

REAGENTS:

1. Deionized water.
2. Potassium cyanide.*
3. Calibration stock solution, 1000 µg/mL CN⁻. Dissolve 0.250 g KCN in 0.1 N KOH to make 100 mL solution. Stable for at least 1 week in polyethylene bottle.
4. Potassium hydroxide (KOH), 0.1 N. Dissolve 5.6 g KOH in deionized water; dilute to 1000 mL.
5. Lead acetate paper.
6. Cadmium carbonate (if sulfide present).
7. Hydrogen peroxide, 30% (if sulfide present).
8. Sodium sulfite, 1 M (if sulfide present).

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: polyvinyl chloride membrane filter, 37-mm diameter, 0.8-µm pore size in 2-piece filter cassette holder, followed by a glass midjet bubbler containing 15 mL 0.1 N KOH.
2. Personal sampling pump, 0.5 to 1 L/min, with splashover protection and flexible connecting tubing.
3. Vials, polyethylene, with screw caps, 20-mL, and plastic tape for sealing.
4. Cyanide ion electrode, (Orion 94-06 or equivalent).
5. Reference electrode.
6. pH meter, readable to 0.1 mV.
7. Magnetic stirrer and stirring bars.
8. Jars, ointment, 60-mL, squat-form with aluminum-lined screw caps.
9. Pipets, 0.05- to 2 and 25-mL, with pipet bulb.
10. Volumetric flasks, 25-mL.
11. Beakers, 50-mL.
12. Analytical balance, readable to 0.1 mg.

SPECIAL PRECAUTIONS: Hydrogen cyanide gas and the cyanide particulates may be fatal if swallowed, inhaled or absorbed through the skin. Work in a hood.

Amyl nitrite is the antidote for cyanide poisoning [7].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at 0.5 to 1 L/min for a total sample size of 10 to 180 L.
NOTE: Maintain bubblers in a vertical position during sampling. Do not allow the solution level to fall below 10 mL.
3. Remove the bubbler stem and tap it gently against the inside wall of the bubbler. Rinse the bubbler stem with 1 to 2 mL of unused 0.1 N KOH. Add the rinse to the bubbler.
4. Quantitatively transfer the contents of the bubbler to a 20-mL vial. Close cap tightly and wrap with plastic tape to avoid sample loss during transit. Label each vial.

SAMPLE PREPARATION:

5. Transfer the filter from the cassette filter holder to a 60-mL ointment jar.
6. Pipet 25.0 mL 0.1 N KOH into the jar. Cap and allow to stand for at least 30 min with occasional shaking to complete extraction. Analyze within 2 h after extraction.
7. Empty the contents of the vial into a 25-mL volumetric flask using 0.1 N KOH to rinse the vial. Add rinse to the volumetric flask. Dilute to the mark with 0.1 N KOH.
NOTE: Sulfide ion irreversibly poisons the cyanide ion specific electrode and must be removed if present. Check for the presence of sulfide ion by touching a drop of sample to a piece of lead acetate paper; the paper will discolor in the presence of sulfide ion. If this test is positive, remove sulfide by one of the following methods:
 - a. Add 1 mL 1 M H₂O₂ and 1 mL 1 M Na₂SO₃ to sample solutions prior to diluting to volume.

- b. Add a small amount (spatula tip) of powdered cadmium carbonate to the sample. Swirl to disperse the solid and recheck the liquid with lead acetate paper. If sulfide ion has not been removed completely, add more cadmium carbonate. Avoid a large excess of cadmium carbonate and long contact time with the solution. When a drop of liquid no longer discolors a strip of lead acetate paper, filter the sample through a small plug of glass wool in a Pasteur pipette and proceed with the analysis.

CALIBRATION AND QUALITY CONTROL:

8. Prepare at least six working standards fresh daily to cover the range 50 to 2000 $\mu\text{g CN}^-$ per sample by diluting aliquots of 1000 $\mu\text{g/mL}$ calibration stock solution with 0.1 N KOH (e.g., 0.05 to 2.0 mL calibration stock solution diluted to 25 mL).
9. Analyze the working standards according to steps 11 and 12 together with the samples and blanks.
10. Prepare a calibration graph on semilog paper by plotting cyanide ion concentration on the logarithmic axis and mV on the linear axis.

MEASUREMENT:

11. Transfer the solution to be measured to a 50-mL beaker. Immerse the cyanide ion electrode and reference electrode in the sample and start the magnetic stirrer.
 12. With the magnetic stirrer on, allow the potential reading to stabilize. Record the mV reading.
- NOTE 1: Potential readings are a function of temperature. Measure samples and working standards at the same temperature (± 2 °C).
- NOTE 2: The cyanide electrode will malfunction if chloride, iodide and bromide ions, which form insoluble silver salts, are present in sufficient quantity. Several metal ions are also known to complex with cyanide such as cadmium, zinc, silver, nickel, cuprous iron and mercury. Consult the electrode instruction manual for the procedure to use when such ions are present.

CALCULATIONS:

13. Read the mass, μg , of cyanide ion present in the sample filter (W_f), sample bubbler (W_b), average media blank filter (B_f) and media blank bubblers (B_b) from the calibration graph.
14. Calculate the concentration (mg/m^3) of particulate cyanide, C_p , and hydrogen cyanide, C_{HCN} , in the air volume sampled, V (L):

$$C_p = \frac{W_f - B_f}{V}, \text{ mg/m}^3 \quad C_{\text{HCN}} = \frac{(W_b - B_b) \cdot 1.04}{V}, \text{ mg/m}^3.$$

where 1.04 is the stoichiometric conversion factor from CN^- to HCN.

NOTE: Particulate cyanides will be collected on the filter. In humid atmospheres, however, it has been observed that during the collection of particulate cyanide, HCN is gradually liberated [2]; therefore, particulate cyanide interference is not completely removed.

EVALUATION OF METHOD:

HCN: Method S288 was issued on September 2, 1977 [4]. Test atmospheres of HCN were generated by calibrated flow from a compressed mixture of HCN in nitrogen [3,8]. The range of HCN concentrations in air was 5 to 21 mg/m^3 for 12-L air samples. Eighteen HCN samples collected at 0.2 L/min for 60 min indicated overall precision of 6.2%, with a 96.7% recovery. An eight-day storage

stability study involving six samples at the OSHA standard concentration level indicated a 92.4% average recovery for the one-day old samples and a 92.6% for eight-day old samples. A collection efficiency study at twice the OSHA standard level, which included backup bubblers, indicated that an average of 99.8% of HCN was collected in the first bubbler. The HCN air generated concentrations were independently confirmed by a titration method [3].

KCN: Method S250 was issued on January 30, 1976 [5]. A set of six weighed KCN samples in the range of 1.8 to 2.5 mg KCN per filter indicated a 97% recovery and a 3.8% measurement precision [2]. Spiking with aqueous or basic solutions of KCN proved unsuccessful (low recovery) because of the cyanide instability in the presence of water and CO₂. Test atmospheres of KCN were generated by atomization of an aqueous solution (162 g/L) of KCN into a dry airstream. Eighteen KCN samples collected in 0.1 N NaOH at 1.5 L/min for 60 min indicated overall precision, \hat{S}_{τ} , of 0.103. Collection was accomplished with cellulose ester membrane filters followed with backup bubblers. The collection efficiency at twice the OSHA level was 100.0% on the filters. Cyanide salts are known to decompose in moist air with liberation of HCN. This instability was determined with two sets of six samples at the one and two times the OSHA level. Each of the samples which were twice the OSHA level were connected with two backup bubblers. Both sets indicated a loss of 16.5%.

REFERENCES:

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METHOD REVISED BY:

J. Palassis, NIOSH/DTMD; S250 and S288 originally validated under NIOSH Contracts CDC-99-74-45 and 210-76-0123, respectively.