

METHOD 8031

ACRYLONITRILE BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8031 is used to determine the concentration of acrylonitrile in water. This method may also be applicable to other matrices. The following compound can be determined by this method:

| Compound Name | CAS No. ^a |
|---------------|----------------------|
| Acrylonitrile | 107-13-1 |

^a Chemical Abstract Services Registry Number.

1.2 The estimated quantitation limit of Method 8031 for determining the concentration of acrylonitrile in water is approximately 10 µg/L.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatographs and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A measured sample volume is micro-extracted with methyl tert-butyl ether. The extract is separated by gas chromatography and measured with a Nitrogen/Phosphorus detector.

3.0 INTERFERENCES

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that leads to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks.

3.2 Samples can be contaminated by diffusion of volatile organics around the septum seal into the sample during handling and storage. A field blank should be prepared from organic-free reagent water and carried through the sampling and sample handling protocol to serve as a check on such contamination.

3.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the

sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph system

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

4.1.2 Column: Porapak Q - 6 ft., 80/10 Mesh, glass column, or equivalent.

4.1.3 Nitrogen/Phosphorus detector.

4.2 Materials

4.2.1 Grab sample bottles - 40 mL VOA bottles.

4.2.2 Mixing bottles - 90 mL bottle with a Teflon lined cap.

4.2.3 Syringes - 10 μ L and 50 μ L.

4.2.4 Volumetric flask (Class A) - 100 mL.

4.2.5 Graduated cylinder - 50 mL.

4.2.6 Pipet (Class A) - 5, 15, and 50 mL.

4.2.7 Vials - 10 mL.

4.3 Preparation

4.3.1 Prepare all materials to be used as described in Chapter 4 for volatile organics.

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 General

5.2.1 Methanol, CH₃OH - Pesticide quality, or equivalent.

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

5.2.3 Methyl tert-butyl ether, CH₃Ot-C₄H₉ - Pesticide quality, or equivalent.

5.2.4 Acrylonitrile, H₂C:CHCN, 98%.

5.3 Stock standard solution

5.3.1 Stock standard solutions - Can be prepared from pure standard materials or can be purchased as certified solutions. Prepare stock standards in organic-free reagent water using assayed liquids.

5.3.2 The stock standard solution may be prepared by volume or by weight. Stock solutions must be replaced after one year, or sooner if comparison with the check standards indicates a problem.

CAUTION: Acrylonitrile is toxic. Standard preparation should be performed in a laboratory fume hood.

5.3.2.1 To prepare the stock standard solution by volume: inject 10 µL of acrylonitrile (98%) into a 100 mL volumetric flask with a syringe. Make up to volume with methanol.

5.3.2.2 To prepare the stock standard solution by weight: Place about 9.8 mL of organic-free reagent water into a 10 mL volumetric flask before weighing the flask and stopper. Weigh the flask and record the weight to the nearest 0.0001 g. Add two drops of pure acrylonitrile, using a 50 µL syringe, to the flask. The liquid must fall directly into the water, without contacting the inside wall of the flask. Stopper the flask and then reweigh. Dilute to volume with organic-free reagent water. Calculate the concentration from the net gain in weight.

5.4 Working standard solutions

5.4.1 Prepare a minimum of 5 working standard solutions that cover the range of analyte concentrations expected in the samples. Working standards of 20, 40, 60, 80, and 100 µg/L may be prepared by injecting 10, 20, 30, 40, and 50 µL of the stock standard solution prepared in Sec. 5.3.2.1 into 5 separate 90 mL mixing bottles containing 40 mL of organic-free reagent water.

5.4.2 Inject 15 mL of methyl tert-butyl ether into each mixing bottle, shake vigorously, and let stand 5 minutes, or until layers have separated.

5.4.3 Remove 5 mL of top layer by pipet, and place in a 10 mL vial.

5.4.4 Keep all standard solutions below 4°C until used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

7.0 PROCEDURE

7.1 Sample Extraction

7.1.1 Pour 40 mL of the sample into a 90 mL mixing bottle. Pipet 15 mL of Methyl tert-butyl ether into the mixing bottle. Shake vigorously for about 2 min. and let stand for about 5 min. Remove about 5 mL of the top layer and store in a 10 mL vial.

7.2 Chromatographic Conditions (Recommended)

| | |
|-----------------------------|--------------------------------------|
| Carrier Gas (He) flow rate: | 35 mL/min. |
| Column Temperature: | 180° C, Isothermal |
| Injection port temperature: | 250° C |
| Detector temperature: | 250° C |
| Detector Current (DC): | 18 volts |
| Gases: | Hydrogen, 3 mL/min; Air, 290 mL/min. |

7.3 Calibration of GC

7.3.1 On a daily basis, inject 3 µL of methyl tert-butyl ether directly into the GC to flush the system. Also purge the system with methyl tert-butyl ether injections between injections of standards and samples.

7.3.2 Inject 3 µL of a sample blank (organic-free reagent water carried through the sample storage procedures and extracted with methyl tert-butyl ether).

7.3.3 Inject 3 µL of at least five standard solutions: one should be near the detection limit; one should be near, but below, the expected concentrations of the analyte; one should be near, but above, the expected concentrations of the analyte. The range of standard solution concentrations used should not exceed the working range of the GC system.

7.3.4 Prepare a calibration curve using the peak areas of the standards (retention time of acrylonitrile under the conditions of Sec. 7.2 is approximately 2.3 minutes). If the calibration curve deviates significantly from a straight line, prepare a new calibration curve with the existing standards, or, prepare new standards and a new calibration curve. See Method 8000, Sec. 7.4.2, for additional guidance on calibration by the external standard method.

7.4 Sample Analysis

7.4.1 Inject 3 μL of the sample extract, using the same chromatographic conditions used to prepare the standard curve. Calculate the concentration of acrylonitrile in the extract, using the area of the peak, against the calibration curve prepared in Sec. 7.3.4.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control procedures.

8.2 Prior to preparation of stock solutions, methanol and methyl tert-butyl ether reagents should be analyzed gas chromatographically under the conditions described in Sec. 7.2, to determine possible interferences with the acrylonitrile peak. If the solvent blanks show contamination, a different batch of solvents should be used.

9.0 METHOD PERFORMANCE

9.1 Method 8031 was tested in a single laboratory over a period of days. Duplicate samples and one spiked sample were run for each calculation. The GC was calibrated daily. Results are presented in Table 1.

10.0 REFERENCES

1. K.L. Anderson, "The Determination of Trace Amounts of Acrylonitrile in Water by Specific Nitrogen Detector Gas Chromatograph", American Cyanamid Report No. WI-88-13, 1988.

TABLE 1
SINGLE LABORATORY METHOD PERFORMANCE

| SAMPLE | CONCENTRATION SPIKE ($\mu\text{g/L}$) | % RECOVERY |
|---------|--|------------|
| A | 60 | 100 |
| B | 60 | 105 |
| C | 40 | 86 |
| D | 40 | 100 |
| E | 40 | 88 |
| F | 60 | 94 |
| Average | | 96 |

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