HYDROGEN CYANIDE

HCN MW: 27.03 CAS: 74-90-8 RTECS: MW6825000

METHOD: 6010, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
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OSHA : 10 ppm (skin)
NIOSH: STEL 4.7 ppm
ACGIH: C 10 ppm (skin)
(1 ppm = 1.105 mg/m^3 @ NTP)

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

SAMPLER: SOLID SORBENT TUBE (soda lime, 600 mg/200 mg)

FLOW RATE: 0.05 to 0.2 L/min

VOL-MIN: 2 L @ 5 ppm
-MAX: 90 L

SHIPMENT: routine

SAMPLE STABILITY: at least 2 weeks @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 2 to 15 mg/m^3 [1] (3-L samples)

BIAS: Not significant

OVERALL PRECISION ($\hat{S}_{rT}$): 0.076 [1]

ACCURACY: ± 15.0%

MEASUREMENT

TECHNIQUE: SPECTROPHOTOMETRY, VISIBLE ABSORPTION

ANALYTE: cyanide ion complex

DESORPTION: 10 mL deionized water; stand 60 min

COLOR DEVELOPMENT: N-chlorosuccinimide/ succinimide oxidizing agent and barbituric acid/pyridine coupling agent; absorption @ 580 nm in 1-cm cuvette

CALIBRATION: standard solutions of KCN in 0.1 N NaOH

RANGE: 10 to 300 µg CN^- per sample [1]

ESTIMATED LOD: 1 µg CN^- per sample [1]

PRECISION ($\hat{S}_r$): 0.041 @ 10 to 50 mg per sample [1]

APPLICABILITY: The working range is 0.3 to 235 ppm (3 to 260 mg/m^3) 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. The method was used to determine HCN in firefighting environments [2].

INTERFERENCES: A high concentration of hydrogen sulfide gives a negative interference.

OTHER METHODS: This is based on the method of Lambert, et al. [3]. NIOSH Method 7904 uses an ion specific electrode for measurement. The method has been adapted for use with a Technicon Autoanalyzer [4].

REAGENTS:

1. Potassium cyanide*, reagent grade.
2. Succinimide, reagent grade.
3. N-Chlorosuccinimide, reagent grade.
4. Barbituric acid, reagent grade.
5. Pyridine, spectrophotometric quality.
6. Phenolphthalein, 1% (w/v) in ethanol or methanol, reagent grade.
7. Hydrochloric acid, concentrated, reagent grade.
8. Sodium hydroxide (NaOH), reagent grade.*
9. Sodium lime (CaO + 5-20% NaOH), reagent grade (Aldrich #26,643-4 or equivalent). Crush and sieve to 10/35 mesh. Store in capped container.*
10. Water deionized-distilled.
11. Sodium hydroxide solution, 0.1 N.*
12. 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 $AgNO_3$ solution (see APPENDIX).
13. Hydrochloric acid solution, 0.15 N.
14. N-Chlorosuccinimide/succinimide oxidizing reagent. Dissolve 10.0 g succinimide in about 200 mL distilled water. Add 1.00 g N-chlorosuccinimide. Stir to dissolve. Adjust volume to 1 liter with distilled water. Stable 6 months when refrigerated.
15. Barbituric acid/Pyridine reagent. Add about 30 mL distilled water to 6.0 g barbituric acid in a 100-mL Erlenmeyer flask. Slowly add 30 mL pyridine with stirring. Adjust the volume to 100 mL with water. Stable 2 months when refrigerated.

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 inlet side. Tubes are commerically available. (SKC, Inc. 226-28 or equivalent.)
2. Spectrophotometer, visible, 580 nm, with cuvettes, 1-cm light path.
3. Personal sampling pump, 0.05 to 0.2 L/min, with flexible connecting tubing.
4. Pipets, volumetric 0.1-, 0.5-, 1.0-, 2.0-, 10.0-mL.
5. Vials, glass or plastic, 15-mL with PTFE-lined caps.
6. Flasks, volumetric, 25-, 50-, 100-, 1000-mL, with stoppers.
7. Pipets, transfer, disposable.
8. Syringes, 10-µL, readable to 0.1 µL.
9. Flask, Erlenmeyer, 100-mL.
10. Syringes, 10-mL, polyethylene with luer tip.
11. Filter cassette, with membrane filter, 13-mm diameter, 0.45-µm pore size, with luer fitting.

* See SPECIAL PRECAUTIONS

SPECIAL PRECAUTIONS: HCN gas and cyanide particulates are highly toxic and may be fatal if swallowed, inhaled, or absorbed through the skin [5]. Soda lime and NaOH are very caustic [5]. Use gloves and a fume hood for 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.
   (i) Transfer the glass wool plug at the tube inlet and the glass fiber filter disk immediately behind it to a third vial.
   (ii) Add 10.0 mL 0.1 N NaOH to each vial.
   (iii) Proceed with step 8.
7. Add 10.0 mL deionized-distilled water to each vial containing a sorbent section. Cap each vial.
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.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards over the range 1 to 300 µg CN^- per sample.
   a. Prepare a working standard solution, 1.00 µg /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 make 0.50-, 1.00-, 1.50-, 2.00- and 2.50- µg CN^- standards.
   c. Analyze together with field samples and blanks (steps 12 through 19).
   d. Prepare calibration graph (absorbance vs. µg CN^-).
10. Determine desorption 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 19).
   e. Prepare a graph of DE vs. µg 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 spectrophotometer according to manufacturer's recommendations and to conditions on p. 6010-1.
13. Pipet a sample aliquot estimated to contain 0.5 to 2.5 µg CN^- into a 25-mL volumetric flask. Alternately, to cover an unknown sample concentration range, pipet 0.5-, 1.00-, and 3.00-mL aliquots into separate 25-mL vol. flasks for each field sample. Larger or smaller aliquots may be taken, based on prior knowledge of expected analyte level.
14. Pipet 0.5 mL 0.1 N NaOH into a 25-mL volumetric flask for reagent blank.
15. Add one drop phenolphthalein solution to each standard or sample.
   NOTE: Add a little deionized-distilled water to increase volume for easier mixing. All solutions should be alkaline (pink) at this point.
16. Starting with the reagent blank, add dropwise 0.15 N HCl, with mixing, until pink color just disappears. CAUTION: HCN may be produced. Work in hood. Immediately add 1.0 mL N-chlorosuccinimide/succinimide oxidizing reagent. Mix and let stand.

NOTE 1: To avoid possible loss of HCN, add the oxidizing agent before proceeding to the next sample.

NOTE 2: Do not prepare more samples than can be analyzed within the 30-minute maximum time for color development.

17. After at least 5 min. standing (but not longer than 15 min), starting with the reagent blank, add 1.0-mL barbituric acid-pyridine coupling reagent. Mix.
18. Adjust sample volume to 25 mL with deionized-distilled water and allow to stand at least 12 min (but not longer than 30 min) for color development.
19. Read absorbance at 580 nm in a 1-cm light path cuvette on a spectrophotometer. If sample absorbance is outside the range of the calibration standards, take an aliquot, re-analyze (steps 12 through 19), and apply the appropriate aliquot factor in calculations.

CALCULATIONS:

20. Calculate the mass, µg, of CN^- in aliquot analyzed. Apply the appropriate aliquot factor to calculate the mass, µg, of CN^- in the original 10-mL solution.
21. Determine the mass, µg 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.
22. 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

EVALUATION OF METHOD:

The method was evaluated 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/m^3 for a 3-L air sample. Twenty-two samples collected at 0.2 L/min for 15 minutes indicated overall precision $\hat{S}_{rT}$ of 0.076 with nearly 100% recovery. Breakthrough occurred after 40 minutes of sampling at the flow rate of 0.2 L/min at an HCN concentration of 148 mg/m^3. 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].

REFERENCES:

[1] Williamson, George. "Method Development Protocol and Backup Data Report on Hydrogen Cyanide"
Internal NIOSH/MRSB Report, Unpubl. NIOSH (1988).
[2] Williamson, George. "Analysis of Air Samples on Project 166 (Firesmoke) on HCN; Sequence NIOSH/MRSB-6366A, Unpubl. NIOSH, (1988).
[3] Lambert, J. L., Ramasamy, J., and J. V. Paukstelis, "Stable Reagents for the Colorimetric Determination of Cyanide by Modified Konig Reactions," Analyt. Chem., 47, 916-918 (1975).
[4] DataChem Laboratories, NIOSH Sequence #6837-K (unpublished, March 21, 1990).
[5] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services. Publ. (NIOSH) 81-123 (1981), available as stock #PB 83-154609 form NTIS, Springfield, VA 22161.
[6] DataChem Laboratories, User Check, NIOSH Sequence #6837-J (unpublished, March 19, 1990).

METHOD WRITTEN BY: George Williamson, NIOSH/DPSE.

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, $Ag[Ag(CN)_2]$. 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