

HYDROGEN CYANIDE

6017

HCN

MW: 27.03

CAS: 74-90-8

RTECS: MW6825000

METHOD: 6017, Issue 1

EVALUATION: PARTIAL

Issue 1: 15 March 2003

OSHA: 10 ppm (skim)
NIOSH: STEL 4.7 ppm
ACGIH: C 10 ppm (skin)
 (1 ppm = 1.105 mg/m³)

PROPERTIES: gas; BP 26 °C; vapor density 0.93 (air = 1.00); d(liq) 0.69 g/mL @ 20 °C; VP 82.7 kPa (620 mm Hg) @ 20 °C; explosive range 5 to 40% v/v in air

SYNONYMS: hydrocyanic acid, prussic acid, formonitrile

| SAMPLING | MEASUREMENT |
|--|--|
| <p>SAMPLER: SOLID SORBENT TUBE (soda lime, 600 mg/200 mg) + glass fiber filter, 5-mm</p> <p>FLOW RATE: 0.05 to 0.2 L/min</p> <p>VOL-MIN: 2 L @ 5 ppm -MAX: 90 L</p> <p>SHIPMENT: routine</p> <p>SAMPLE STABILITY: at least 2 weeks @ 25 °C [1]</p> <p>BLANKS: 2 to 10 field blanks per set</p> | <p>TECHNIQUE: ION CHROMATOGRAPHY (IC) / DC AMPEROMETRY</p> <p>ANALYTE: CN⁻</p> <p>DESORPTION: 10 mL deionized water; agitate; let stand 60 min</p> <p>INJECTION LOOP VOLUME: 50 µL</p> <p>ELUENT: 0.5 M NaAc 0.1 M NaOH 0.5% ethylenediamine</p> <p>COLUMNS: HPIC-AS7 or equivalent anion separator, HPIC-AG7 or equivalent anion micro guard</p> <p>DETECTOR: 0.0 V applied Ag⁰ vs. AgCl reference</p> <p>CALIBRATION: standard solutions of KCN in 0.1 N NaOH</p> <p>RANGE: 10 to 300 µg CN⁻ per sample [2]</p> <p>ESTIMATED LOD: 1 µg CN⁻ per sample [2]</p> <p>PRECISION (S_r): 0.041</p> |
| ACCURACY | |
| <p>RANGE STUDIED: not determined</p> <p>BIAS: not determined</p> <p>OVERALL PRECISION (S_r): not determined</p> <p>ACCURACY: not determined</p> | |

APPLICABILITY: The working range is 0.3 to 235 ppm (0.3 to 260 mg/m³) for a 3-L air sample. This method is applicable to STEL measurements. Particulate cyanides are trapped by the initial glass fiber membrane disk. This method is more sensitive and subject to fewer interferences than NIOSH Method 7904, which uses ion-specific electrode analysis [3].

INTERFERENCES: A high concentration of hydrogen sulfide gives a negative interference. Any component with the same retention time as cyanide will interfere.

OTHER METHODS: This method is based on NIOSH 6010 which uses the same collection procedure with a VISIBLE ABSORPTION detection system [4]. The method has been adapted for use with a Technicon Autoanalyzer [5]. NIOSH Method 7904 uses an ion-specific electrode for measurement and has been used to determine HCN in firefighting environments [6].

REAGENTS:

1. Potassium cyanide, reagent grade.*
2. Sodium acetate trihydrate, A.C.S. grade.
3. Ethylenediamine, 99%.
4. Sodium hydroxide (NaOH), reagent grade.*
5. Sodium lime (CaO + 5 to 20% NaOH), reagent grade (Aldrich #26,643-4, or equivalent). Crush and sieve to 10/35 mesh. Store in capped container.*
6. Water, deionized or distilled.
7. Sodium hydroxide solution, 0.1 N.*
8. Calibration stock solution. 1 mg/mL CN⁻: Dissolve 0.125 g KCN in 0.1 N NaOH in a 50-mL volumetric flask. Dilute to mark with 0.1 N NaOH. Standardize by titration with standard AgNO₃ solution (see APPENDIX).
9. Eluent, 0.5 M sodium acetate, 0.1 M NaOH, 0.5% ethylenediamine: Dissolve 60 g sodium acetate + 4 g NaOH pellets in 800 mL H₂O. Add 5 mL ethylenediamine. Bring to 1 L with distilled water.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: Glass tube, 9 cm long, 7-mm OD, 5-mm ID, with plastic caps, containing two sections (front = 600 mg; back = 200 mg) granular soda lime 10/35 mesh, separated and contained with silanized glass wool plugs, with a 5-mm diameter glass fiber filter disk placed before the plug on the inlet side (SKC, Inc. 226-28, or equivalent).
2. Personal sampling pump, 0.05 to 0.2 L/min, with flexible connecting tubing.
3. DIONEX DX-500 or equivalent ion chromatograph.
4. DIONEX ED-40 or equivalent electrochemical detector.
5. DIONEX or equivalent amperometry cell with silver working electrode and silver chloride reference.
6. DIONEX AS7 column with AG7 guard column or equivalent.
7. Autosampler.
8. Autosampler vials.
9. Vials, 15- to 20-mL, for sample preparation.
10. In-line filters, 0.45-µm.
11. Micropipettors with disposable tips.
12. Flasks, volumetric, 25-, 50-, 100-, 1000-mL, with stoppers
13. Pipettes, transfer, disposable.

SPECIAL PRECAUTIONS: HCN gas and cyanide particulates are highly toxic and may be fatal if swallowed, inhaled, or absorbed through the skin [7]. Soda lime and NaOH are very caustic [7]. Use gloves and a fume hood when handling these chemicals.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.05 and 0.2 L/min for a total sample size of 0.6 to 90 L.
4. Cap tube. Pack securely for shipment.

SAMPLE PREPARATION:

5. Score each sampler with a file. Break sampler at score line.
6. Transfer front and back sorbent sections to separate vials. Discard glass wool plugs separating and retaining sorbent sections.

NOTE: An estimate of particulate cyanide may be obtained by analyzing the initial glass fiber filter disk as follows; however, no evaluation data are available for particulate cyanides determined in this manner:

- a. Transfer the glass fiber disk and glass wool plug immediately behind it at the tube inlet to a third vial.
- b. Add 10.0 mL 0.1 N NaOH to each vial.
- c. Proceed with step 8.

7. Add 10.0 mL deionized-distilled water to each vial containing a sorbent section and cap.
8. Allow to stand 60 minutes, with occasional agitation. Transfer to a 10-mL plastic syringe fitted with an in-line 0.45- μm filter. Collect the filtrate in a clean vial. (If samples are allowed to stand for a period of time filtration may not be necessary.)

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards over the range 1 to 250 $\mu\text{g CN}^-$ per sample.
 - a. Prepare a working standard solution, 1.00 $\mu\text{g/mL CN}^-$, by diluting 100 μL of calibration stock solution to 100 mL with 0.1 N NaOH.
 - b. Pipet 0.5-, 1.00-, 1.50-, 2.00-, and 2.50-mL of the working standard solution into 25-mL volumetric flasks to produce 0.5-, 1.00-, 1.50-, 2.00-, and 2.50- $\mu\text{g CN}^-$ standards
 - c. Analyze together with field samples and blanks (steps 12 through 14).
 - d. Prepare calibration graph (peak height in nA vs. $\mu\text{g CN}^-$).
10. Determine desorbent efficiency (DE) at least once for each lot of soda lime used for sampling. Prepare at least three tubes at each of five levels plus three media blanks.
 - a. Remove and discard back sorbent section of a blank sampler.
 - b. Inject a known amount of calibration stock solution directly onto the soda lime with a microliter syringe.
 - c. Cap and allow to stand overnight.
 - d. Desorb (steps 5 through 8) and analyze together with working standards and blanks (steps 12 through 14).
 - e. Prepare a graph of DE vs. $\mu\text{g CN}^-$ 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 ion chromatograph according to manufacturer's instructions to conditions given on page 6017-1.
13. Inject 50- μL sample aliquot. For manual operation, inject 2 to 3 mL of sample from filter/syringe to ensure complete rinse of sample loop.

NOTE: All samples, eluents, and water flowing through the IC must be filtered to avoid plugging system valves or columns.
14. Measure peak height.

NOTE: If sample peak height exceeds linear calibration range, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.

CALCULATIONS:

15. Calculate the mass, μg , of CN^- in an aliquot analyzed. Apply the appropriate aliquot factor to calculate the mass, μg , of CN^- in the original 10-mL solution.
16. Determine the mass, $\mu\text{g CN}^-$ (corrected for DE), 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. If $W_b > W_f/10$, report breakthrough and possible sample loss.
17. Calculate concentration, C, of HCN in the air volume sampled V(L).

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 1.039}{V}, \text{mg / m}^3$$

where 1.039 = conversion factor, CN^- to HCN

NOTE: $\mu\text{g/L} \equiv \text{mg/m}^3$

EVALUATION OF METHOD:

Only the analytical procedure was evaluated for this method. The sampler, the soda lime tube, was evaluated for NIOSH method 6010 by sampling the test atmospheres of HCN generated from a compressed mixture of HCN in nitrogen [1]. The range of HCN concentration was equivalent to 2 to 15 mg/m³ for a 3-L air sample. Twenty-two samples collected at 0.2 L/min for 15 minutes indicated overall precision \bar{S}_{RT} of 0.076 with nearly 100% recovery. Breakthrough occurred after 40 minutes of sampling at a flow rate of 0.2 L/min at an HCN concentration of 148 mg/m³. Sample tubes spiked with solutions of KCN and analyzed after storage indicated that the samples of cyanide ions were stable on the tube for at least 2 weeks. Analysis of 22 tubes which were spiked with KCN standard solutions in the range 10 to 50 µg indicated a recovery of nearly 100% with a pooled precision of 0.041. Desorption efficiency may be poor, below 10 µg CN⁻ [6].

This ion chromatographic (IC) procedure for the determination CN⁻ was developed by Wisconsin Occupational Health Laboratory (WOHL) in 1997 [2]. Desorption, quantifiable limit, and linear range were investigated and found comparable to method 6010. WOHL also demonstrated that recovery below 10 µg was questionable.

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METHOD WRITTEN BY:

LeRoy Dobson, Wisconsin Occupational Health Laboratory, Madison, WI.

APPENDIX: STANDARDIZATION OF CALIBRATION STOCK SOLUTION

Titrate an aliquot of the cyanide standard stock solution (Reagent 12) with standard silver nitrate (AgNO_3) solution. The end point is the first formation of a white precipitate, $\text{Ag}[\text{Ag}(\text{CN})_2]$. Calculate the cyanide concentration with the following equation:

$$M_c = 52.04 V_a (M_a/V_c)$$

Where:

- M_c = cyanide concentration (mg/mL).
- V_a = volume (mL) of standard silver nitrate solution.
- M_a = concentration (moles/L) of standard silver nitrate solution.
- V_c = volume (mL) of calibration stock solution titrated.