. compounds similar in analytical behavior to the analytes of interest but which are not expected to be present in the sample) recommended to encompass the range of the temperature program used in this method. From stock standard solutions prepared as in Section 5.5, add a volume to give 750 μ g 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/ μ L. Add 10 μ L 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 5.8.2).

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 heated purge-and-trap (Method 5030). Method 5030 may be used directly on ground water samples or low-concentration contaminated soils and sediments. For high-concentration soils or sediments, methanolic extraction, as described in Method 5030, may be necessary prior to purge-and-trap analysis.

7.2 Gas chromatographic conditions (Recommended)

7.2.1 Column 1:

Helium flow rate = 30 mL/min
Temperature program:
Initial temperature = 110°C, hold for 1.5 minutes
Program = 110°C to 150°C, heating as rapidly as possible
Final temperature = 150°C, hold for 20 minutes.

7.2.2 Column 2:

Helium flow rate = 40 mL/min
Temperature program:
Initial temperature = 80°C, hold for 4 minutes
Program = 80°C to 120°C at 50°C/min
Final temperature = 120°C, hold for 12 minutes.

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 (heated purge-and-trap method using Tenax as the trap packing material) or the direct injection method. If the internal standard calibration technique is used, add 10 µL of the 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).

7.4.2 Follow Method 8000 for 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. Figure 1 illustrates the chromatographic separation of acrolein and of acrylonitrile using Column 1.

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, 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 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 parameter of interest at a concentration of 25 mg/L in water.

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 gives single laboratory accuracy and precision 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, Section 8.10).

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 In a single laboratory, the average recoveries and standard deviations presented in Table 4 were obtained using Method 5030. Seven replicate samples were analyzed at each spike concentration.

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

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. 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 (in preparation).
4. Going, J., et al., Environmental Monitoring Near Industrial Sites - Acrylonitrile, Office of Toxic Substances, U.S. EPA, Washington, DC, EPA 560/6-79-003, 1979.
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. Kerns, E.H., et al. "Determination of Acrolein and Acrylonitrile in Water by Heated Purge and Trap Technique," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, 1980.
7. "Evaluation of Method 603," Final Report for EPA Contract 68-03-1760 (in preparation).

TABLE 1.
CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Compound	<u>Retention time (min)</u>		Method detection limit ^a (µg/L)
	Col. 1	Col. 2	
Acrolein	10.6	8.2	0.7
Acrylonitrile	12.7	9.8	0.5

^a Based on using purge-and-trap, Method 5030.

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

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

^a Sample EQLs are highly matrix dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

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

TABLE 3.
CALIBRATION AND QC ACCEPTANCE CRITERIA^a

Analyte	Range for Q (µg/L)	Limit for S (µg/L)	Range for x (µg/L)	Range P, P _s (%)
Acrolein	45.9 - 54.1	4.6	42.9 - 60.1	88-118
Acrylonitrile	41.2 - 58.8	9.9	33.1 - 69.9	71-135

Q = Concentration measured in QC check sample, in µg/L.
S = Standard deviation of four recovery measurements, in µg/L.
R = Average recovery for four recovery measurements, in µg/L.
P, P_s = Percent recovery measured.

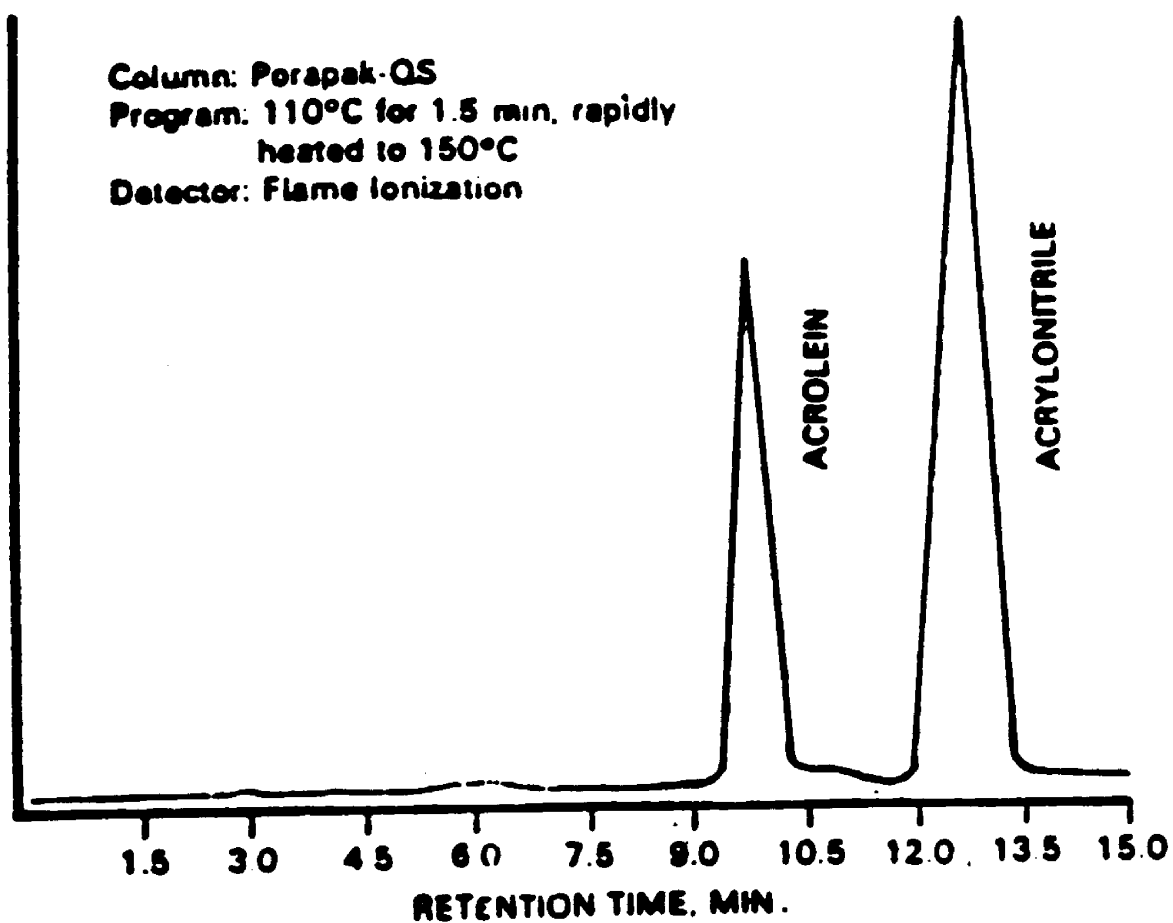
^a Criteria from 40 CFR Part 136 for Method 603 and were calculated assuming a QC check sample concentration of 50 µg/L.

TABLE 4.
SINGLE LABORATORY ACCURACY AND PRECISION

Parameter	Spike conc. (µg/L)	Average recovery (µg/L)	Standard deviation (µg/L)	Average percent recovery	Sample matrix
Acrolein	5.0	5.2	0.2	104	AW
	50.0	51.4	0.7	103	AW
	5.0	4.0	0.2	80	POTW
	50.0	44.4	0.8	89	POTW
	5.0	0.1	0.1	2	IW
	100.0	9.3	1.1	9	IW
Acrylonitrile	5.0	4.2	0.2	84	AW
	50.0	51.4	1.5	103	AW
	20.0	20.1	0.8	100	POTW
	100.0	101.3	1.5	101	POTW
	10.0	9.1	0.8	91	IW
	100.0	104.0	3.2	104	IW

AW = ASTM Type II water.
POTW = Prechlorination secondary effluent from a municipal sewage treatment plant.
IW = Industrial wastewater containing an unidentified acrolein reactant.

Figure 1
Gas Chromatogram of Acrolein and Acrylonitrile



METHOD 8030A
ACROLEIN AND ACRYLONITRILE BY GAS CHROMATOGRAPHY

