Method no.:	ID-120
Matrix:	Air
OSHA Standards:	HCN Gas: 10 ppm CN: 5.0 mg/m³
Collection Procedure:	The sample is drawn through a cassette containing a 37-mm mixed cellulose ester filter ahead of a midget impinger containing 10 mL of 0.1 N NaOH.
Recommended Air Volume:	90 liters with a maximum of 120 liters
Recommended Sampling Rate:	Maximum of 1.0 liters per minute
Analytical Procedure:	The filter is extracted using 0.1 N NaOH and analyzed separately from the impinger solution. A potentiometric analytical procedure with the Ion Specific Electrode for cyanide is used to determine sample concentrations.
Detection Limit:	0.25 ppm cyanide in solution
Precision:	$(CV_T) = 0.11$
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1. Introduction

This method describes the collection and analysis of airborne cyanide and hydrogen cyanide gas.

1.1 History

Several methods for CN^- determination have been developed which are based on colorimetric reactions.

1.2 Uses

HCN gas is used for exterminating rodents and insects in ships and for killing insects on trees, etc. NaCN is used for extracting Au and Ag from ores, extrapolating baths, fumigating citrus and other fruit trees, ships, railway cars, warehouses, making other cyanides and case hardening steel. (8.4)

1.3 Physical Properties (8.4)

For HCN gas: Colorless gas or liquid; characteristic odor; very weakly acidic (does not redden litmus): burns in air with a blue flame: intensely poisonous even when mixed with air.

Physical Constants for HCN:

Specific Gravity: 0.941
Melting Point: 13.4 °C
Boiling Point: 25.6 °C
Molecular Weight: 27.03

For NaCN as a representative CN salt, physical constants are:

Melting Point: 563 °C
Boiling Point: 1496 °C
Molecular Weight: 49.02

2. Working Range and Detection Limit

2.1 The working range is 0.25 ppm to 25 ppm cyanide.

2.2 The detection limit is about 0.25 ppm cyanide for linear response.

3. Precision and Accuracy

The following precision and accuracy data are based on 57 quality control samples prepared by the QC department of the OSHA Analytical Laboratory and analyzed there. They were mixed cellulose ester filters spiked with a CN salt solution in the range of 200-400 µg CN^-. The calculated (CV) = 0.11 with a standard deviation = 0.10. The mean recovery 0.997.

4. Interferences

4.1 Ions that form insoluble silver salts such as Cl^-, I^-, Br^- (8.1) (i.e., ion conc. greater than 1/10 the CN conc.).

4.2 Many transition and heavy metals that form very stable cyanide complexes such as Fe^{+2}, Fe^{+3}, Co^{+3}, Ni^{+2}, Cu^+, Ag^+, Cd^+, Hg^{+2},etc. The extent of complexation is dependent upon the concentration of metal ions present, cyanide concentration and the solution pH. (8.1)

4.3 Sulfide ion. Presence of sulfide ion in the sample solution will poison the electrode. (8.3)

5. Advantages and Disadvantages

5.1 The procedure is quick and simple and has a large concentration range.

5.2 High concentration samples can quickly damage the electrode.

5.3 Impinger solutions can easily be lost during collection.

5.4 Particulate CN^- collected on a filter converts to HCN upon exposure to moisture in the air. Studies show approximately 16% conversion. (8.1)

5.5 Strong reducing solutions in the atmosphere or sulfide contaminants cause damage to the electrode. (8.1)

6. Sampling Procedure Summary

6.1 The sample is drawn through a cassette containing a 37-mm mixed cellulose ester membrane filter ahead of a midget impinger containing 10 mL of 0.1 N NaOH. A flow rate of 1.0 L/min and a minimum sampling time of 60 minutes are recommended. The filter is used to collect particulate cyanide while the impinger collects HCN gas.

6.2 The filter cassettes are plugged. Within 1 hour of sampling, transfer the filter to a screwcap vial. The vial is sealed with OSHA tape, and sent to the laboratory for analysis.

6.3 The impinger solutions are transferred to leak proof vials with Teflon lined caps. Vinyl or waterproof tape is used around the caps to prevent leakage during shipment. The tape is wrapped around the cap in the direction the cap is turned. The vials are also sealed with an official OSHA seal and sent to the laboratory for analysis.

6.4 Analysis should be completed as soon as possible to avoid losses due to decomposition or volatilization of HCN.

7. Analytical Procedure

7.1 Apparatus

7.1.1 Cyanide Ion Specific Electrode Orion Model 9406 or equivalent.

7.1.2 Orion single junction reference electrode Model 900100 or equivalent.

7.1.3 Magnetic stirrer and Teflon stirring bars or battery operated stirring rod.

7.1.4 Millivolt meter (with expanded scale) Orion Ionalyzer 940 or equivalent.

7.1.5 Calibrated personal sampling pump.

7.1.6 Midget impinger and filter cassette assembly.

7.1.7 Associated laboratory glassware including volumetric flasks, plastic beakers, pipettes, etc.

7.2 Reagents

7.2.1 0.1 N NaOH solution - 4.0 g NaOH is added to approximately 600 mL deionized water and the solution is diluted to 1 liter. The solution is stored in a polyethylene bottle.

7.2.2 1000 ppm CN^- standard solution - 1.88 g NaCN reagent grade or better is added to approximately 600 mL 0.1 N NaOH. The solution is diluted to 1 liter with 0.1 N NaOH and stored in a polyethylene bottle. The solution is stable for at least 6 months.

7.2.3 Lead acetate paper.

7.2.4 Cadmium carbonate. ACS reagent grade or better.

7.3 Safety Precautions

7.3.1 Cyanide compounds are powerful poisons which prevent the utilization of oxygen by the body tissues. Cyanides which contact the skin or eyes should be washed off immediately since they can be absorbed through the skin.

7.3.2 Disposal of samples should be accomplished by pouring down a sink with copious amounts of tap water. In no case should cyanide standards come in contact with acids since this will produce deadly hydrogen cyanide gas.

7.4 Standard Preparation

7.4.1 All previously cleaned glassware is rinsed with 0.1 N NaOH and deionized water prior to use.

7.4.2 Standard solutions are prepared by appropriate dilution of stock 1000 ppm CN^- solution. All dilutions are made using 0.1 N NaOH. 100 ppm, 25 ppm, 10 ppm, 1 ppm, and 0.1 ppm solutions are made in the following manner:

Standard Solution used	Dilution	Final Concn
1000 ppm CN	10 mL:100mL	100 ppm CN^-
100 ppm	25 mL:100mL	25 ppm
100 ppm	10 mL:100mL	10 ppm
10 ppm	10 mL:100mL	1 ppm
1 ppm	10 mL:100mL	0.1 ppm

7.5 Sample Preparation

7.5.1 The volume of each impinger sample solution is measured and recorded. If an analysis other than hydrogen cyanide is to be done, then an aliquot of the sample is measured out for cyanide analysis into a 25-mL volumetric flask and diluted to volume with 0.1 N NaOH. The entire sample may be used as the aliquot if no other analyses are required.

7.5.2 Filter samples are transferred to a 50-mL plastic beaker and desorbed with 25 mL 0.1 N NaOH for at least 30 minutes with occasional agitation. If an analysis other than cyanide is to be done, then an aliquot of the sample is measured out for cyanide analysis into a 25-mL volumetric flask and diluted to volume with 0.1 N NaOH. The entire sample may be used as the aliquot if no other analyses are required.

7.5.3 A bulk sample is prepared by weighing out 1 g of the sample and dissolving it in enough 0.1 N NaOH to give a total volume of 25 mL. Sulfide ion contamination of the sample solution is determined by touching a drop of the sample solution to a piece of lead acetate paper. Discoloration of the test paper indicates sulfide ion contamination. If no sulfide is indicated, proceed to 7.6. (8.2)

7.5.4 Sulfide ion contamination can be removed from the sample solutions by addition of a small amount (spatula tip) of cadmium carbonate to the sample. The solution pH must be in the range 11-13. After each addition of cadmium carbonate, the sample is swirled and rechecked for sulfide ion presence prior to addition of more cadmium carbonate. (Note: Avoid a large excess of cadmium carbonate and long contact times.)

7.5.5 When a drop of liquid no longer discolors the strip of lead acetate paper, solids are removed by filtering the sample solution through a plug of glass wool contained in a small glass funnel. The funnel is not rinsed since the sample has already been diluted to volume.

7.6 Analysis

7.6.1 The cap is removed from the CN^- ion specific electrode. (Note: The electrode should be stored dry with a cap over the end.) Polish the end of the electrode with some deionized water and a polishing strip (94-82-01) for about 30 seconds. This will remove buildup and improve electrode response. Do this before and after electrode use.

7.6.2 The single junction reference electrode is filled with saturated KCl filling solution (90-00-01). (Note: The reference electrode should be stored empty and dry as response time will be quicker.) It should be stored dry only after it has been thoroughly cleaned and rinsed.

7.6.3 The potentiometer, Orion 940 Ionalyzer or Altex Selection 5000, is used following manufacturer's instructions. Plug the electrodes into the appropriate jacks on the back of the instrument.

7.6.4 Samples and standards are placed in 50-mL polyethylene beakers, Each is analyzed in the relative mV or concentration mode. (Note: See instrument instructions for use of either mode. See Table 1 for the instructions for the Orion 940.) A battery operated stirring rod is inserted into the solution before each analysis. The reproducibility of sample concentration is dependent on constant electrode temperature and constant stirring rate.

7.6.5 The electrodes are placed into the solution at about the same depth each time, making sure the stirring rod does not contact the electrodes.

7.6.6 Electrodes should be removed from solutions reading higher than the 25 ppm CN^- standard and an aliquot should be taken and diluted to 25 mL with 0.1 N NaOH for analysis. Failure to remove the electrode immediately will cause damage to the electrode and shorten its life. If the electrode is exposed to a sample of high concentration it should be quickly removed from the solution, polished with a polishing strip and rinsed well. Check its response in a standard solution to be sure it is giving a reproducible reading before proceeding.

7.6.7 Electrode voltage readings are allowed to stabilize for each sample. They stabilize faster in higher concentration solutions than in lower ones. The stable reading is recorded. Between samples, the electrodes are rinsed with deionized water and carefully blotted dry prior to introduction into the next one to avoid contamination. If the next sample is not immediately ready for determination, the electrodes should be placed in 0.1 N NaOH solution to reduce electrode stabilization time.

7.6.8 Typical voltage readings for 1, 10, and 25 ppm CN standard solutions are 115 mV, 175 mV, and 200 mV ±20 mV. Standards should be read at the beginning of the sample run and also at the end. Selected standards should be read between sample determinations to bracket sample values obtained.

7.6.9 The 1 ppm CN^- standard mV reading should be logged into the QC worksheet near the bench along with the I.S.E. and reference electrode ID numbers. The analyst initials and date should be included.

7.7 Calculations

7.7.1 Since the instrument was calibrated in the concentration mode the readings are simply plotted versus concentration of standards in ppm using the colorimetric or AA least squares plotting programs. Both of these curves give the sample ppm of CN.

7.7.2 The equation for calculating the air concentration of CN^- in mg/m^3 is:

$$mg/m^3 = \frac{(Sample\ ppm\ \times dilution\ factor - blank\ ppm)\ \times 25\ mL}{Air\ Volume\ (L)}$$

7.7.3 The equation for calculating the air concentration of HCN gas in ppm is:

(result from equation in 7.7.2) × (1.038) × (0.906)

where the gravimetric factor = 1.038 for HCN from CN and the ppm in air conversion factor = 0.906 for HCN.

This may be entered in the Auto AA program by combining the factors and entering the result as a "gravimetric factor" of 0.9404. [09404 = (1.038)(0.906)]

8. References

8.1 Instrument Manual Cyanide Ion Activity Electrode Model 9406, Orion Research Inc.

8.2 Draft Report Cyanide (as CN) Method Number S250, validation date Jan. 30, 1976.

8.3 Cyanide in Air, P&CAM 116 NIOSM Manual of Analytical Methods, issued Sept. 7, 1972, revised Dec. 1, 1973.

8.4 Merck Index, Tenth Edition 1983 page 696.

Table 1

Analysis using the Orion 940 follows a menu array. Answer the questions of the menu appropriately by using the "Yes", "No" and the numeric keys as follows:

- OPERATOR MENU? - "Answer "YES".
- CHANGE ELECTRODE ID? - Answer "YES".
- ELECTRODE 1 = NH3 IS THIS CORRECT? - Answer "NO" to change the ID. Continue to answer "NO" until CN^- is displayed as a choice. Use the numeric keys to select CN^-. The display will change to...
- ELECTRODE 1 = CN- IS THIS CORRECT? - Answer "YES".
- SET ABSOLUTE OR RELATIVE MILLIVOLTS? - Answer "NO".
- CHANGE THE pH OR ISE LIMITS? - Answer "NO".
- SET TIMER? - Answer "NO".
- CHANGE PRINT INTERVAL? - Answer "NO".
- SET TEMPERATURE? - Answer "NO".
- CHANGE THE TIME AND DATE? - Answer "NO".
- ENTER STANDBY MODE? - Enter "SPEED 0" to continue.
- CALIBRATE CN-? - Answer "YES".
- CALIBRATE BY DIRECT MEASUREMENT? - Answer "YES".
- ENTER NUMBER OF STANDARDS (1-5) - Enter 2 to standardize on the 1 and 10 ppm standards.
- DO BLANK CORRECTION? - Answer "NO".

- 1-CN- ELECTRODE IN STANDARD 1? - Place the electrodes into the 1 ppm standard and answer "YES". Wait for the reading to stabilize.

- STD 1 = 1.16 CAL AS 1.00? - Use the numeric keys to change to "CAL AS 1.0011 if necessary then answer "YES".

- 1-CN- ELECTRODE IN STANDARD 2? - Place the electrodes into the 10 ppm standard and answer "YES". Wait for the reading to stabilize.

- STD 2 = 10.00 CAL AS 10.00? - Correct if necessary and answer "YES".

- SLOPE = -59.2 mV/DEC YES TO CONTINUE - Record the slope value in your log book and press "YES".

- MEASURE 1-CN-? - Place electrodes in the first standard and answer "YES".

- 1-CN- = 1.00 READY 23.1°C - Record this concentration value for the standard. Rinse the electrodes and blot dry. Place the electrodes in the next sample or standard. Record the values shown (when the READY message is given).