ACETONE CYANOHYDRIN 2506

$(CH_3)_2C(OH)CN$ MW: 85.11 CAS: 75-86-5 RTECS: OD9275000

METHOD: 2506, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA: no PEL
NIOSH: C 1 ppm/15 min
ACGIH: no TLV
(1 ppm = 3.48 mg/m^3)

PROPERTIES: liquid; d 0.932 g/mL @ 19 °C; BP 95 °C; MP –19 °C; VP 110 Pa (0.8 mm Hg) @ 20 °C

SYNONYMS: 2-cyano-2-propanol; 2-methyllactonitrile; 2-hydroxy-2-methylpropanenitrile

SAMPLING

SAMPLER: SOLID SORBENT TUBE (Porapak QS, 100 mg/50 mg)

FLOW RATE: 0.2 L/min

VOL-MIN: 0.3 L @ 1 ppm
-MAX: 12 L

SHIPMENT: in refrigerated container @ 0 °C

SAMPLE STABILITY: at least 5 days if stored at @ 0 °C immediately following collection

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.33 to 16.7 mg/m^3 [1] (3-L samples)

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{rT}$): 0.093 [1]

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPH, NP (THERMIONIC) DETECTOR

ANALYTE: acetone cyanohydrin

DESORPTION: 1 mL ethyl acetate; ultrasonicate 60 min

INJECTION VOLUME: 5 µL, 1 µL flush

TEMPERATURE-INJECTION: 100 °C
-DETECTOR: 100 °C
-COLUMN: 70 °C

CARRIER GAS: N_2, 33 mL/min

COLUMN: PTFE, 2 m × 3.2-mm OD, packed with 5% OV-17 on 40/60 mesh Chromosorb T (APPENDIX)

CALIBRATION: solutions of acetone cyanohydrin in ethyl acetate

RANGE: 1 to 50 µg per sample

ESTIMATED LOD: 0.1 µg per sample [1]

PRECISION ($\bar{S}_r$): 0.042 [1]

APPLICABILITY: The working range is 0.1 to 4.8 ppm (0.33 to 17 mg/m^3) for a 3-L air sample. However, coadsorbed water vapor will decompose the analyte unless the samples are refrigerated immediately after collection.

INTERFERENCES: Acetone, methyl methacrylate and methanol do not interfere with the analysis. Methacrylamide does not elute from the column under the conditions given above. The gas chromatograph must be modified to eliminate contact of analyte with heated glass or metal surfaces.

OTHER METHODS: This method was originally designated P&CAM 340 [2].

REAGENTS:

1. Desiccant, bagged, for field use.
2. Acetone cyanohydrin, 98% or better.*
3. Ethyl acetate, chromatographic quality.
4. Silicone oil (OV-17).
5. Coated Chromosorb-T, 40/60 mesh, for GC stationary phase (APPENDIX).
6. Calibration stock solution, ca. 1.8 mg/mL. Inject 2.0 µL acetone cyanohydrin into 1.0 mL ethyl acetate. Compute the actual concentration from analyte density.
7. Nitrogen, purified.
8. Hydrogen, purified.
9. Air, filtered.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID; two sections (front = 100 mg; back= 50 mg) of pre-extracted 50/80 mesh Porapak QS held in place and separated by silanized glass wool plugs. Tubes are commercially available (SKC, Inc. #226-59-09, or equivalent).
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Refrigerant, bagged ("Blue Ice," or equivalent).
4. Gas chromatograph, NPD, integrator, and column (page 2506-1 and APPENDIX).
5. Vials, 2-mL, glass, PTFE-lined crimp caps.
6. Ultrasonic bath, water.
7. Syringe, 10-µL, readable to 0.1 µL.
8. Pipet, 1-mL, with pipet bulb.
9. Spatula.

SPECIAL PRECAUTIONS: Acetone cyanohydrin is extremely toxic; it is readily decomposed by water to form hydrogen cyanide and acetone. Perform all work with the analyte in a hood. Avoid dermal contact with acetone cyanohydrin. It is readily absorbed through the skin and will decompose in the body, with release of HCN, to induce cyanosis [3].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.1 and 0.2 L/min for a total sample size between 0.3 and 12 L.
4. Cap the samplers with PTFE tape and plastic (not rubber) caps. Pack the samplers in a plastic bag containing bagged refrigerant. Ship in a refrigerated container at 0 °C.

SAMPLE PREPARATION:

5. Bring the samples to room temperature before uncapping. Remove the end caps from the sorbent tube.
6. Remove the front glass wool plug. Place it in a vial along with the front (larger) sorbent section. Transfer the separating glass wool plug along with the back sorbent section to a separate vial.
7. Add 1.0 mL ethyl acetate to each vial. Attach crimp cap to each vial.
8. Agitate the samples in an ultrasonic waterbath for 60 min.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards over the range 0.1 to 50 µg acetone cyanohydrin per sample.
   a. Add aliquots of calibration stock solution or a serial dilution thereof to 1.0 mL ethyl acetate in 2-mL vials. Attach crimp cap to each vial.
   b. Analyze together with samples and blanks (steps 12 and 13).
   c. Prepare calibration graph (peak area vs. µg acetone cyanohydrin).

10. Determine desorption efficiency (DE) at least once for each lot of samplers used for sampling in the calibration range (step 9). Prepare three tubes at each of five levels plus three media blanks.
    a. Remove and discard back sorbent section of a media blank sampler.
    b. Inject a known amount of calibration stock solution or a serial dilution thereof directly onto front sorbent section with a microliter syringe.
    c. Cap the tube. Allow to stand overnight.
    d. Desorb (steps 6 through 8) and analyze together with working standards and blanks (steps 12 and 13).
    e. Prepare a graph of DE vs. µg acetone cyanohydrin recovered.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

12. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2506-1. Inject sample aliquot manually using solvent flush technique, or auto sampler. t_r = 3.2 min under these conditions.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the sample solution with ethyl acetate, reanalyze and apply the appropriate dilution factor in calculations.
13. Measure peak area.

CALCULATIONS:

14. Determine the mass, µg (corrected for DE), of acetone cyanohydrin found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of acetone cyanohydrin in the air volume sampled, V (L):

$$C = \frac{W_f + W_b - B_f - B_b}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD [1]:

Calibration curve: Over the range 2.5 to 250 ng acetone cyanohydrin injected (0.5 to 50 µg per sample), the correlation coefficients of NPD response with mass injected ranged from 0.998 to 0.999 for peak height and from 0.990 to 0.996 for peak area.

Recovery of spiked samples after storage for one week at room temperature was ≥98% over the range 0.5 to 50 µg per sample. Independent verification of sample concentrations generated dynamically was not possible. The method was evaluated by evaporating 1, 10, or 50 µg of analyte from U-tubes onto the sorbent tube. Three liters of humid air (RH = 80%) were then drawn through the tube at 0.2 L/min for 15 min. Two sets of six samples at each level were generated. One set of six samples at each level was stored for one day at room temperature. The other sample sets were stored for five to seven days at 0 °C. Recovery was ≥ 89% (S_r = 10.6%). Experiments also showed that storage of 1 or 10 µg samples collected as above, but stored at ambient temperature for four days, gave recoveries of 62 to 80%.

A maximum of 2% mass breakthrough to the backup section was obtained when 10 to 100 µg aliquots of analyte were evaporated from U-tubes into a stream of humidified air (RH = 80%) onto the sorbent at 0.2 L/min for 60 min. Recovery from the primary sorbent section for all samples was ≥ 92%.

REFERENCES:

[1] Glaser, R. and P. Fey. Development of a Quantitative Sampling and Analytical Method for Acetone Cyanohydrin in Air (1981), available as Order No. PB 83-139-444 from NTIS, Springfield, VA 22161.
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 7, P&CAM 340, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-141 (1981).
[3] Criteria for a Recommended Standard...Occupational Exposure to Nitriles, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-212 (1978).

METHOD WRITTEN BY:

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APPENDIX: COLUMN PREPARATION AND GC MODIFICATION

1. Stationary phase preparation:

Weigh 10 g Chromosorb T into a glass Petri dish or small bowl. Dissolve 0.5 g OV-17 in 50 mL acetone; pour this solution over the Chromosorb T. Using a small spatula, slowly stir the stationary phase into the solution while evaporating the solvent away under a stream of nitrogen. Avoid crushing the soft Chromosorb T. A portion of the coated Chromosorb T will adhere to the glass; do not attempt to recover this material. Continue to stir the support into the solution until the solvent has completely evaporated. After the solvent has evaporated, allow the coated Chromosorb T to dry completely under the nitrogen stream. Refrigerate the coated Chromosorb T at 0 °C until it is packed into the GC column.

2. Column preparation, GC modification:

Although the column dimensions are 2 m long × 3.2-mm OD, a longer piece of PTFE tubing (2.3 m) should be used in order to allow fitting to the chromatograph. Measure the length of the injector zone from the injector port to the point of column attachment in the oven. Push a plug of silanized glass wool this distance (about 10 to 20 cm) into the front (injector) end of the column. Add the packing material from the other end of the column under vacuum to a point about 1 cm before the detector end of the column. A 2-m column requires ca. 5 g of packing material. Seal the detector end of the column with a 0.5-cm plug of silanized glass wool. If it is necessary to replace transfer lines (see below), do not fill the column completely; leave about 1 cm open at the detector end after insertion of the glass wool. Use plastic (nylon, PTFE, etc.) compression fittings to connect the column to the instrument. Slide the injection port compression fittings onto the column directly over the silanized glass wool plug. Remove the septum retainer fitting, the septum, and the injector liner from the GC injection port. Push the empty end of the column through the oven side of the injection port to the point where it is just flush with the external port opening. If the column is made from thin-walled PTFE tubing, do not tighten the compression fitting over the soft column packing; otherwise, the Chromosorb T may be crushed and a plug may develop that will block carrier flow. Trim any column overhang away from the outer edge of the injection port. It may be necessary to slide a small piece of oversize glass or PTFE tubing over the column into the injection port in order to center the column with the septum retainer fitting. Be careful not to block any holes drilled in the port for carrier flow. Gently tighten the compression fitting around the column over the glass wool plug. Replace the septum and septum retainer fitting.

Because the analyte is thermally labile, it must not contact hot metallic or glass surfaces in the gas chromatograph. To eliminate this contact, push the end of the column into the detector port up to the detector itself. If the design of the instrument does not permit the column to be pushed up to the detector, the transfer line from the end of the column to the detector must be replaced with low dead-volume PTFE tubing. Use a 1.6-mm ID × 2.6-mm OD × 1 cm long PTFE plug to seal the detector end of

the column. Determine the length of transfer line needed from the column end fitting to the bottom of the detector jet. Force a piece of 1.6-mm OD PTFE tubing equal to this length plus the length of the PTFE plug, through the center to the back end of the plug. Insert the PTFE plug, back end first, into the opening at the detector end of the column. Push the compression fitting over the column where the PTFE plug was inserted. Attach the column to the chromatograph, pushing the transfer line as close as possible to the bottom of the detector jet. Gently tighten the compression fitting around the column. Once the column has been installed in the instrument, pressurize it with nitrogen. Check the column for a flow of 33 mL/min. Check the compression fittings for leaks; gently tighten them as necessary. After it has been determined that there is flow through the column, condition it at 125 °C for 1 to 2 h. A diagram of a column where the transfer line has been replaced is shown in Figure 1.

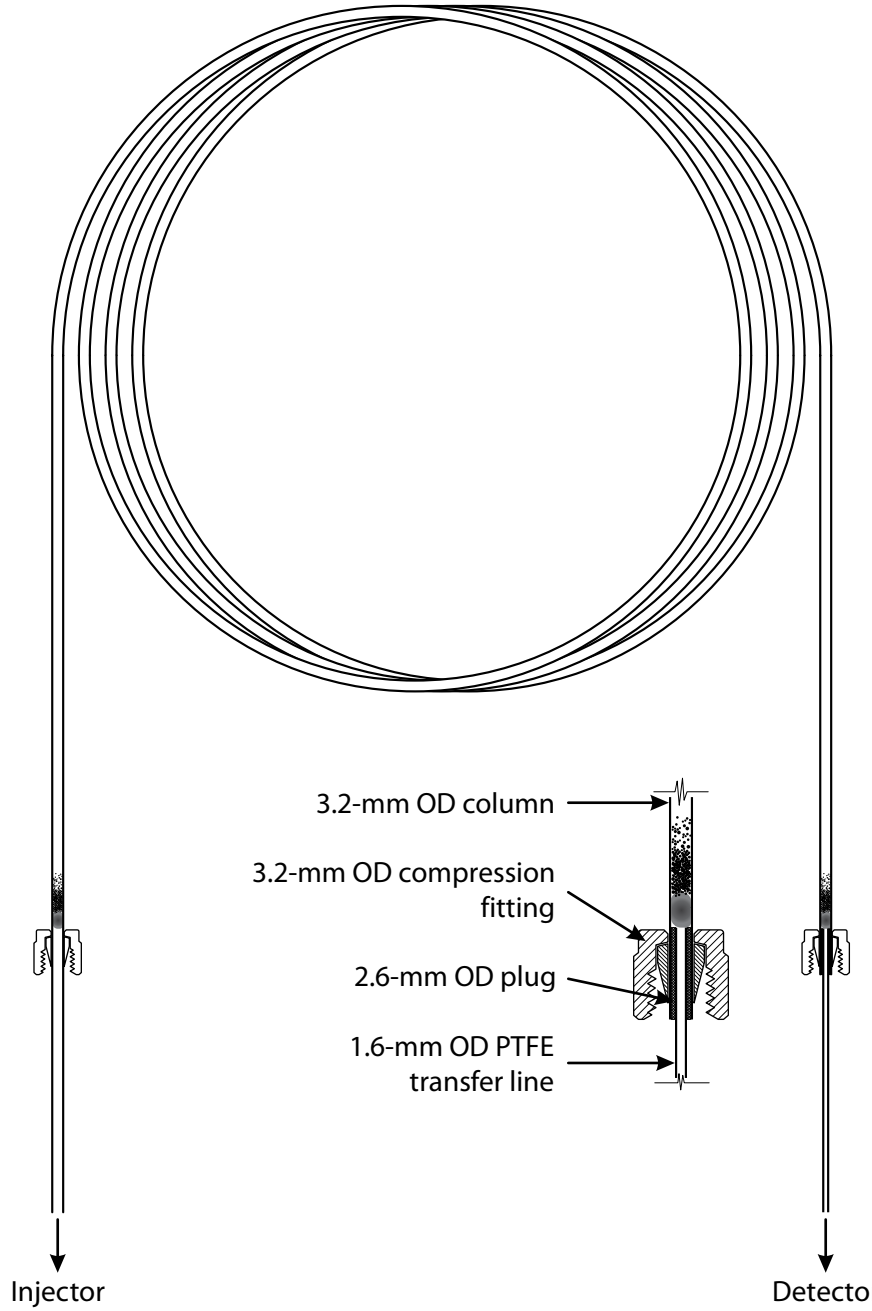

Figure 1. All-PTFE gas chromatograph system used for the determination of acetone cyanohydrin.