

## Hydrogen Cyanide



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Method number:	1015
Version:	1.0
Target concentration:	10 ppm (11 mg/m <sup>3</sup> )
OSHA PEL:	10 ppm (11 mg/m <sup>3</sup> ); Skin
ACGIH TLV:	4.7 ppm (5 mg/m <sup>3</sup> ) Ceiling as CN; Skin
Procedure:	Diffusive samples are collected by exposing ULTRA II Passive Samplers, field loaded with 600 mg of soda lime, to workplace air. Samples are extracted with water and analyzed by ion chromatography using an electrochemical detector.
Recommended sampling time:	240 min
Sampling rate:	28.4 mL/min at 25 °C and 760 mmHg
Reliable quantitation limit:	0.44 ppm (0.48 mg/m <sup>3</sup> )
Standard error of estimate at the target concentration:	9.8% <sup>*</sup> <sup>*</sup> For diffusive samplers when sampling site atmospheric pressure and temperature are known. When either or both of these values are unknown, see Section 4.5 for applicable standard errors of estimate.
Special requirements:	When using an ULTRA II Passive Sampler report the temperature and uncorrected sampling site atmospheric pressure.
Status of method:	Fully validated method. This method has been subjected to the established validation procedures of the Methods Development Team.

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Michael Simmons

Methods Development Team  
Industrial Hygiene Chemistry Division  
OSHA Salt Lake Technical Center  
Sandy UT 84070-6406

## 1. General Discussion

For assistance with accessibility problems in using figures and illustrations presented in this method, please contact the Salt Lake Technical Center (SLTC) at (801) 233-4900. This procedure was designed and tested for internal use by OSHA personnel. Mention of any company name or commercial product does not constitute endorsement by OSHA.

### 1.1 Background

#### 1.1.1 History

Previous to this method OSHA used a 37-mm mixed cellulose ester filter, followed by a bubbler containing 10 mL of 0.1 N NaOH, for the collection of hydrogen cyanide and particulate cyanide with analysis by ion specific electrode (OSHA Method ID-120).<sup>1</sup> In addition, OSHA occasionally used a solid sorbent tube containing a glass fiber prefilter, followed by two sections of soda lime, for sampling hydrogen cyanide (NIOSH Method 6010).<sup>2</sup> In theory both sampling methods work by collecting particulate cyanide on the prefilter and hydrogen cyanide using the bubbler or sorbent. Particulate cyanide, however, will decompose on the prefilter forming hydrogen cyanide, which then passes through the filter and is collected by the bubbler or sorbent, resulting in inaccurate hydrogen cyanide and particulate cyanide exposure results. A study by OSHA indicates that as much as 40% of particulate cyanide can be stripped off the prefilter and collect in the bubbler when using OSHA Method ID-120.<sup>3</sup> Since OSHA has separate PELs for particulate cyanide and hydrogen cyanide neither method can insure accurate hydrogen cyanide exposure results. The use of a passive sampler for monitoring hydrogen cyanide eliminates the potential for particulate cyanide decomposition within the sampler helping to insure more accurate determinations of personal workplace exposure to hydrogen cyanide.

Soda lime, the same medium used in NIOSH Method 6010, was chosen as the sampling medium. Soda lime is a mixture of chemicals consisting of mostly calcium hydroxide but also 6-18% water and 5-20% sodium hydroxide.<sup>4</sup> The ULTRA II Passive Sampler was selected since the sampling medium can be easily loaded and unloaded from the sampler in the field. Limiting the time the sampling medium spends in the sampler is desirable because it is caustic and sometimes clumps together.

Samples are desorbed using water and analyzed by ion chromatography using pulsed amperometric detection with disposable silver working electrodes. The disposable silver working electrode, sold by Dionex Corporation, along with the detection waveforms used in this method were developed and described by Cheng et al.<sup>5</sup>

When using OSHA Method ID-120 the presence of sulfide, which causes a positive interference, was determined by placing a drop of the bubbler sample solution on lead acetate paper. If the lead acetate paper changed red then cadmium carbonate was added to the sample to remove the sulfide interference. However, addition of excess

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<sup>1</sup> Cyanide (OSHA Method ID-120), 1998. U.S. Department of Labor, Occupational Safety and Health Administration Web site. <http://www.osha.gov/dts/sltc/methods/validated/id120/id120.html> (accessed January 2009).

<sup>2</sup> Williamson, G. Hydrogen Cyanide (NIOSH Method 6010), 1994. Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health web site. <http://www.cdc.gov/niosh/docs/2003-154/pdfs/6010.pdf> (accessed January 2008).

<sup>3</sup> Simmons, M. *Effect of Humidity on the Collection of Particulate Cyanide & Use of Coated Filters for the Collection of Hydrogen Cyanide and Particulate Cyanide (Study)*; U.S. Department of Labor, Occupational Safety and Health Administration. Unpublished work, March 2010.

<sup>4</sup> *The Merck Index*, 12<sup>th</sup> ed.; Budavari, S., Ed.; Merck & Co. Inc.: Whitehouse Station, NJ, 1996; p 1469.

<sup>5</sup> Cheng, J.; Jandik, P.; Avdalovic, N. Pulsed amperometric detection of sulfide, cyanide, iodide, thiosulfate, bromide and thiocyanate with microfabricated disposable silver working electrodes in ion chromatography. *Anal. Chim. Acta* **2005**, 536, pp 267-274.

cadmium carbonate could result in low recoveries for cyanide. In this method sulfide is separated from cyanide by the analytical column. However, sampling hydrogen cyanide in the presence of hydrogen sulfide will result in some cyanide reacting with sulfide on the sample medium producing thiocyanate. If cyanide is suspected to have reacted with sulfide, indicated by the detection of sulfide, the sample should also be analyzed for thiocyanate. The micrograms thiocyanate found is mathematically converted into equivalent micrograms cyanide and used in the final exposure calculation.

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)<sup>6</sup>

Human physiological response to various air concentrations of hydrogen cyanide are listed below in Table 1.1.2. Workplace exposure can occur from inhalation and through skin absorption. Reported symptoms of exposure to hydrogen cyanide include “lightheadedness, breathlessness, feeling shaky, headache, and nausea”. Individuals who have become exposed to acute levels of hydrogen cyanide, which did not result in death, have shown a complete and rapid recovery once removed from the source of exposure. Reported symptoms of chronic exposure to cyanide include “headache, weakness, irritation of the throat, vomiting, and effort dyspnea”. Thyroid gland enlargement along with “lacrimation, abdominal colic, salivation, and nervous instability” has also been reported.

Table 1.1.2

Human Physiological Response to Various Air Concentrations of HCN <sup>‡</sup>	
response	concn (ppm)
immediately fatal	270
fatal after 10 min	181
fatal after 30 min	135
fatal after 0.5 – 1 hr or later (dangerous to life)	110-135
tolerated for 0.5 – 1 hr without immediate or late effects	45-54
slight symptoms after several hours	18-36

<sup>‡</sup>Adapted from Hartung<sup>7</sup>

1.1.3 Workplace exposure

Hydrogen cyanide is used as a chemical building block in the production of chemicals used in various industries. Estimates of use “for hydrogen cyanide in the United States are adiponitrile for nylon, 41%; acetone cyanohydrin for acrylic plastics, 28%; sodium cyanide for gold recovery, 13%; cyanuric chloride for pesticides and other agriculture products, 9%; chelating agents such as EDTA, 4%; and methionine for animal feed, 2%”. Other minor uses of hydrogen cyanide include the “manufacturing of ferrocyanides, acrylates, lactic acid, pharmaceuticals, and specialty chemicals”. The use of hydrogen cyanide as a fumigant is decreasing.<sup>8</sup> United States production of hydrogen cyanide in 2003 was 2.019 billion pounds.<sup>9</sup>

<sup>6</sup> American Conference of Governmental Industrial Hygienists, Inc. *Documentation of the Threshold Limit Values and Biological Exposure Indices*, 7th ed.; Cincinnati, OH, 2001; Vol. 2, pp. Hydrogen Cyanide – 1 through Hydrogen Cyanide – 6.

<sup>7</sup> Hartung, R.; Cyanides and Nitriles. In *Patty's Industrial Hygiene and Toxicology*, 4<sup>th</sup> ed.; Clayton, G. D., Clayton, F. E., Eds.; John Wiley & Sons, Inc.: New York, 1994; Vol. II, Part D, pp 3119-3136.

<sup>8</sup> *Kirk-Othmer Encyclopedia of Chemical Technology*, 4<sup>th</sup> ed.; Kroschwitz, J. I., Ex. Ed.; John Wiley & Sons, Inc.: New York, 1993; Vol. 7, pp 753 - 765.

<sup>9</sup> Toxicological Profile for Cyanide, July 2006. Centers for Disease Control and Prevention, Agency for Toxic Substances & Disease Registry web site. <http://www.atsdr.cdc.gov/toxprofiles/tp8.html> (accessed May 2010).

#### 1.1.4 Physical properties and descriptive information<sup>10,11</sup>

synonyms:	hydrocyanic acid; prussic acid; formonitrile
IMIS number <sup>12</sup> :	1440
CAS number:	74-90-8
molecular weight:	27.03
boiling point:	25.6 °C
melting point:	-13.4 °C
molecular formula:	HCN
vapor pressure:	620 mmHg at 20 °C
vapor density:	0.941 (air = 1.0)
appearance:	colorless gas
odor:	some individuals may detect a bitter almond odor
solubility:	miscible with water, alcohol; slightly soluble in ether
flash point:	-17.78 °C, closed cup
explosive limits:	lower, 5.6%; upper, 40% by volume in air

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This method was validated according to the OSHA SLTC "Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis"<sup>13</sup>. The Guidelines define analytical parameters, specify required laboratory tests, statistical calculations and acceptance criteria. The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters. Air concentrations listed in ppm are referenced to 25 °C and 760 mmHg (101.3 kPa).

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## 2. Sampling Procedure

All safety practices that apply to the work area being sampled should be followed. The sampling equipment should be attached to the worker in a manner that will not interfere with work performance or safety.

### 2.1 Apparatus

#### 2.1.1 ULTRA II Passive Sampler

Samples are collected with an ULTRA II Passive Sampler field loaded with 600 mg of soda lime from a sorbent vial. OSHA policy is to not reuse the sampler.

For this validation the ULTRA II Passive Samplers were purchased from SKC Inc. (catalog no. 590-259). The soda lime, purchased in bulk from SKC Inc., is the same medium placed in an active sorbent tube (catalog no. 226-28) also sold by SKC Inc. Six hundred milligrams of soda lime was placed into 4-mL sorbent vials, with PTFE-lined cap and with threads compatible with the vial adapter on the ULTRA II, and then used to load the sampler just prior to sampling.

2.1.2 A thermometer and barometer are required to determine the sampling site air temperature and atmospheric pressure.

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<sup>10</sup> *The Merck Index*, 12<sup>th</sup> ed.; Budavari, S., Ed.; Merck & Co. Inc.: Whitehouse Station, NJ, 1996; p 822.

<sup>11</sup> American Conference of Governmental Industrial Hygienists, Inc. *Documentation of the Threshold Limit Values and Biological Exposure Indices*, 7th ed.; Cincinnati, OH, 2001; Vol. 2, p. Hydrogen Cyanide – 1.

<sup>12</sup> Hydrogen Cyanide (Chemical Sampling Information), 2007. U.S. Department of Labor, Occupational Safety and Health Administration Web site. [http://www.osha.gov/dts/chemicalsampling/data/CH\\_246400.html](http://www.osha.gov/dts/chemicalsampling/data/CH_246400.html) (accessed January 2010).

<sup>13</sup> Eide, M.; Simmons, M.; Hendricks, W. *Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis*; <http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf> OSHA Salt Lake Technical Center, U.S. Department of Labor: Sandy, UT, 2009 (accessed May 2010).

## 2.2 Reagents

None Required

## 2.3 Technique

### 2.3.1 SKC Inc. ULTRA II Passive Sampler

Remove the sampler from its re-sealable plastic package.

Remove the white plastic plug from the back of the sampler. Remove the cap from the sorbent vial and carefully screw the sorbent vial onto the sampler vial adaptor without spilling any soda lime. Invert the sampler and vial assembly and gently tap the sampler until all the soda lime has been transferred into the sampler. Unscrew the sorbent vial and reinsert the white plastic plug onto the back of the sampler. Place the cap and sorbent vial into the re-sealable plastic package for storage. Do not throw away the cap and sorbent vial. It is recommended that the sampler be loaded immediately before use. If this is not possible then load the sampler on the day of use.

Record the start time on the sampler label and on the Form OSHA-91A. Remove the cover when ready to begin sampling. CAUTION - The sampler immediately begins to sample when the cover is removed.

Attach the sampler to the worker near his/her breathing zone with the perforations in the sampler facing forward. Assure that the area directly in front of the sampler is unobstructed throughout the sampling period.

Sample for up to 240 min when using ULTRA II Passive Samplers loaded with soda lime to collect TWA (long-term) samples. The sampling rate for hydrogen cyanide using ULTRA II Passive Samplers loaded with soda lime is 28.4 mL/min at 25 °C and 760 mmHg.

Sample for 15 min when using ULTRA II Passive Samplers loaded with soda lime to collect short-term samples. The sampling rate for hydrogen cyanide using ULTRA II Passive Samplers loaded with soda lime is 28.4 mL/min at 25 °C and 760 mmHg.

At the end of the sampling period, immediately detach the sampler from the worker and attach the cover. Record the stop time on the sampler label and also on the Form OSHA-91A.

Hold the sampler with the plastic plug facing upwards and remove the plug. Screw the sorbent vial onto the sampler vial adaptor and invert the sampler and vial assembly. Gently tap or shake the sampler until all the soda lime has been transferred back into the sorbent vial. Detach the sorbent vial from the sampler and attach the vial cap. Place the vial and sampler in its re-sealable plastic package, close the package, and seal it with a Form OSHA-21.

Prepare a blank in a low background area by loading and then unloading a sampler as described above. Return the vial to its re-sealable plastic package, close the package, and seal it with a Form OSHA-21.

Verify that the sampling times are properly recorded on the Form OSHA-91A for each sample. Also, identify blank samples on this form.

Record the room temperature and atmospheric pressure at the sampling site on the Form OSHA-91A.

List any compounds that could be considered potential interferences, especially hydrogen sulfide.

Submit the samplers to the laboratory for analysis as soon as possible. If delay is unavoidable, store the samples in a refrigerator as a precaution.

Ship any bulk sample(s) in a container separate from the air samples.

### 3. Analytical Procedure

Adhere to the rules set down in your laboratory's Chemical Hygiene Plan<sup>14</sup> (for example OSHA SLTC adheres to: "The OSHA SLTC Chemical Hygiene Plan"). Avoid skin contact and inhalation of all chemicals and review all appropriate MSDSs before beginning the analytical procedure. Follow all applicable quality assurance practices established in your laboratory's internal quality system (for example OSHA SLTC follows: "The OSHA SLTC Quality Assurance Manual").

#### 3.1 Apparatus

Ion chromatograph with an electrochemical and conductivity detector. A Dionex ISC-3000 Ion Chromatography System equipped with an Integrated DC Detector/Chromatography module, an AS Autosampler with a 100 place tray, an SP Pump, an EO Eluent Organizer with pressure regulator, an ED Electrochemical detector and a CD Conductivity detector were used in this validation.

IC column and guard column that can separate cyanide from potential interferences. A Dionex IonPac® AS15 analytical column (250-mm × 4-mm i.d.) and a Dionex IonPac® AG15 guard column (50-mm × 4-mm i.d.) were used in this validation.

IC column and guard column that can separate thiocyanate from potential interferences. A Dionex IonPac® AS16 analytical column (250-mm × 4-mm i.d.) and a Dionex IonPac® AG16 guard column (50-mm × 4-mm i.d.) were used in this validation.

A means to integrate chromatograms. Dionex Chromeleon software was used in this validation.

A mechanical rotator. A Fisher Roto-Rack that accepts 4-mL vials was used in this validation.

Autosampler vials. National Scientific Company clear glass 2-mL screw thread vials with PTFE-lined septum caps were used in this validation.

Polypropylene vial racks for 2 and 4-mL vials.

Analytical balance capable of weighing at least 0.01 mg. An Ohaus Galaxy 160D balance was used in this validation.

A means to dispense and dilute solutions. A Hamilton Microlab 540B dual syringe diluter/dispenser was used in this validation.

Water purifier. A Barnstead NANOpure Diamond system was used to produce 18.0 MΩ-cm DI water in this validation.

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<sup>14</sup> Occupational Exposure to Hazardous Chemicals in Laboratories. *Code of Federal Regulations*, Part 1910.1450, Title 29, 2003.

Syringe and filters certified for ion chromatography for the filtration of sample solutions prior to analysis. Pall Corporation ion chromatography certified Acrodisc® 25 mm syringe filters with 0.2 µm Supor® (PES) membranes were used in this validation.

Class A 2-L volumetric flask.

Standard preparation vials. Wheaton 20-mL glass scintillation vials were used in this validation.

### 3.2 Reagents

Sodium Hydroxide (NaOH), [CAS no. 1310-73-2]. The sodium hydroxide used in this validation was a 99.995% trace metal basis grade (lot no. 17130TD) purchased from Sigma Aldrich (Milwaukee, WI).

Cyanide (CN<sup>-</sup>) 1000 mg/L standard solution. The 1000 mg/L (1000 µg/mL) cyanide standard used in this validation was (lot no. 1013925) purchased from CPI International (Santa Rosa, CA).

Thiocyanate (SCN<sup>-</sup>) 1000 mg/L standard solution. The 1000 mg/L (1000 µg/mL) cyanide standard used in this validation was (lot no. 1907227) purchased from Ricca Chemical Company (Arlington, TX).

Eluent [62.5 mM NaOH]: Add 5 g of NaOH to a 2-L volumetric flask, dilute to mark with 18.0 MΩ-cm DI water and mix well. Transfer eluent to appropriate container(s) and degas. Store eluent under a helium blanket to avoid reaction with carbon dioxide in the air.

Extraction solvent. The extraction solvent used is 18.0 MΩ-cm DI water. The extraction efficiency is affected by extraction solvent, the sampling medium, and the technique used to extract the samples. Other reagents and techniques than those described in this method can be used provided they are tested as specified in the validation guidelines<sup>15</sup>.

### 3.3 Standard preparation

Prepare a concentrated stock standard of 100 µg/mL using a 1000 µg/mL cyanide standard using the eluent as the diluent. Prepare working analytical standards by diluting milliliter amounts of the concentrated stock standard with measured amounts of eluent. For example, to prepare a target level standard of 73.5 µg/sample cyanide, add 2.1 mL of 100 µg/mL concentrated stock into a 10 mL volumetric flask and dilute to the mark with eluent. If necessary, prepare thiocyanate working analytical standards in the same manner.

Bracket sample concentrations with standard concentrations. If upon analysis, sample concentrations fall outside the range of prepared standards, prepare and analyze additional standards to confirm instrument response, or dilute high samples with extraction solvent and reanalyze the diluted samples.

### 3.4 Sample preparation

For each sample break the Form OSHA-21 seal, remove the 4-mL sorbent vial from the re-sealable plastic package and write the sample number on the vial.

Add 3.5 mL of 18.0 MΩ-cm DI water to each vial.

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<sup>15</sup> Eide, M.; Simmons, M.; Hendricks, W. *Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis*; <http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf> OSHA Salt Lake Technical Center, U.S. Department of Labor: Sandy, UT, 2009 (accessed May 2010).

Place the 4-mL vials on a mechanical rotator and rotate at approximately 40 rpm for 60 min.

Remove the vials from the rotator and allow samples to settle for 15 min.

Filter 2 mL of each sample and transfer the filtrate to 2-mL glass autosampler vials and seal with PTFE caps.

Analyze as described in Section 3.5.

### 3.5 Analysis

Sampling hydrogen cyanide in the presence of hydrogen sulfide will result in some cyanide reacting with sulfide on the sample medium producing thiocyanate. If cyanide is suspected to have reacted with sulfide, indicated by the detection of sulfide, the sample should also be analyzed for thiocyanate. The micrograms thiocyanate found is converted mathematically into equivalent micrograms cyanide and used in the final exposure calculation (see Section 3.7).

Analyze all samples for cyanide as described in Section 3.5.1. If cyanide and sulfide are both detected analyze the sample for thiocyanate as described in Section 3.5.2.

#### 3.5.1 Analytical conditions for analysis of cyanide

##### IC conditions

column: Dionex IonPac® AS15 column (250-mm x 4-mm i.d.) and AG15 guard column (50-mm x 4-mm i.d.)  
run time: 20 min  
injection volume: 25.0 µL\*  
eluent: 62.5 mM NaOH  
flow rate: 1.0 mL/min  
pump pressure: ~ 1000 psi  
column temperature: 30 °C  
retention times: ~ 4.8 min (sulfide)  
~ 5.8 min (cyanide)  
~ 17.2 min (thiosulfate)

\*Injection volume can be increased if lower quantitation limits are desired for the analysis of short term samples.

##### electrochemical detector conditions

detector mode: pulsed amperometric  
reference electrode: Ag/AgCl (3 M KCl)  
working electrode: silver (disposable electrode)  
counter electrode: titanium (detector cell body)

waveform:

cyanide waveform <sup>†</sup>				
time (s)	potential (V)	gain	ramp	integration
0.00	-0.100	Off	Off	Off
0.20	-0.100	On	Off	On
0.90	-0.100	Off	Off	Off
0.91	-1.000	Off	Off	Off
0.93	-0.300	Off	Off	Off
1.00	-0.300	Off	Off	Off

<sup>†</sup>Use manufacture recommended waveform



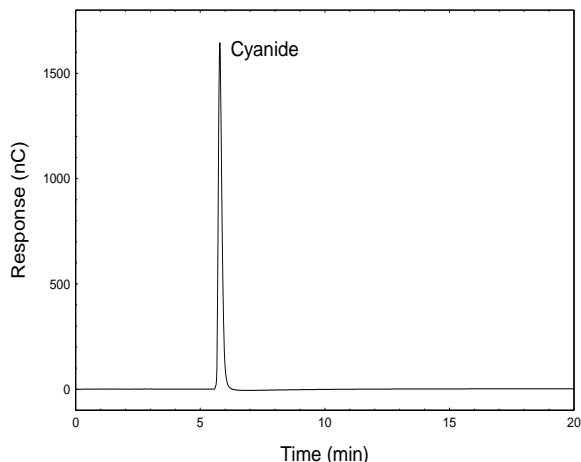


Figure 3.5.1.1. Chromatogram obtained at the target concentration with the recommended analytical conditions.

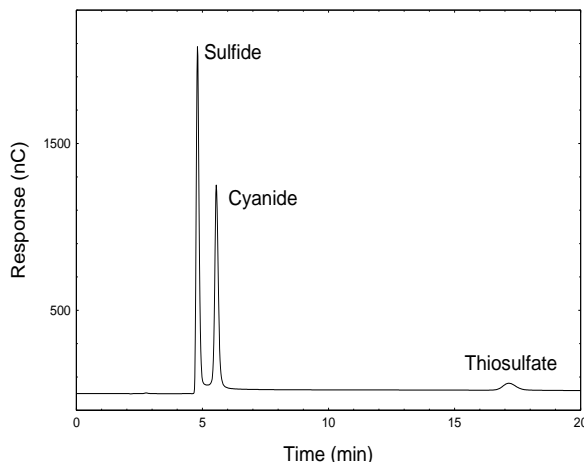


Figure 3.5.1.2. Chromatogram obtained when a sample was taken from a test atmosphere containing the target concentration of HCN and 11 ppm of H<sub>2</sub>S.

### 3.5.2 Analytical conditions for analysis of thiocyanate

Thiocyanate may be analyzed by pulsed amperometric detection with a silver electrode using the same column and eluent as described below.<sup>16</sup> However, using a conductivity detector is preferable due to the larger linear dynamic range of the detector.

#### IC conditions

column:	Dionex IonPac® AS16 column (250-mm x 4-mm i.d.) and AG16 guard column (50-mm x 4-mm i.d.)
run time:	11.5 min
injection volume:	25.0 µL*
eluent:	62.5 mM NaOH
flow rate:	1.0 mL/min
pump pressure:	~ 1600 psi
column temperature:	30 °C
retention times:	~ 9.8 min (thiocyanate)

\*Injection volume can be increased if lower quantitation limits are desired for the analysis of short term samples.

#### conductivity detector and suppressor conditions

cell heater temp:	35 °C
temp compensation:	1.7 %/°C
suppressor (current):	4-mm ASRS (155 mA)

<sup>16</sup> Cheng, J.; Jandik, P.; Avdalovic, N. Pulsed amperometric detection of sulfide, cyanide, iodide, thiosulfate, bromide and thiocyanate with microfabricated disposable silver working electrodes in ion chromatography. *Anal. Chim. Acta* **2005**, 536, pp 267-274.

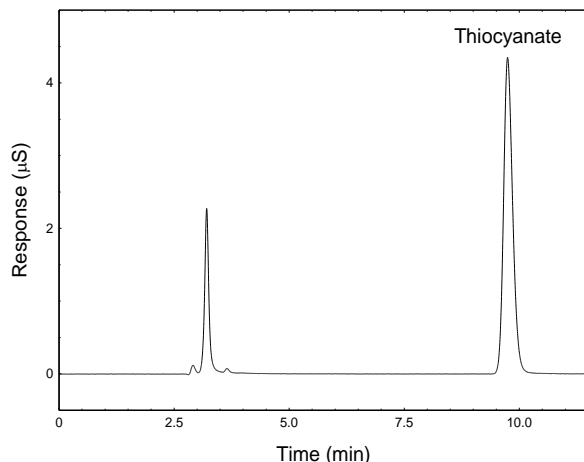


Figure 3.5.2. Chromatogram obtained at the concentration of 31.5 μg/sample of thiocyanate with the recommended analytical conditions.

3.5.3 An external standard calibration method is used. A calibration curve can be constructed by plotting response of standard injections versus micrograms of analyte per sample. Bracket the samples with freshly prepared analytical standards over a range of concentrations.

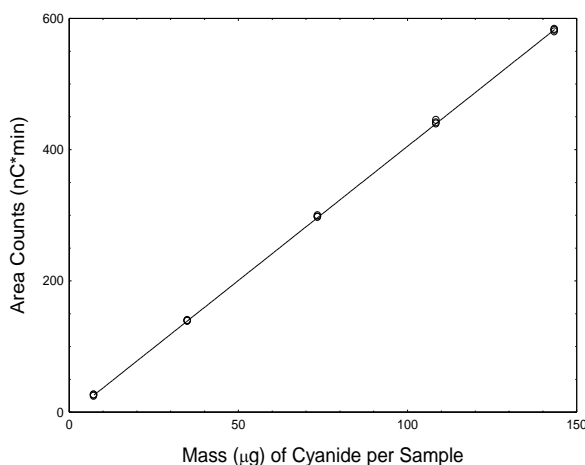


Figure 3.5.3.1 Calibration curve for cyanide ( $y = 4.09x - 3.98$ ).

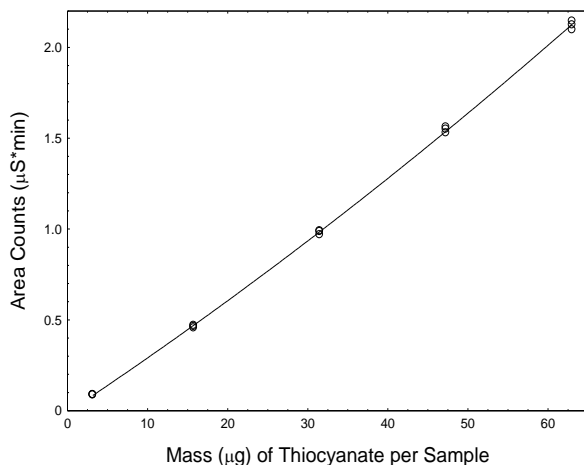


Figure 3.5.3.2. Calibration curve for thiocyanate ( $y = 7E-05x^2 + 0.0292x - 0.009$ ).

### 3.6 Interferences (analytical)

3.6.1 Any compound that produces a detector response and has a similar retention time as the analyte is a potential interference. If any potential interferences were reported, they should be considered before samples are extracted.

3.6.2 When necessary, the identity of an analyte peak can be confirmed with additional analytical techniques (Section 4.10).

### 3.7 Calculations

The amount of hydrogen cyanide per sample is obtained from the appropriate calibration curve in terms of micrograms per sample, uncorrected for extraction efficiency. This total amount is

then corrected by subtracting the total amount (if any) found on the blank. The air concentration is calculated using the following formulas.

$$R_{SS} = R_{NTP} \left( \frac{T_{SS}}{T_{NTP}} \right)^{\frac{3}{2}} \left( \frac{P_{NTP}}{P_{SS}} \right)$$

where  $R_{SS}$  is the sampling rate at the sampling site (mL/min)  
 $R_{NTP}$  is the sampling rate at NTP (28.4 mL/min)  
 $T_{SS}$  is the temp at the sampling site (K)  
 $T_{NTP}$  is 298.2 K  
 $P_{SS}$  is the sampling site pressure (mmHg)  
 $P_{NTP}$  is 760 mmHg

$$C_M = \frac{\left[ \left( \frac{M_{CN} GF_{CN}}{E_{E(CN)}} \right) + \left( \frac{M_{SCN} GF_{SCN}}{E_{E(SCN)}} \right) \right] 1000}{R_{SS} t}$$

where  $C_M$  is HCN concn by weight in air (mg/m<sup>3</sup>)  
 $M_{CN}$  is micrograms per sample CN<sup>-</sup>  
 $M_{SCN}$  is micrograms per sample SCN<sup>-</sup>  
 $GF_{CN}$  is the CN<sup>-</sup> gravimetric factor (1.039 HCN/CN<sup>-</sup>)  
 $GF_{SCN}$  is the SCN<sup>-</sup> gravimetric factor (0.465 HCN/SCN<sup>-</sup>)  
 $E_{E(CN)}$  is the CN<sup>-</sup> extraction efficiency (decimal form)  
 $E_{E(SCN)}$  is the SCN<sup>-</sup> extraction efficiency (decimal form)  
 $R_{SS}$  is the sampling rate at the sampling site (mL/min)  
 $t$  is the sampling time (min)

$$C_V = \frac{C_M V_M}{M_r}$$

where  $C_V$  is concn of HCN by volume (ppm)  
 $V_M$  is 24.46 (molar volume at NTP)  
 $C_M$  is concn by weight (mg/m<sup>3</sup>)  
 $M_r$  is molecular weight of HCN (27.03)

If the sampling site temperature is not provided, assume that it is 22.2 °C. If the sampling site atmospheric pressure is not given, calculate an approximate value based on the sampling site elevation from the following equation.

$$P_{SS} = AE^2 - BE + 760$$

where  $P_{SS}$  is the approximate atmospheric pressure (mmHg)  
 $E$  is the sampling site elevation (ft)  
 $A$  is  $3.768 \times 10^{-7}$  mmHg/ft<sup>2</sup>  
 $B$  is 0.02741 mmHg/ft

#### 4. Method Validation

General instruction for the laboratory validation of OSHA sampling and analytical methods that employ chromatographic analysis is presented in "Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis"<sup>17</sup>. These Guidelines detail required validation tests, show examples of statistical calculations, list validation acceptance criteria, and define analytical parameters. Air concentrations listed in ppm are referenced to 25 °C and 760 mmHg (101.3 kPa).

##### 4.1 Detection limit of the analytical procedure (DLAP)

The DLAP is measured as the mass of analyte introduced onto the chromatographic column. Ten analytical standards were prepared with equally descending increments of cyanide with the highest standard containing 1.2 µg/mL. This is the concentration that would produce a peak approximately 10 times the response of a reagent blank at or near the chromatographic retention time of the analyte. These standards and the reagent blank were analyzed with the recommended analytical parameters (25-µL injection volume). The data obtained were used to determine the required parameters (standard error of estimate and slope) for the calculation of the DLAP. Values of 0.46 and 0.80 were obtained for the slope and standard error of estimate respectively. The calculated DLAP of 5.2 ng did not produce a detector response so the DLAP

<sup>17</sup> Eide, M.; Simmons, M.; Hendricks, W. *Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis*; <http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf> OSHA Salt Lake Technical Center, U.S. Department of Labor: Sandy, UT, 2009 (accessed May 2010).

was set to 7.5 ng cyanide.

Table 4.1  
Detection Limit of the Analytical Procedure

concentration ( $\mu\text{g/mL}$ cyanide)	mass on column (ng)	area counts (nC*min)
0.0	0.0	0.00
0.3	7.5	1.06
0.4	10.0	2.34
0.5	12.5	3.76
0.6	15.0	4.84
0.7	17.5	6.27
0.8	20.0	7.32
0.9	22.5	8.53
1.0	25.0	11.1
1.1	27.5	11.4
1.2	30.0	12.6

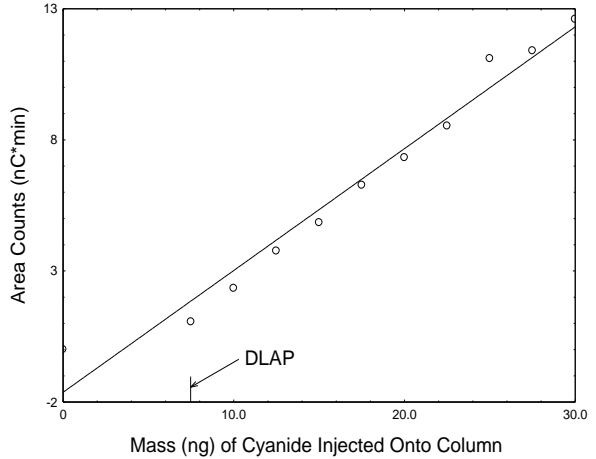


Figure 4.1. Plot of data to determine DLAP ( $y = 0.46x - 1.63$ ).

#### 4.2 Detection limit of the overall procedure (DLOP) and reliable quantitation limit (RQL)

The DLOP is measured as mass per sample and expressed as equivalent air concentrations based on the recommended sampling parameters. Ten samplers were spiked with equally descending increments of analyte, such that the highest sampler loading was  $4.55 \mu\text{g/sample}$ . This is the amount spiked on a sampler that would produce a peak approximately 10 times the response of a sample blank at or near the chromatographic retention time of the analyte. These spiked samplers and the sample blank were analyzed with the recommended analytical parameters, and the data obtained used to calculate the required parameters (standard error of estimate and the slope) for the calculation of the DLOP. Values of 2.98 and 0.94 were obtained for the slope and standard error of estimate respectively. The calculated DLOP of  $0.95 \mu\text{g}$  cyanide did not produce a detector response so the DLOP was set to  $1.4 \mu\text{g/sample}$  cyanide or  $1.45 \mu\text{g/sample}$  hydrogen cyanide ( $0.19 \text{ ppm}$  or  $0.21 \text{ mg/m}^3$ ).

Table 4.2  
Detection Limit of the Overall Procedure

mass per sample ( $\mu\text{g}$ cyanide)	area counts (nC*min)
0.00	0.00
1.40	0.92
1.75	2.33
2.10	3.72
2.45	4.83
2.80	5.99
3.15	7.18
3.50	8.41
3.85	9.70
4.20	10.95
4.55	12.32

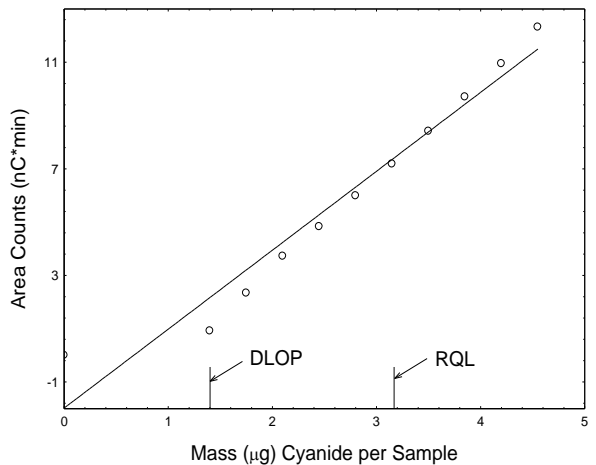


Figure 4.2.1. Plot of data to determine the DLOP/RQL ( $y = 2.98x - 1.98$ ).

The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line parameters that were obtained for the calculation of DLOP providing 75% to 125% of the analyte is recovered. The RQL is 3.2 µg/sample cyanide or 3.3 µg/sample hydrogen cyanide (0.44 ppm or 0.48 mg/m<sup>3</sup>). Recovery at this concentration is 97.8%.

When short-term samples are collected, the air concentration equivalent to the reliable quantitation limit becomes larger. For example, the reliable quantitation limit is 7.0 ppm (7.7 mg/m<sup>3</sup>) for hydrogen cyanide when 0.426 L is sampled (15 min sample).

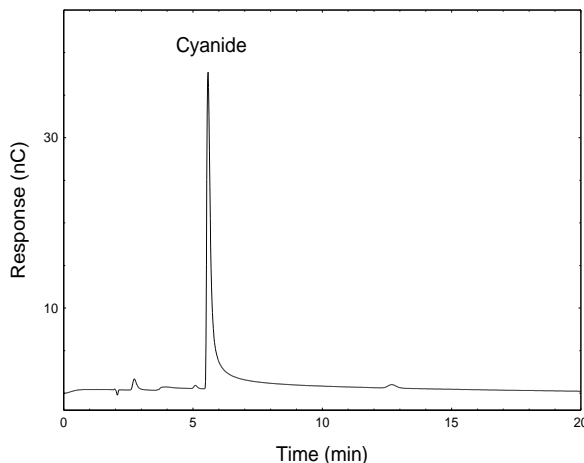


Figure 4.2.2. Chromatogram of the RQL for cyanide.

#### 4.3 Precision of the analytical method

The precision of the analytical method measured as the mass equivalent to the standard error of estimate determined from the linear regression of data points from standards over a range that covers 0.1 to 2 times the target concentration. A calibration curve was constructed and shown in Section 3.5.3 from the three injections of five standards. The standard error of estimate was 1.5 µg/sample cyanide.

Table 4.3  
Instrument Calibration

× target concn (µg/sample cyanide)	0.1×	0.5×	1.0×	1.5×	2.0×
area counts	24.14	138.45	299.31	440.93	581.75
(nC*min)	26.03	139.67	297.04	444.68	583.25
	26.08	138.62	296.86	439.07	579.59

#### 4.4 Storage stability test

Storage samples for hydrogen cyanide were prepared by collecting samples from a dynamically generated controlled test atmosphere using the recommended sampling time. The concentration of hydrogen cyanide in the test atmosphere was the target concentration (9.8 ppm or 10.8 mg/m<sup>3</sup>), and the relative humidity was 80% at 21 °C. Eighteen storage samples were prepared. Three samples were analyzed on the day of generation. The other fifteen samples were stored in a closed drawer at ambient temperature (about 20 °C). At 3-4 day intervals three samples were selected and analyzed. Sample results are not corrected for extraction efficiency. Results were calculated using the sampling rate determined in Section 4.7 converted to its equivalent sampling rate at sampling site temperature and pressure.

Table 4.4  
Storage Test for Hydrogen Cyanide

time (days)	ambient storage recovery (%)		
0	100.8	100.0	105.1
4	96.0	101.0	95.3
7	99.3	95.0	107.5
11	93.5	105.1	LIA
14	102.1	103.7	97.3
18	93.4	97.3	104.1

LIA = lost in analysis

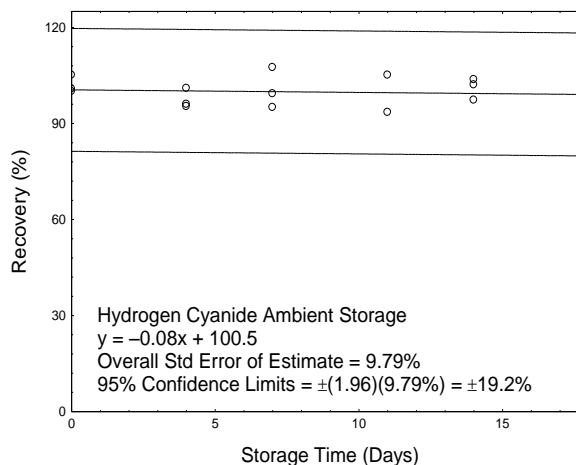


Figure 4.4. Ambient storage test for hydrogen cyanide.

#### 4.5 Precision (overall procedure)

The precision of the overall procedure at the 95% confidence level is obtained by multiplying the standard error of estimate by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). Ninety-five percent confidence intervals are drawn about the regression line in the storage stability figure shown in Section 4.4.

##### 4.5.1 ULTRA II Passive Sampler precision

The precisions of the overall procedure at the 95% confidence level for the ambient temperature (20 °C) 18-day storage test (at the target concentration) are given in Table 4.5.1. They each include an additional 8.7% for sampling rate variation<sup>18,19</sup>. There are different values given, depending on whether both, either or neither temperature (*T*) or atmospheric pressure (*P*) are known at the sampling site. If the sampling site temperature is unknown, it is assumed to be 22.2 ± 15 °C (72 ± 27 °F) and a variability of ±7.7% is included. If the atmospheric pressure is not known, it is estimated from the sampling site elevation and a variability of ±3% is included.

Table 4.5.1  
Standard Error of Estimate  
and Precision of the Overall Procedure

known condition	error (%)	precision (± %)
both <i>T</i> & <i>P</i>	9.79	19.2
only <i>T</i>	10.2	20.0
only <i>P</i>	12.5	24.5
neither <i>T</i> nor <i>P</i>	12.8	25.1

##### 4.5.2 Recovery

The recovery of hydrogen cyanide, in the form of cyanide, from samples used in an 18-day storage test remained above 99.1% when the samples were stored at 20 °C.

<sup>18</sup> Hendricks, W. Development of a Protocol for Laboratory Testing of Diffusive Samplers, 1996. U.S. Department of Labor, Occupational Safety and Health Administration Web Site. <http://osha.gov/dts/sltc/methods/studies/3movm/3movm.html> (accessed 2010).

<sup>19</sup> Hendricks, W. Determination of the Sampling Rate Variation for SKC 575 Series Passive Samplers, 1998. U.S. Department of Labor, Occupational Safety and Health Administration Web Site. <http://osha.gov/dts/sltc/methods/studies/skc575/skc575.html> (accessed January 2010).

#### 4.6 Reproducibility

Six samples were prepared by sampling a dynamically generated controlled test atmosphere similar to that used in the collection of the storage samples. The concentration of hydrogen cyanide in the test atmosphere was the target concentration (9.86 ppm or 10.9 mg/m<sup>3</sup>), and the relative humidity was 80% at 21 °C. The samples were submitted to the OSHA Salt Lake Technical Center for analysis. The samples were analyzed after being stored for 13 days at ambient temperature (about 20 °C). Sample results were corrected for extraction efficiency. No sample result for hydrogen cyanide had a deviation greater than the precision of the overall procedure determined in Section 4.5. Theoretical masses for hydrogen cyanide were determined using the sampling rate determined in Section 4.7 converted to its equivalent sampling rate at sampling site temperature and atmospheric pressure.

Table 4.6.1  
Reproducibility Data for Hydrogen Cyanide  
Collected on ULTRA II Passive Samplers  
Loaded with Soda Lime

theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
86.1	83.5	97.0	-3.0
86.1	82.9	96.3	-3.7
86.1	83.3	96.7	-3.3
86.1	87.8	102.0	2.0
86.1	82.9	96.3	-3.7
86.1	84.4	98.0	-2.0

#### 4.7 Sampling rate and capacity

The sampling rate and sampler capacity were determined with samples collected for increasing time intervals from a dynamically generated controlled test atmosphere. The concentration of the test atmosphere was two times the target concentration (19.7 ppm or 21.8 mg/m<sup>3</sup>) at 80% relative humidity and 21 °C. The preliminary sampling rate was determined by averaging the nine values for the 0.5, 1 and 2 hour samples. Horizontal lines were placed 10% above and 10% below the preliminary sampling rate. The sampling rate is 28.4 mL/min at 760 mmHg and 25 °C and represents the average of all values between the lines. The standard deviation and RSD are 1.25 mL/min and 4.40%, respectively. The data obtained are shown in Table 4.7 and Figure 4.7. Mass collected is corrected for extraction efficiency. The recommended sampling time is 240 min (4 hours).

Sampler capacity is exceeded when the plotted sampling rate decreases rapidly as the sampler becomes saturated. Sampler capacity was not exceeded even after 10 hours of sampling at two times the target concentration.

Table 4.7  
Determination of Sampling Rate  
and Time

time (h)	sampling rate (mL/min)		
	first	second	third
0.083	28.55	29.65	28.19
0.167	28.44	29.71	28.00
0.5	28.57	28.85	28.76
1	31.09	29.77	31.24
2	28.24	27.30	26.05
3	27.64	26.95	26.63
4	28.74	26.71	28.25
6	27.94	27.08	28.40
8	28.80	27.53	27.43
10	27.76	28.08	30.43

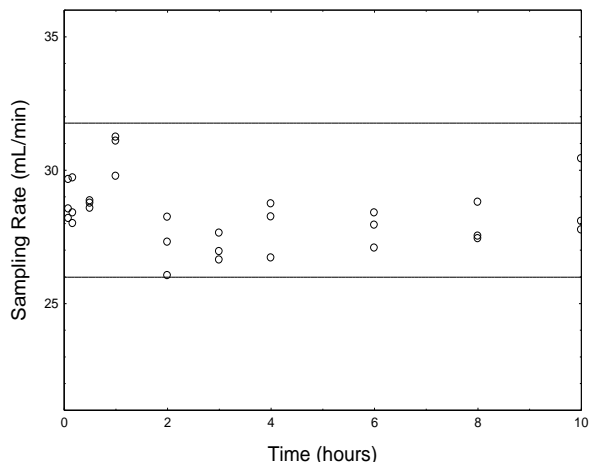


Figure 4.7. Plotted data to determine the sampling rate and recommended sampling time.

#### 4.8 Extraction efficiency and stability of extracted samples

The extraction efficiency is affected by the extraction solvent, the internal standard, the sampling medium, and the technique used to extract the samples. Other reagents and techniques than described in this method can be used provided they are tested as specified in the validation guidelines.<sup>20</sup>

##### Extraction efficiency

The extraction efficiency of cyanide was determined by liquid-spiking four vials, each containing 600 mg of soda lime, at each concentration level. These samples were stored overnight at ambient temperature and then extracted and analyzed. The overall mean extraction efficiency over the range of 0.1 to 2 times the target concentration was 97.9%. The extraction efficiency at the RQL was 91.2%. The presence of water had no significant effect on extraction efficiency. The extraction efficiencies for the RQL and for the wet samplers are not included in the overall mean. Wet soda lime was prepared by exposing the samplers to humid air (80% relative humidity at 21 °C) for 240 min. The data obtained are shown in Table 4.8.1.

Table 4.8.1  
Extraction Efficiency of Cyanide from Soda Lime

level	µg per sample	sample number				mean
		1	2	3	4	
× target concn						
0.1	7.48	96.0	94.8	93.6	93.6	94.5
0.25	18.7	101.2	96.2	97.6	97.1	98.0
0.5	37.4	98.4	99.2	98.3	99.2	98.8
1.0	74.8	97.7	97.9	97.4	97.3	97.6
1.5	112.2	100.2	99.7	100.1	100.0	100.0
2.0	150.6	100.4	99.7	97.0	96.7	98.4
RQL	3.15	93.1	91.6	90.5	89.7	91.2
1.0 (wet)	74.8	97.0	97.9	96.9	97.1	97.2

<sup>20</sup> Eide, M.; Simmons, M.; Hendricks, W. *Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis*; <http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf> OSHA Salt Lake Technical Center, U.S. Department of Labor: Sandy, UT, 2009 (accessed June 2009).



## Stability of extracted samples

The stability of extracted samples was examined by reanalyzing the target concentration samples 24, 48, and 72 hours after the initial analysis. After the original analysis was performed two vials were recapped with new septa which were replaced after each reanalysis. The remaining two vials retained their punctured septa throughout the test. All samples were allowed to stand in the autosampler tray at room temperature (20 °C). The samples were reanalyzed with freshly prepared standards. Diff is the difference between the initial analysis and the subsequent analysis. Each septum was punctured one time for each injection. The data obtained are shown in Table 4.8.2.

Table 4.8.2  
Stability of Extracted Samples for Cyanide

initial (%)	punctured septa replaced						punctured septa retained						
	24 h (%)	diff (%)	48 h (%)	diff (%)	72 h (%)	diff (%)	initial (%)	24 h (%)	diff (%)	48 h (%)	diff (%)	72 h (%)	diff (%)
97.7	98.8	1.1	97.8	0.1	98.8	1.1	97.4	98.7	1.3	98.9	1.5	98.6	1.2
97.9	98.9	1.0	98.6	0.7	99.4	1.5	97.3	98.6	1.3	99.0	1.7	99.1	1.8
			mean							mean			
97.8	98.8	1.0	98.2	0.4	99.1	1.3	97.4	98.6	1.3	99.0	1.6	98.8	1.5

## 4.9 Sampling interferences

The tested sampling interferences, with the exception of hydrogen sulfide, had no significant effect on the ability of ULTRA II Passive Samplers loaded with soda lime to collect and retain hydrogen cyanide. If cyanide is suspected to have reacted with sulfide, indicated by the detection of sulfide, the sample should also be analyzed for thiocyanate. The micrograms thiocyanate found is mathematically converted into equivalent micrograms cyanide and used in the final exposure calculation as described in Sections 3.5 and 3.7.

### Reverse diffusion

Reverse diffusion was tested by sampling a dynamically generated controlled test atmosphere containing two times the target concentration (19.3 ppm or 21.3 mg/m<sup>3</sup>) of hydrogen cyanide at 80% relative humidity and 21 °C. Six samplers were exposed to the test atmosphere for 60 min. Sampling was discontinued and

Table 4.9.1  
Reverse Diffusion of Hydrogen Cyanide from ULTRA II  
Passive Samplers Loaded with Soda Lime

set	mass (µg)			mean
	1	2	3	
first	42.6	42.3	39.9	41.6
second	40.6	43.6	41.0	41.7
second/first				100.2

the samplers were separated into two sets of 3 samplers each. The generation system was flushed with contaminant-free air. Sampling was resumed with a set of three samples exposed to contaminant-free air at 80% relative humidity and 21 °C for 180 min and then all six samplers were analyzed. The data obtained are shown in Table 4.9.1.

### Low humidity

The effect of low humidity was tested by sampling a dynamically generated controlled test atmosphere containing two times the target concentration (19.7 ppm or 21.7 mg/m<sup>3</sup>) of hydrogen cyanide at 20% relative humidity and 21 °C. Three samplers were exposed to the test atmosphere for 240 min. All of the samples were immediately analyzed. Results were calculated using the average sampling rate determined in Section 4.7 converted to its equivalent sampling rate at sampling site temperature and pressure. The results were 92.4%, 93.0%, and 100.2% of theoretical.

### Low concentration

The effect of low concentration was tested by sampling a dynamically generated controlled test atmosphere containing 0.1 times the target concentration (0.99 ppm or 1.09 mg/m<sup>3</sup>) of hydrogen cyanide at 80% relative humidity and 21 °C. Three samplers were exposed to the test atmosphere for 240 min. All of the samples were immediately analyzed. Results were calculated using the average sampling rate determined in Section 4.7 converted to its equivalent sampling rate at sampling site temperature and pressure. The results were 96.2%, 97.0%, and 104.1% of theoretical.

### Chemical sampling interference

The effect of a potential chemical sampling interference was tested by sampling a dynamically generated controlled test atmosphere containing one times the target concentration (9.4 ppm or 10.4 mg/m<sup>3</sup>) of hydrogen cyanide at 80% relative humidity and 21 °C and the interference. The interference was hydrogen sulfide at approximately its permissible exposure level (10.7 ppm or 12.9 mg/m<sup>3</sup>). Three samplers were exposed to the test atmosphere for 240 min. All of the samples were immediately analyzed. Results were calculated using the average sampling rate determined in Section 4.7 converted to its equivalent sampling rate at sampling site temperature and pressure. The results were 76.1%, 75.8%, and 76.9% of theoretical indicating that hydrogen sulfide is an interferent. Stability of the sample solutions was demonstrated by analyzing the sample solutions 19 days later for hydrogen cyanide. The results were 74.2%, 77.9%, and 79.6% of theoretical.

When the samples were also analyzed for thiocyanate, as described in Section 3.5 and results calculated as shown in Section 3.7, the results were 94.6%, 97.1%, and 96.0% of theoretical.

The interference study with hydrogen sulfide was repeated with results similar to those reported above demonstrating the appropriateness of the thiocyanate correction. Thiocyanate tests were performed, using a target concentration of 31.5 µg/sample, which is approximately the amount found on a sampler when a test atmosphere of 10 ppm hydrogen cyanide and 11 ppm of hydrogen sulfide was sampled. These tests were performed to support the analysis of thiocyanate and are shown below.

### DLOP and RQL for thiocyanate

Ten samplers were spiked with equally descending increments of analyte, such that the highest sampler loading was 0.210 µg/sample. This is the amount spiked on a sampler that would produce a peak approximately 10 times the response of a sample blank at or near the chromatographic retention time of the analyte. These spiked samplers and the sample blank were analyzed with the recommended analytical parameters for thiocyanate, and the data obtained used to calculate the required parameters (standard error of estimate and the slope) for the calculation of the DLOP. Values of 0.025 and 0.00017 were obtained for the slope and standard error of estimate respectively. The DLOP was calculated to be 0.020 µg/sample.

Table 4.9.2  
Detection Limit of the Overall Procedure

mass per sample ( $\mu\text{g}$ thiocyanate)	area counts ( $\mu\text{S}\cdot\text{min}$ )
0.000	0.00000
0.028	0.00067
0.049	0.00122
0.070	0.00227
0.091	0.00239
0.112	0.00283
0.133	0.00348
0.154	0.00385
0.175	0.00452
0.196	0.00488
0.210	0.00532

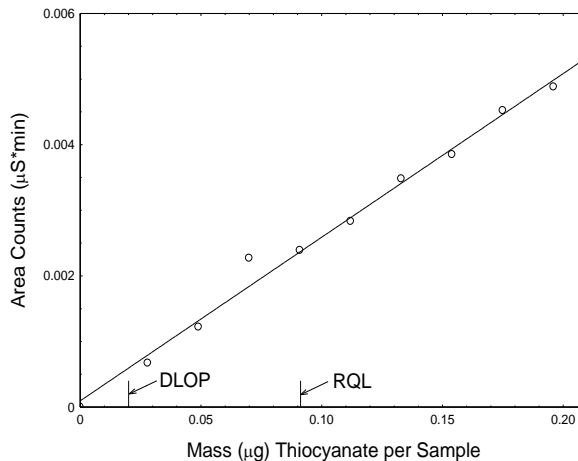


Figure 4.9.1. Plot of data to determine the DLOP/RQL ( $y = 0.0249x + 0.000095$ ).

The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line parameters that were obtained for the calculation of DLOP providing 75% to 125% of the analyte is recovered. The calculated value of the RQL was 0.067  $\mu\text{g}/\text{sample}$  thiocyanate. The nearest spiking amount to the calculated RQL, 0.070  $\mu\text{g}/\text{sample}$  thiocyanate, had a recovery of 125%; therefore, the RQL was set to 0.091  $\mu\text{g}/\text{sample}$ . Recovery at this concentration is 102%.

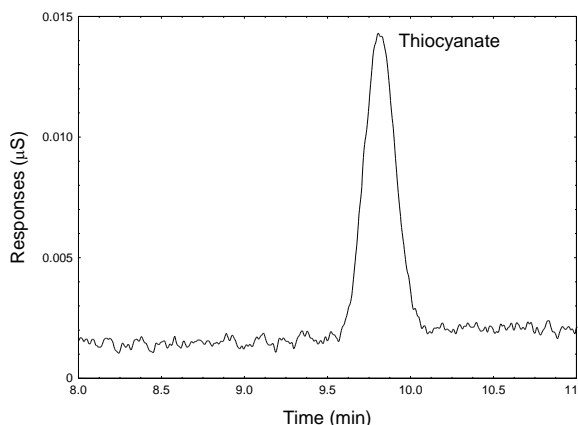


Figure 4.9.2. Chromatogram of the RQL (0.091  $\mu\text{g}/\text{sample}$ ) for thiocyanate.

Precision of the analytical method for thiocyanate

The precision of the analytical method measured as the mass equivalent to the standard error of estimate determined from the linear regression of data points from standards over a range that covers 0.1 to 2 times the target concentration. A calibration curve was constructed and shown in Section 3.5.3 from the three injections of five standards. The standard error of estimate was 0.81  $\mu\text{g}/\text{sample}$  thiocyanate.

Table 4.9.3  
Instrument Calibration

$\times$ target concn ( $\mu\text{g}/\text{sample}$ thiocyanate)	0.1 $\times$	0.5 $\times$	1.0 $\times$	1.5 $\times$	2.0 $\times$
area counts	0.087	0.456	0.969	1.530	2.097
( $\mu\text{S}\cdot\text{min}$ )	0.088	0.464	0.986	1.550	2.124
	0.089	0.470	0.991	1.562	2.145

### Extraction efficiency

The extraction efficiency of thiocyanate was determined by liquid-spiking four vials, each containing 600 mg of soda lime, at each concentration level. These samples were stored overnight at ambient temperature and then extracted and analyzed. The overall mean extraction efficiency over the range of 0.1 to 2 times the target concentration was 96.9%. The extraction efficiency at the RQL was 99.3%. The presence of water had no significant effect on extraction efficiency. The extraction efficiencies for the RQL and for the wet samplers are not included in the overall mean. Wet soda lime was prepared by exposing the samplers to humid air (80% relative humidity at 21 °C) for 240 min. The data obtained are shown in Table 4.9.4.

Table 4.9.4  
Extraction Efficiency of Thiocyanate from Soda Lime

<u>level</u>		<u>sample number</u>					
$\times$ target concn	$\mu\text{g}$ per sample	1	2	3	4	mean	
0.1	3.15	97.5	97.8	97.2	98.2	97.7	
0.25	7.88	96.9	97.0	97.4	96.5	97.0	
0.5	15.7	96.6	96.8	97.3	96.6	96.8	
1.0	31.5	95.9	97.6	96.7	97.3	96.9	
1.5	47.2	96.6	96.5	97.0	96.4	96.6	
2.0	63.0	95.7	96.1	96.8	96.2	96.2	
RQL	0.091	99.1	99.5	98.9	99.7	99.3	
1.0 (wet)	31.5	94.1	92.6	94.2	93.6	93.6	

### Stability of extracted samples

The stability of extracted samples was examined by reanalyzing the target concentration samples 24, 48, and 72 hours after the initial analysis. After the original analysis was performed two vials were recapped with new septa which were replaced after each reanalysis. The remaining two vials retained their punctured septa throughout the test. All samples were allowed to stand in the autosampler tray at room temperature (20 °C). The samples were reanalyzed with freshly prepared standards. Diff is the difference between the initial analysis and the subsequent analysis. Each septum was punctured one time for each injection. The data obtained are shown in Table 4.9.5.

Table 4.9.5  
Stability of Extracted Samples for Thiocyanate

initial (%)	<u>punctured septa replaced</u>						<u>punctured septa retained</u>						
	24 h (%)	diff (%)	48 h (%)	diff (%)	72 h (%)	diff (%)	24 h (%)	diff (%)	48 h (%)	diff (%)	72 h (%)	diff (%)	
95.9	96.8	0.9	96.0	0.1	96.3	0.4	96.7	97.0	0.3	96.8	0.1	96.0	-0.7
97.6	97.5	-0.1	97.1	-0.5	98.8	1.2	97.3	96.8	-0.5	96.3	-1.0	97.1	-0.2
			mean							mean			
96.8	97.2	0.4	96.6	-0.2	97.6	0.8	97.0	96.9	-0.1	96.6	-0.4	96.6	-0.4

### 4.10 Qualitative analysis

When necessary, the identity of an analyte peak can be confirmed by an additional analytical technique or alternate column. Several examples are briefly described:

Cyanide can be analyzed using a Dionex IonPac® AS7 column using pulsed amperometric detection with a 75 mM NaOH/100 mM NaAc eluent (see Dionex Product Manual for IonPac®)

AS7).<sup>21</sup>

Cyanide can also be analyzed by ion chromatography using ion-exclusion chromatography with pulsed amperometric detection (see Dionex Application Note 227).<sup>22</sup> The cyanide is converted to hydrogen cyanide using an eluent of methanesulfonic acid and detected with a platinum electrode. This analytical technique also has advantages if large amounts of sulfide are present since the cyanide elutes before the sulfide. (Caution: this technique will generate hydrogen cyanide gas. Pump column waste stream into a concentrated sodium hydroxide solution to prevent off-gassing of hydrogen cyanide.)

Another technique is analysis of hydrogen cyanide by headspace GC-NPD: Place 200  $\mu\text{L}$  aliquots of working standard solutions and filtered sample solutions into separate 2-mL GC autosampler vials and seal. Using a 200- $\mu\text{L}$  syringe inject 200  $\mu\text{L}$  of 1:1 phosphoric acid into each vial. Heat vials in a 60  $^{\circ}\text{C}$  water bath for 20 min; this will allow the acid to react with the cyanide releasing hydrogen cyanide into the headspace of the vial. Allow vials to cool to room temperature before analysis. Analyze hydrogen cyanide by injecting 10  $\mu\text{L}$  of the headspace, using a 25- $\mu\text{L}$  gas tight syringe, and separating with an HP-PLOT/Q column. An example of analytical conditions is given by Calafat and Stanfill.<sup>23</sup> Hydrogen cyanide results will be low when sulfide is present in the sample.

#### 4.11 Generation of test atmospheres

A dynamically generated test atmosphere, as diagramed in Figure 4.11, was set up in a walk-in hood. House air was humidified and regulated using a Miller Nelson Model 401 Flow-Temperature-Humidity Control System. A measured flow (typically 43 or 83  $\mu\text{L}$  per min) of a 1.0 M NaCN water solution was pumped through a 0.53-mm uncoated fused silica capillary tube into a single port septum inlet adaptor connected to a 500-mL 4 neck round bottom flask, using a Series D ISCO Syringe Pump with Controller. Through a second neck of the flask, using an inlet adaptor, was pumped 1 L/min of nitrogen. The third neck of the flask was connected to the inlet manifold and the fourth was internally threaded to accept a nylon bushing with o-ring that held a thermometer. In the flask was placed 20 mL of 1:1 sulfuric acid and a magnetic stir bar. The sulfuric acid solution was constantly stirred using a magnetic stir bar and maintained at a constant temperature of 30  $^{\circ}\text{C}$  (HCN has a boiling point of 25.6  $^{\circ}\text{C}$ ) using a round bottom flask heater.

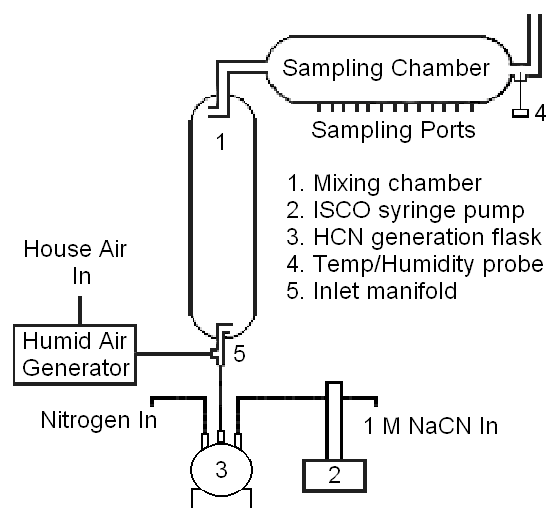


Figure 4.11. Diagram of apparatus used to generate test HCN atmospheres.

The 1 M NaCN solution was continuously pumped into the inside wall of the round bottom flask, allowed to flow down into the sulfuric acid solution, where it reacted with the acid and formed hydrogen cyanide gas. The hydrogen cyanide gas was swept out of the flask at 1 L/min with nitrogen into the inlet manifold and mixed with 100 L/min of dilution air. The gas mixture then flowed continuously into the mixing chamber (76-cm  $\times$  15-cm) and then into the sampling

<sup>21</sup> Product Manual for IonPac® AS7 & IonPac® AG7, 2008. Dionex. [www.dionex.com](http://www.dionex.com) (accessed March 2010), Document No. 031299.

<sup>22</sup> Application Note 227: Determination of Total Cyanide in Municipal Wastewater and Drinking Water Using Ion-Exclusion Chromatography with Pulsed Amperometric Detection (ICE-PAD). Dionex. [www.dionex.com](http://www.dionex.com) (accessed March 2010).

<sup>23</sup> Calafat, A. M.; Stanfill, S. B. Rapid quantitation of cyanide in whole blood by automated headspace gas chromatography. *J Chromatogr B* **2002**, 772, pp 131-137.

chamber (67-cm x 8-cm). Samples were collected in the sampling chamber. Temperature and humidity were measured near the exit of the sampling chamber using an Omega Digital Thermo-hygrometer model RH411. With the exception of low humidity tests OSHA generates test atmospheres at 80% relative humidity and 22 °C resulting in an absolute humidity of 15.5 mg/L H<sub>2</sub>O. The air velocity in the sampling chamber was 0.4 m/s.

The exact concentration of the 1 M NaCN solution used to generate the hydrogen cyanide test atmosphere was determined by analyzing a small aliquot using a NIST traceable standard to calibrate the analytical instrument. The theoretical concentration of the test atmosphere was used for calculating sample recoveries.

Bubblers containing 0.1 N NaOH were initially used, at a sampling rate of 50 mL/min, to verify the theoretical concentration of the test atmosphere generated inside the sampling chamber. A PAC III Dräger monitor, calibrated using an independent source of hydrogen cyanide, was also occasionally used as an additional check on theoretical test atmosphere concentrations. The monitor was connected to the sampling chamber by placing a two port calibration adaptor over the monitor sensor cap and attaching one port via a sampling tube to the sampling chamber and the second port to a vacuum pump. The flow rate past the sensor was ~0.05 L/min.