HYDROGEN CYANIDE 6010

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

METHOD: 6010, Issue 3 **EVALUATION:** FULL **Issue 1:** 16 May 1989
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OSHA: 10 ppm (11 mg/m^3) (skin)
NIOSH: STEL 4.7 ppm (5 mg/m^3) (skin)
IDLH: 50 ppm [1]
OTHER OELs: Refs. [2, 3]

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), with glass fiber pre-filter

FLOW RATE: 0.025 to 0.05 L/min

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

SHIPMENT: routine

SAMPLE STABILITY: at least two weeks at 25 °C [4]

BLANKS: 3 field blanks min. per set

ACCURACY

RANGE STUDIED: 2 to 15 mg/m^3 (3-L samples) [4]

BIAS: negligible

OVERALL PRECISION ($\hat{S}_{rT}$): 0.076 [4]

ACCURACY: ±15%

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 1 M NaOH

RANGE: 10 to 300 µg CN^- per sample [4]

ESTIMATED LOD: 1 µg CN^- per sample [4]

PRECISION ($\bar{S}_r$): 0.041 @ 10 to 50 µg CN^- per sample [4]

APPLICABILITY: The method is applicable to STEL measurements of HCN gas. The working range is 0.3 to 235 ppm (3 to 260 mg/m^3) for a 3-L air sample. Particulate cyanides are trapped by an initial glass fiber filter (pre-filter) that precedes the sorbent tube. This method is more sensitive and subject to fewer interferences than NIOSH Method 7904 [5], which uses ion specific electrode analysis. The method has been used to measure HCN in firefighting environments [6].

INTERFERENCES: A high concentration of hydrogen sulfide (H_2S) can cause a negative interference by reaction with cyanide to form thiocyanate.

OTHER METHODS: The procedure is based on the method of Lambert et al. [7]. NIOSH Method 7904 relies on the use of ion selective electrodes for measurement of CN^- [5]. A related method, which employs diffusive sampling onto soda lime sorbent, followed by desorption and ion chromatography with electrochemical detection, has been promulgated by OSHA [8].

REAGENTS:

1. Potassium cyanide,* reagent grade.
2. Succinimide, reagent grade.
3. N-Chlorosuccinimide, reagent grade.
4. Barbituric acid, reagent grade.
5. Pyridine, spectroscopic quality.
6. Phenolphthalein, 1% (w/v) in ethanol or methanol, reagent grade.
7. Hydrochloric acid, conc., reagent grade.
8. Sodium hydroxide, reagent grade.
9. Soda lime (CaO + 5-20% NaOH), reagent grade. Crush and sieve to 10/35 mesh; store in a sealed container.
10. Water, deionized (18 MΩ-cm).
11. NaOH solution, 0.1 M.
12. Calibration stock solution, 1 mg/mL CN^-: Dissolve 0.125 g KCN in ≈40 mL 0.1 M NaOH in a 50-mL volumetric flask. Dilute to the mark with 0.1 M NaOH. Standardize by titration with $AgNO_3$ (see APPENDIX).
13. HCl solution, 0.15 M.
14. N-Chlorosuccinimide/succinimide oxidizing reagent: Dissolve 10.0 g succinimide in ≈200 mL deionized (DI) water. Add 1.00 g N-chlorosuccinimide; agitate to dissolve. Adjust volume to 1 L with DI H_2O. Solution is stable for 6 months when kept at ≈4 °C.
15. Barbituric acid/pyridine reagent: Add ≈30 mL DI H_2O to 6.0 g barbituric acid in a 100-mL Erlenmeyer flask. Slowly add 30 mL pyridine with stirring. Adjust volume to 100 mL with DI H_2O. Solution is stable for 2 months when kept at ≈4 °C.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, length 9 cm, 7-mm OD/5-mm ID, with plastic caps, containing two sorbent sections of granular soda lime 10/35 mesh (front = 600 mg; back = 200 mg), separated by and contained within silanized glass wool plugs. A 5-mm dia. glass fiber filter is placed before the inlet.
   NOTE: Tubes are commercially available.
2. Spectrophotometer, Visible (580 nm), with 1-cm light path cuvettes.
3. Personal sampling pump, 0.025-0.05 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 polytetrafluoroethylene (PTFE)-lined caps.
6. Flasks, volumetric, 25-, 50-, 100-, and 1000-mL, with stoppers.
7. Pipets, transfer, disposable.
8. Laboratory wipes.
9. Syringes, 10-mL, polyethylene with Luer tip readable to 0.1 µL.
10. Flask, Erlenmeyer, 100-mL.
11. Luer-lock PTFE membrane filters, 13-mm dia., 0.45-µm pore size, to fit onto 10-mL syringes.

SPECIAL PRECAUTIONS: HCN gas and cyanide are highly toxic and may be fatal if swallowed, inhaled or absorbed through skin [1]. Soda lime and NaOH are very caustic [1]. Wear appropriate personal protection during sampling activities and analysis. It is essential that suitable gloves, eye protection, laboratory coat, etc., be used when working with these chemicals. Perform sample preparation and analysis in a clean, well-ventilated area that is well removed from any possible contamination.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in the line.
2. Break both ends of the sampling tube immediately prior to sampling. Attach the glass fiber filter to the inlet of the sorbent tube. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.025 and 0.05 L/min (e.g., 0.033 L/min) for a total sample size of 0.6 to 90 L.

4. Remove the sorbent tube from the sampling apparatus, cap both ends and pack securely for shipment to the laboratory. Discard the pre-filter.

SAMPLE PREPARATION:

5. Score each sample tube with a file and break sampler at the score line.
6. Transfer front and back sorbent sections to separate 15-mL vials. Discard glass wool plugs.
7. Add 10.0 mL DI H_2O to each vial containing a sorbent section. Seal each vial.
8. Allow to stand 60 min. with occasional agitation. Transfer to a 10-mL plastic syringe fitted with a 0.45-µm PTFE filter, and collect the filtrate in a clean vial.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standard solutions 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 M NaOH.
   b. Pipet 0.50, 1.00, 1.50, 2.00, and 2.50 mL of the working standard solution into 25-mL volumetric flasks to make up 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 an unused (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 18).
    e. Prepare a graph of DE vs. µg CN^- recovered.
11. Analyze at least three quality control blind spikes and at least three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

12. Set spectrophotometer to record absorbance at 580 nm.
13. Pipet a sample aliquot estimated to contain 0.5 to 2.5 µg CN^- into a 25-mL volumetric flask. Alternatively, to cover an unknown sample range, pipet 0.50-, 1.00- and 3.00-mL aliquots into separate 25-mL volumetric flasks for each field sample. Larger or smaller aliquots may be taken, based on prior knowledge of the expected analyte level.
14. Pipet 0.5 mL 0.1 M NaOH into a 25-mL volumetric flask for each standard or sample.
15. Add one drop of phenolphthalein solution to each standard and sample.
    NOTE: Add a small portion of DI H_2O to increase volume for easier mixing. All solutions should be alkaline (pink) at this juncture.
16. Starting with the reagent blank, add 0.15 M HCl dropwise, with mixing, until reaching the point at which the pink color just disappears. CAUTION: HCN may be produced, so this step must be carried out in a fume 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 of barbituric acid/pyridine coupling reagent and mix.

18. Adjust sample volume to 25 mL with DI H_2O and allow to stand for at least 12 min (but no longer than 30 min.) for color development.
19. Using the spectrophotometer, read the absorbance at 580 nm using a 1-cm light path cuvette. If sample absorbance is outside the range of the calibration standards, remove an aliquot, dilute and reanalyze. Apply appropriate dilution factor in calculations.

CALCULATIONS:

20. From the absorbance readings, calculate the mass of CN^- (µg) in each aliquot analyzed. Apply the appropriate dilution factor to calculate the mass of CN^- (µg) in the original 10-mL solution.
21. Determine the mass of CN^- (µg), corrected for desorption efficiency (DE), found in the front (W_f) and back (W_b) sections of the sorbent tube. Also determine the average background mass of 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 the concentration, C, of HCN in the air volume sampled, V(L):

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

(where 1.039 = conversion factor for CN^- to HCN).

EVALUATION OF METHOD:

The method was initially evaluated by sampling test atmospheres of HCN generated from a compressed gas mixture of HCN in nitrogen [4]. The range of HCN concentrations was equivalent to 2 to 15 mg/m^3 for a 3-L air sample. For 22 samples, an overall precision $\hat{S}_{rT}$ of 0.076 was obtained with nearly 100% recovery. Breakthrough was observed to occur at [HCN] ≈150 mg/m^3 for sample volumes ≈10 L. Sample tubes spiked with KCN standard solutions (n=22) in the range of 10 to 50 µg per sample indicated recoveries of nearly 100% with a pooled precision $\bar{S}_r$ of 0.041. Sample tubes similarly spiked with KCN solutions were analyzed after storage and demonstrated that the samples were stable for at least two weeks. Sample collection of [HCN] in nitrogen of 130 mg/m^3 at 50 mL/min for 7.3 minutes (0.36 L sample volume) resulted in quantitative recoveries [9]. Further evaluation of the method was carried out in test atmospheres of HCN generated in air of low (20%) and high (80%) relative humidity [9]. It was found that a sampling rate of 50 mL/min resulted in quantitative recoveries for HCN concentrations at 0.1 – 2× the OSHA PEL, while sampling at 200 mL/min gave recoveries <90% in this concentration range; similar results were obtained for both low and high humidity conditions. In consideration of these observations, the maximum sampling flow rate recommended for the method is 0.05 L/min.

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APPENDIX: STANDARDIZATION OF CYANIDE CALIBRATION STOCK SOLUTION

Titrate an aliquot of the cyanide standard stock solution (KCN in NaOH) with standard silver nitrite ($AgNO_3$) solution. The end point is the first formation of a white precipitate, $Ag[Ag(CN)_2]$. Calculate the cyanide concentration by using the following equation:

$$M_c = 52.04 * V_a * \left(\frac{M_a}{V_c}\right)$$

where: M_c = cyanide concentration (mg/mL)
V_a = volume (mL) of standard $AgNO_3$ solution
M_a = concentration (moles/L) of standard $AgNO_3$ solution
V_c = volume (mL) of cyanide calibration stock solution titrated