Method number:	PV2193
Control number:	T-PV2193-8906-01-CH
Target concentration:	0.3 ppm (0.6 mg/m^3)
Procedure:	Samples are collected by drawing a known volume of air through sampling tubes containing XAD-2 adsorbent which have been coated with 2-(hydroxymethyl)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 (3 L) (ceiling) 120 minutes at 0.2 L/min (24 L) (upper limit)
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 chloride is 0.3 ppm (0.6 mg/m^3). Direct collection on various media was not successful. The media tried were charcoal tubes, XAD-2 tubes, XAD-7 tubes, silica gel tubes, Tenax tubes, and acid coated XAD-7 tubes. The major problem with these tubes was the low retention of the cyanogen chloride when humid air (89-91% RH) was drawn through them. Since direct collection was a failure, derivatizing the cyanogen chloride was next attempted with an XAD-2 tube coated with 2-(hydroxymethyl)piperidine. The cyanogen chloride stabilized by forming a derivative, showing good desorption efficiencies, retention efficiencies, and storage.

1.1.2 Potential workplace exposure (Ref. 5.1)

Workers are exposed to cyanogen chloride in chemical manufacturing. Cyanogen chloride is generated in cyanide recovery processes. It is used as a fumigant. It is also used as a military poison gas.

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

Chronic exposure to cyanogen chloride causes irritation to the respiratory tract and to exposed skin surfaces. Cyanogen chloride forms hydrocyanic acid 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 500 ppm for 3 minutes was fatal to mice, 120 ppm for 3.5 minutes was fatal to cats, and 48 ppm for 6 hours was fatal to dogs. In a workplace exposure, 48 ppm for 10 minutes was fatal for a male worker.

1.1.4 Physical properties (Ref. 5.1 and 5.2)

CAS:	506-77-4
IMIS:	C146
RTECS:	27681 (GT2275000)
DOT:	UN1589
Compound:	ClC=N
Synonyms:	chlorcyan; chlorocyanide; chlorocyan; chlorine cyanide
Molecular weight:	61.48
Freezing point:	- 6 ^{0}C
Boiling point:	13.8 ^{0}C
Odor:	pungent above 1 ppm
Molecular formula:	CNCl

1.2 Limit defining parameters

1.2.1 The detection limit of the analytical procedure is 0.02 ng. This is the smallest amount of cyanogen chloride that could be detected under normal operating conditions.

1.2.2 The overall detection limit is 0.02 µg. This corresponds to 0.00265 ppm based on the 1 mL desorption volume, and 3 liter 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 column and GC parameters.

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. and 6-mm o.d. The tube is packed with a 150 mg front section and a 75 mg backup section of the XAD-2 coated with 2-(hydroxymethyl)piperidine. 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 towards the pump.

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

2.2.5 Seal the sampling tubes with plastic caps immediately after sampling. 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 sample (break ends, seal, & transport) except 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 liquid spiked at each loading of 0.226 µg (0.03 ppm), 1.13 µg (0.15 ppm), and 2.26 µg (0.3 ppm). They were compared to standards prepared by spiking cyanogen chloride

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 then analyzed by GC-NPD. The overall average desorption was 98.5% recovered (Table 2.3).

Table 2.3
Cyanogen Chloride
Desorption Efficiency

tube #	% recovered		
	µg spiked 0.226	µg spiked 1.13	µg spiked 2.26
1	90.0	100	100
2	100	100	105
3	100	100	95.7
4	100	96.9	95.7
5	100	95.0	97.4
6	100	100	97.9
average	98.3	98.7	98.6

overall average = 98.5%
standard deviation = ±3.17

2.4 Retention efficiency

Six tubes were liquid spiked with 8.7 µg (1.15 ppm) cyanogen chloride, allowed to equilibrate overnight, and had 24 liters humid air (91% RH) pulled through them. They were opened, desorbed, and analyzed by GC-NPD. There was no cyanogen chloride found on the backup portions of the tubes (Table 2.4). Six tubes were liquid spiked with 8.86 µg (1.17 ppm) cyanogen chloride, allowed to equilibrate overnight, and had 10 liters dry air (11% RH) pulled through them. They were opened, desorbed, and analyzed by GC-NPD. There was no cyanogen chloride found on the backup portions of the tubes (Table 2.4). The retention efficiency averaged 95.3% for humid air samples and 99.9% for dry air.

Table 2.4
Cyanogen Chloride
Retention Efficiency

tube #	humid or dry	% recovered		total
		'A'	'B'	
1	humid	99.3	0.0	99.3
2	humid	92.6	0.0	92.6
3	humid	93.7	0.0	93.7
4	humid	95.6	0.0	95.6
5	humid	93.0	0.0	93.0
6	humid	97.5	0.0	97.5
average	humid			95.3%
7	dry	98.8	0.0	98.8
8	dry	99.6	0.0	99.6
9	dry	99.1	0.0	99.1
10	dry	102	0.0	102
11	dry	99.9	0.0	99.9
12	dry	99.9	0.0	99.9
average	dry			99.9%

2.5 Storage

Sampling tubes were spiked with 8.86 µg (1.17 ppm) and stored at room temperature until opened and analyzed. The recoveries averaged 97.6 % for the 14-days stored (Table 2.5).

Table 2.5
Cyanogen Chloride
Storage Study

day	% recovered
7	96.6
7	96.4
7	96.7
14	99.1
14	100
14	95.4
14	99.7
14	98.8
14	96.1

average = 97.6%

2.6 Precision

The precision was calculated using the area counts from six injections of each standard at concentrations of 0.226, 1.13, 2.26, and 4.52 µg/ml.

Table 2.6
Cyanogen Chloride
Precision Study

injection #	0.226 µg/mL	1.13 µg/mL	2.26 µg/mL	4.52 µg/mL
1	24157	113110	228810	477110
2	21586	105450	229030	469670
3	21368	106390	238030	442220
4	24341	110500	241450	478630
5	21885	98812	247350	437170
6	24077	111900	250210	446920
average	22902	107694	239147	458620
SD	±1300	±5301	±9005	±18603
CV	0.0568	0.0492	0.0377	0.0406

pooled CV = 0.0467

Where:

$$CV\ \left(Coefficient\ of\ Variation\right) = \frac{\left(standard\ deviation\right)}{\left(average\right)}$$

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

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 10 and 24 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 60-m x 0.32-mm i.d. (0.5 µm d_f RTX-5) capillary column.

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

3.1.4 Two milliliter vials with PTFE-lined caps.

3.1.5 A 1.0-µL syringe or other convenient size for sample injection.

3.1.6 Pipettes for dispensing the desorbing solution.

3.1.7 Gas-tight syringes, 100-µL, or other convient size to make standards.

3.2 Reagents

3.2.1 Purified GC grade hydrogen and air.

3.2.2 Cyanogen chloride 98% purity.

3.2.3 Toluene, Reagent grade.

3.2.4 2-(Hydroxymethyl)piperidine, Reagent grade.

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 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 chloride onto a 150 mg portion of XAD-2 coated with 2-HMP.

3.4.2 Stock solutions of cyanogen chloride in methanol were prepared to spike the coated resin. A stock solution of 125 µL/mL cyanogen chloride in methanol corresponds to 275 µg/mL based on a pressure of 656-mmHg and 21°C. A 150 mg portion of the coated resin spiked with 10 µL of this stock solution would have 2.75 µg/mL cyanogen chloride when desorbed with 1 mL Toluene.

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**	**(^{0}C)**
Nitrogen(make-up):	30	Injector:	180
Hydrogen(carrier):	1	Detector:	250
Hydrogen(detector):	2	Column:	135
Air:	30		
Injection size:	1.0 µL		
Elution time:	30.99 min		
Chromatogram:	(See Figure 1)		

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 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.

3.6.3 Cyanogen forms the same derivative as cyanogen chloride.

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 chloride in solution.

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

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

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

$$volume\ of\ analyte = (moles\ of\ analyte)(molar\ volume)$$

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

* 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:

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

Where:

µg/mL = concentration of analyte in sample
24.46 = Molar volume (liters/mole) at 25 °C and 760 mmHg
MW = Molecular weight (g/mole)
DV = Desorption volume, 1.0 mL
10 L = Air volume, L
DE = Desorption efficiency, decimal

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 and lab coat at all times in laboratory areas.

4 Recommendations for further study

Collection studies should be performed. A different column may allow an internal standard of dimethylformamide to be used at a concentration of 0.2 µL/mL. With the column used in this study, the dimethylformamide came out in the Toluene as a negative peak.

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. 155.

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

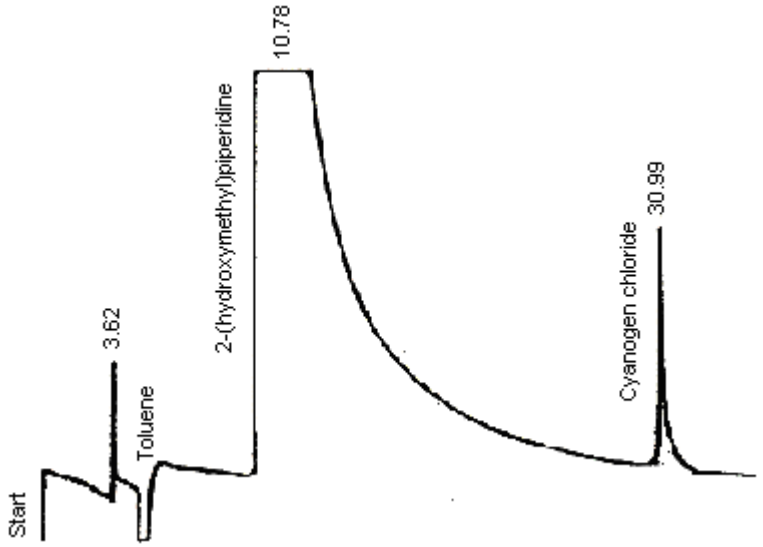

Figure 1. Standard of 2.26 µg/mL Cyanogen Chloride in Toluene