Cyanogen

Method no.:	PV2104
Target concentration:	10 ppm (20 mg/m3) OSHA TWA PEL
Procedure:	Samples are collected by drawing a known volume of air through sampling tubes containing XAD-2 adsorbent which have been coated with 2-(hydroxmethyl) piperidine. Samples are desorbed with toluene and analyzed by gas chromatography with a nitrogen-phosphorous detector (GC-NPD).
Air volume and sampling rate studied:	15 minutes at 0.2 L/min for 3 liters
upper limit:	60 minutes at 0.2 L/min for 12 liters
Status of method:	Partially Validated Method. This method has been only partially evaluated and is presented for information and trial use.

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1 General Discussion

1.1 Background

1.1.1 History of procedure

The OSHA PEL for cyanogen is 10 ppm (20 mg/m^3). Direct collection on various media was not attempted as cyanogen reacts with water to form hydrogen cyanide and cyanate, and would react with any water collected from the humidity in the air. The collection of the cyanogen with a XAD-2 tube coated with 2-(hydroxymethyl) piperidine (2-HMP XAD-2) was attempted and found to be successful. The cyanogen was stabilized by forming a derivative, and demonstrated good desorption efficiencies, retention efficiencies, and storage.

1.1.2 Potential workplace exposure (Ref 5.1)

Workers are exposed to cyanogen in chemical manufacturing. Cyanogen is used as a fumigant, in welding and cutting heat-resistant metals, and as a rocket and missile propellant.

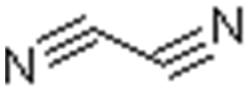
1.1.3 Toxic Effects (This section is for information purposes only and should not be taken as the basis for OSHA policy.) (Ref 5.1)

Chronic exposure to cyanogen causes irritation to the respiratory tract and to exposed skin surfaces. Cyanogen forms hydrocyanic acid and cyanate in vivo. Exposure causes hoarseness, conjunctivitis, and edema of the eyelid; further exposure causes hemorrhagic exudate of the bronchi and trachea, followed by pulmonary edema, and death. In laboratory tests, exposure to 100 ppm for 2-3 hours was fatal to cats, and at 400 ppm for 2 hours was fatal to rabbits.

1.1.4 Physical properties (Ref 5.1 and 5.2):

CAS:	460-19-5
IMIS:	0800
Synonyms:	carbon nitride: dicyanogen; dicyan; ethedinitride; nitriloacetonitrile; oxalic acid dinitrile; oxalyl cyanide; oxalonitrile
Molecular weight:	52.04
Freezing point:	- 27.9 °C
Boiling point:	- 20.7 °C
Odor	none up to 250 ppm, after that almond-like
Molecular formula:	C_2N_2
RTECS:	27697 (GT1925000)
DOT:	UN 1026

Structure:



1.2 Limit defining parameters

1.2.1 The detection limit of the analytical procedure is 0.1 µg. This is the smallest amount of cyanogen that could be detected under normal operating conditions.

1.2.2 The overall detection limit is 0.1 µg. This corresponds to 0.016 ppm based on the 1-mL desorption volume, and 3 liters air volume (all ppm amounts in this study are based on a 3-L air volume).

1.3 Advantages

1.3.1 The sampling procedure is convenient.

1.3.2 The analytical method is reproducible and sensitive.

1.3.3 Reanalysis of samples is possible.

1.3.4 It may be possible to analyze other compounds at the same time.

1.3.5 Interferences may be avoided by proper selection of GC parameters and column.

1.4 Disadvantages

None known.

2 Sampling procedure

2.1 Apparatus

2.1.1 A calibrated personal sampling pump, the flow of which can be determined within ±5% at the recommended flow of 0.1 L/min sampling rate with the sampling tube in line.

2.1.2 Samples are collected using sampling tubes containing XAD-2 coated with 2-(hydroxymethyl) piperidine. The tubes are 8-cm x 4-mm i.d., 6-mm o.d. The tube is packed with a 150 mg front section and a 75 mg backup section. There is a silanized glass wool plug before and after each section.

2.2 Sampling technique

2.2.1 The ends of the sampling tubes are opened immediately before sampling.

2.2.2 Connect the sampling tubes to the sampling pump with flexible tubing.

2.2.3 Tubes should be placed in a vertical position to minimize channeling, with the smaller section toward the pump.

2.2.4 Air being sampled should not pass through any hose or tubing before entering the sampling tube.

2.2.5 Immediately after sampling, seal the sampling tubes with plastic caps. Then seal each sample lengthwise with a Form OSHA-21 seal.

2.2.6 With each batch of samples, submit at least one blank tube from the same lot used for samples. This tube should be subjected to exactly the same handling as the samples (break ends, seal, & transport) except that no air is drawn through it.

2.2.7 Transport the samples (and corresponding paperwork) to the lab for analysis.

2.2.8 Bulks submitted for analysis must be shipped in a separate container from the samples.

2.3 Desorption efficiency

Six tubes were spiked with cyanogen gas at each loading of 3.64 µg (0.57 ppm), 16.5 µg (2.58 ppm), 32.9 µg (5.15 ppm), and 64.0 µg (10.0 ppm). They were compared to standards prepared by spiking cyanogen into a solution of 15 mg/mL 2-(hydroxymethyl) piperidine in toluene.

Samples and standards were allowed to react overnight. The samples were opened; each section placed into a separate 2-mL vial, desorbed with 1 mL of the desorbing solution for 30 minutes with occasional shaking, and analyzed by GC-NPD. The overall average was 99.0% recovered (Table 2.3).

Table 2.3
Desorption Efficiency

tube #	% recovered			
	0.05 x PEL (3.64 μg)	0.25 x PEL (16.5 μg)	0.5 x PEL (32.9 μg)	1 x PEL (64.0 μg)
1	99.3	97.9	94.4	96.2
2	98.6	99.1	101	97.9
3	103	100	102	98.2
4	97.4	95.8	100	101
5	98.8	101	100	98.2
6	100	99.9	99.9	95.5
average	99.5	99	99.6	97.8

overall average = 99.0
standard deviation = ±2.09

2.4 Retention efficiency

Six tubes were spiked with 35-μL cyanogen gas [64.3 μg (10.1 ppm) cyanogen] allowed to equilibrate overnight, and had 12-liters humid air (93% RH) pulled through them. They were then opened, desorbed, and analyzed by GC-NPD. There was no cyanogen found on the backup portions of the tubes (Table 2.4). The retention efficiency averaged 99.8%.

Table 2.4
Retention Efficiency

tube #	% recovered 'A'	% recovered 'B'	total % recovered
1	96.6	0.0	96.6
2	102	0.0	102
3	97.5	0.0	97.5
4	99.6	0.0	99.6
5	101	0.0	101
6	102	0.0	102
average			99.8

2.5 Storage

Sampling tubes were spiked with 63.6 μg (9.96 ppm) cyanogen and stored at room temperature until opened and analyzed. The recoveries averaged 98.6 % for the 13 days stored (Table 2.5).

Table 2.5
Storage Study

day	% recovered
6	97.9
6	94.3
6	96.4
6	98.2
6	99.2
13	102
13	101
13	99.8
13	97.6
13	100

average = 98.6%

2.6 Precision

The precision was calculated using the area counts from six injections of each standard at concentrations of 3.64 µg/mL, 16.5 µg/mL, 32.9 µg/mL, and 64.0 µg/mL. The pooled coefficient of variance (Pooled CV) was 0.0257 (Table 2.6).

Table 2.6
Precision Study

injection number	3.64 µg/mL	16.5 µg/mL	32.9 µg/mL	64.0 µg/mL
1	129360	617890	1260600	2004500
2	130840	578030	1298100	2048300
3	127230	582110	1307300	1927600
4	124970	615870	1294900	1959700
5	132100	574430	1300200	1914100
6	127550	617730	1300700	1915500
average	128675	597577	1293533	1961617
standard deviation	±2606	±21496	±16689	±54586
CV	0.0203	0.0360	0.0130	0.0278
pooled CV	0.0257			

Where:

$$Pooled\ CV = \sqrt{\frac{A1(CV1)^2 + A2(CV2)^2 + A3(CV3)^2 + A4(CV4)^2}{A1 + A2 + A3 + A4}}$$

A1, A2, A3, A4 = number of injections at each level
CV1, CV2, CV3, CV4 = coefficients of variation at each level

2.7 Air volume and sampling rate studied

2.7.1 The air volume studied is 3 liters. Retention efficiencies were studied at 12 liters with no loss of sample, so larger air volumes can be taken.

2.7.2 The sampling rate studied is 0.2 liters per minute.

2.8 Interferences

Suspected interferences should be listed on sample data sheets.

2.9 Safety precautions

2.9.1 Sampling equipment should be placed on an employee in a manner that does not interfere with work performance or safety.

2.9.2 Safety glasses should be worn at all times.

2.9.3 Follow all safety practices that apply to the workplace being sampled.

3 Analytical method

3.1 Apparatus

3.1.1 Gas chromatograph equipped with a nitrogen-phosphorous detector.

3.1.2 GC column capable of separating the analyte and an internal standard from any interference. The column used in this study was a 30-m x 0.32-mm i.d. (0.5-µm d_f SP2250) capillary column,

3.1.3 An electronic integrator or some other suitable method of measuring peak areas.

3.1.4 2-mL vials with PTFE-lined caps.

3.1.5 A 1-µL syringe or other convenient size for sample injection.

3.1.6 Pipettes for dispensing the desorbing solution.

3.1.7 Gas tight syringe 25-µL or other convenient size for preparing standards.

3.2 Reagents

3.2.1 Purified GC grade hydrogen, nitrogen, and air.

3.2.2 Cyanogen 98% purity.

3.2.3 Toluene, Reagent grade.

3.2.4 2-(Hydroxymethyl) piperidine, Reagent grade.

3.2.5 Dimethyl formamide (Internal standard), Reagent grade.

3.2.6 Desorbing solution is 0.2 µL/mL dimethyl formamide in toluene.

3.3 Sample preparation

3.3.1 Sample tubes are opened and the front and back section of each tube are placed in separate 2-mL vials.

3.3.2 Each section is desorbed with 1-mL of the desorbing solution of 0.2 µL/mL dimethyl formamide in toluene.

3.3.3 The vials are sealed immediately and allowed to desorb for 30 minutes with occasional shaking.

3.4 Standard preparation

3.4.1 Standards are prepared by spiking a known quantity of cyanogen onto a 150 mg portion of the 2-HMP XAD-2.

3.4.2 Cyanogen gas was spiked onto the resin using a gas-tight syringe. A spike of 35 µL corresponds to 64.0-µg cyanogen at 657 mmHg, 22°C, and a 98% purity gas. This is equal to 10.0 ppm based on a 3-L air volume, or 2.5 ppm based on a 12-liter air volume.

3.4.3 A series of standards are prepared covering the range from detection limit to the highest sample. The standards should bracket the samples. At least five differing concentrations should be made so that there are enough data points to plot a curve.

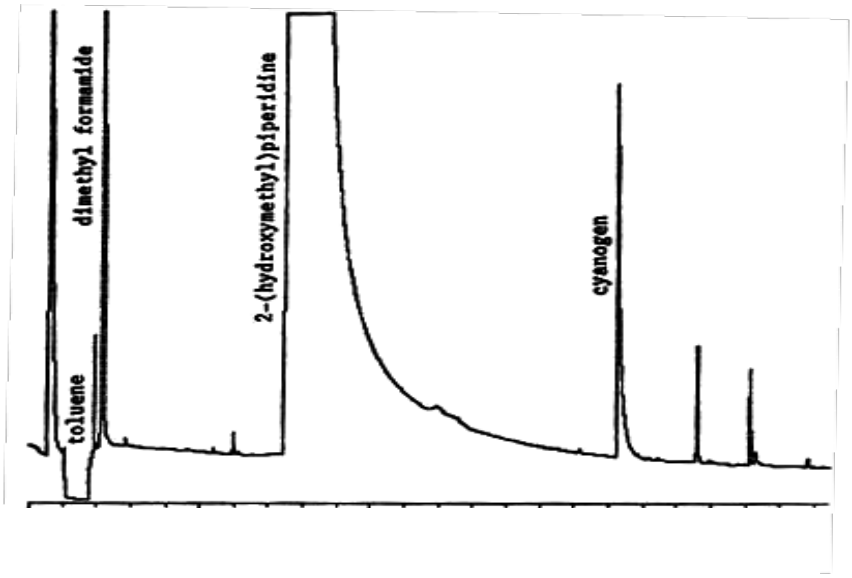
3.5 Analysis

3.5.1 Gas chromatograph conditions.

Flow rates	**(mL/min)**	**Temperature**	**(°C)**
Nitrogen (make-up):	30	Injector:	180
Hydrogen (carrier):	1	Detector:	250
Hydrogen (detector):	2	Column:	140
Air:	30		

Injection size:	1 µL
Elution time:	34.4 min

` Chromatogram:



3.5.2 Peak areas are measured by an integrator or other suitable means.

3.6 Interferences (analytical)

3.6.1 Any compound having the general retention time of the analyte or the internal standard used is interference. Possible interferences should be listed on the sample data sheet. GC parameters should be adjusted if necessary so these interferences will pose no problems.

3.6.2 It was found that cyanogen chloride formed the same derivative.

3.6.3 Retention time data on a single column is not considered proof of chemical identity. Samples over the target concentration should be confirmed by GC/Mass Spec or other suitable means.

3.7 Calculations

3.7.1 A curve with area counts versus concentration is calculated from the calibration standards.

3.7.2 The area counts for the samples are plotted with the calibration curve to obtain the concentration of cyanogen in solution.

3.7.3 To calculate the concentration of analyte in the air sample the following formulas are used:

$$\text{mass of analyte, } \mu g = \frac{(\mu g / mL)(\text{desorption volume, } mL)}{(\text{desorption efficiency, decimal})}$$

$$\text{moles of analyte} = \frac{(\text{mass of analyte, } \mu g)(1\,g)}{(\text{molecular weight})(10^6\,\mu g)}$$

$$\text{analyte volume} = (\text{moles of analyte})(\text{molar volume})$$

$$ppm = \frac{(\text{analyte volume})(10^6)^*}{(\text{air volume, } L)}$$

* All units must cancel.

3.7.4 The above equations can be consolidated to form the following formula. To calculate the ppm of analyte in the sample based on a 10-liter air sample:

$$ppm = \frac{(\mu g / mL)(DV)(24.46)}{(10\,L)(DE)(MW)}$$

µg/mL = Concentration of analyte in sample or standard
24.46 = Molar volume (liters/mole) at 25°C and 760 mmHg.
MW = Molecular weight (g/mole)
DV = Desorption volume
10 L = 10 liter air sample
DE = Desorption efficiency

3.7.5 This calculation is done for each section of the sampling tube and the results added together.

3.8 Safety precautions

3.8.1 All handling of solvents should be done in a hood.

3.8.2 Avoid skin contact with all solvents.

3.8.3 Wear safety glasses at all times.

4 Recommendations for further study

Collection studies should be performed.

5 References

5.1 "Documentation of the Threshold Limit Values and Biological Exposure Indices", Fifth Edition, American Conference of Governmental Industrial Hygienists Inc., Cincinnati, OH, 1986, p. 154.

5.2 Windholz, M., "The Merck Index", Tenth Edition, Merck & Co., Rahway N.J., 1983, p. 385.