

IX. APPENDIX I
METHODS FOR SAMPLING CYANIDES
IN AIR AND CALIBRATION

The same sampling and analytical methods are used for atmospheric hydrogen cyanide and the particulate cyanides. They can be collected and analyzed separately or by insertion of a filter can be simultaneously collected and individually analyzed. A sampling period of about 10 minutes is necessary to provide an amount of cyanide readily amenable to analysis by the cyanide selective electrode.

Sampling

All glassware is washed in detergent solution, rinsed in tap water, and then rinsed with distilled or deionized water. Ten ml of an absorbing solution (0.1 M NaOH) is poured into an all-glass midget impinger using a graduated cylinder to measure the volume. The fritted inlet of the impinger should have a porosity approximately equal to that of Corning EC (170-220 micron maximum pore diameter). A membrane prefilter (0.45 μm pore size) should be inserted (by means of an in-line cassette or similar device) before the impinger when sampling for particulate cyanides is to be performed. Sampling for HCN and/or the particulate cyanides is performed for at least 10 minutes at a rate of 2 liters/minute, but the total volume of air sampled should not exceed 200 liters. A personal sampling pump or other satisfactory source of suction may be used for sampling provided it is calibrated as outlined below. Alternate sampling systems may be used, providing the required volume of air is sampled from the breathing zone of the worker.

After sampling, the fritted impinger stem can be removed and cleaned in the following manner. Tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Wash the stem with a small amount (1-2 ml) of unused absorbing solution and add the wash to the impinger bottle. Then the impinger bottle is sealed with a hard, non-reactive stopper (preferably Teflon) and an appropriate identifying number attached to it. Do not seal with rubber. The stoppers on the impinger bottle should be tightly sealed to prevent leakage during shipping. If it is preferred to ship the fritted impingers with the stems in, the outlets of the stem should be sealed with Parafilm or other nonrubber covers, and the ground glass joints should be sealed, ie, taped to secure the top tightly. Upon completion of sampling for the particulate cyanides, plastic caps should be replaced on the inlet and outlet tubes of the cassette and an appropriate identifying number attached to it.

Care should be taken to minimize spillage or loss by evaporation at all times. Refrigerate samples if analysis cannot be done within a day. Whenever possible, hand delivery of the samples is recommended. Otherwise, special impinger shipping cases should be used to ship the samples.

A "blank" fritted impinger should be handled as the other samples (fill, seal, and transport) except that no air is sampled through this fritted impinger. Where a prefilter has been used for the collection of particulate cyanides, the filter cassettes are capped and placed in an appropriate cassette shipping container. One filter disc should be handled like the other samples (seal and transport) except that no air is sampled through it, and this is labeled as a blank.

Certain cyanide compounds, especially calcium cyanide, may hydrolyze at sufficiently high relative humidities, resulting in losses of collected sample as HCN gas. In such cases, it may be advisable to minimize losses by keeping the sampling time as short as possible, then storing it in a refrigerator until analysis.

It should be noted that when sampling for HCN without a prefilter, particulates will pass through the midget impinger. Likewise, when sampling for particulate cyanides by means of a midget impinger without a prefilter, HCN gas will also be collected and will constitute a positive interference.

Calibration

Since the accuracy of an analysis can be no greater than the accuracy of measurement of the volume of air sampled, the accurate calibration of a sampling device is essential to the correct interpretation of an instrument's indication. The frequency of calibration is dependent upon the use, care, and handling to which the pump is subjected. Pumps should be calibrated if they have been subjected to misuse or if they have just been repaired or received from a manufacturer. If the pump receives hard usage, more frequent calibration may be necessary.

Ordinarily, pumps should be calibrated in the laboratory both before they are used in the field and after they have been used to collect a large number of field samples. The accuracy of calibration is dependent on the type of instrument used as a reference. The choice of calibration instrument will depend largely upon where the calibration is to be performed. For laboratory testing, a soapbubble flow meter or wet-test

meter is recommended, although other standard calibrating instruments, such as a spirometer or dry-gas meter, can be used. The actual setup will be connected in sequence to the filter cassette or fritted impinger unit which will be followed by the sampler pump. In this way, the calibration instrument will be at atmospheric pressure. If the personal sampler pump is used, each pump must be calibrated separately. If the buret is used, it should be set up so that the flow is toward the narrow end of the unit.

Care must be exercised in the assembly procedure to ensure that seals at the joints are airtight and that the length of connecting tubing is kept to a minimum. Calibration should be performed under the same conditions of pressure and temperature as those encountered in use. The calibrated pump rotameter should be used to set the flow rate in the field.

X. APPENDIX II

METHOD FOR ANALYSIS OF CYANIDE SAMPLES

Principle of the Method

Atmospheric samples are taken with midget impingers that contain 10 ml of 0.1M NaOH.

Particulate cyanides are collected on membrane filters and leached with 10 ml of 0.1M NaOH.

Samples are analyzed using the cyanide ion selective electrode.

Range and Sensitivity

The ultimate range and sensitivity of the method have not been established at this time. The recommended range of the method is 0.013-13 mg/cu m in air (approximately 0.0117-11.7 ppm of HCN).

Interference

Sulfide ion irreversibly poisons the cyanide ion selective electrode and must be removed if found in the sample. Check for the presence of sulfide ion by touching a drop of sample to a piece of lead acetate paper. The presence of sulfide is indicated by discoloration of the paper.

Sulfide is removed by the addition of a small amount (spatula tip) of powdered cadmium carbonate to the sample at pH 11-13. Swirl to disperse the solid, and recheck the liquid by again touching a drop to a piece of lead acetate paper. If sulfide ion has not been removed completely, add more cadmium carbonate. Avoid a large excess of cadmium carbonate and long contact time with the solution.

When a drop of liquid no longer discolors a strip of lead acetate paper, remove the solid by filtering the sample through a small plug of glass wool and proceed with the analysis.

Precision and Accuracy

The precision and accuracy of this method have not been completely determined at this time. No collaborative tests have been performed on this method.

Apparatus

(a) Sampling and Calibration Equipment

(1) A filter unit (if needed) consisting of the filter media and cassette filter holder.

(2) A midget fritted impinger containing the absorbing solution or reagent.

(3) A pump suitable for delivering desired flow rates. The sampling pump is protected from splashover or water condensation by an absorption tube loosely packed with a plug of glass wool and inserted between the exit arm of the impinger and the pump.

(4) An integrating volume meter such as a dry-gas or wet-test meter.

(5) Thermometer

(6) Manometer

(7) Stopwatch

(b) Analytical Equipment

- (1) Cyanide ion selective electrode
- (2) Single junction reference electrode
- (3) Expanded scale millivolt-pH meter
- (4) Associated laboratory glassware
- (5) Plastic bottles
- (6) Magnetic stirrer and stirring bars

Reagents

The reagents described must be made up using ACS reagent grade or better grade of chemical.

(a) Distilled or deionized water

(b) Potassium cyanide

(c) Sodium hydroxide 0.1 M. Dissolve 2.0 g NaOH in doubly distilled water and dilute to 500 ml.

(d) Potassium cyanide standards

(1) Dissolve 0.65 g KCN in 0.1 M NaOH and dilute to 100 ml with additional 0.1 M NaOH for 0.1 M [cyanide ion] (2600 $\mu\text{g}/\text{ml}$).

(2) Dilute 10 ml of 0.1 M [cyanide ion] to 100 ml with 0.1 M NaOH for 0.01 M [cyanide ion] (260 $\mu\text{g}/\text{ml}$).

(3) Dilute 10 ml of 0.01 M [cyanide ion] to 100 ml with 0.1 M NaOH for 0.001 M [cyanide ion] (26 $\mu\text{g}/\text{ml}$).

(4) Dilute 10 ml of 0.001 M [cyanide ion] to 100 ml with 0.1 M NaOH for 0.0001 M [cyanide ion] (2.6 $\mu\text{g}/\text{ml}$).

(5) Dilute 10 ml of 0.0001 M [cyanide ion] to 100 ml with

0.1 M NaOH for 0.00001 M [cyanide ion] (0.26 $\mu\text{g}/\text{ml}$).

- (e) Lead acetate paper
- (f) Cadmium carbonate

Procedure

- (a) Cleaning of equipment

All glassware is washed in detergent solution, rinsed in tap water, and then rinsed with distilled or deionized water.

- (b) Analysis of Samples

(1) For HCN, transfer the contents of the impinger to a 15-ml volumetric flask. Wash the impinger several times with 1 or 2 ml of 0.1 M NaOH and add to the contents of the flask. Add sufficient 0.1 M NaOH to the flask to make up 15 ml and mix the contents. Test for sulfide and if necessary remove it according to the procedure given above. The loss of solution in these steps (sulfide testing and filtering) should not be made up; sufficient solution should remain for cyanide electrode determination and the sample volume for calculations is therefore 15 ml. This solution is transferred to a 50-ml beaker. For the particulate cyanides, remove the filter from the cassette with tweezers, place in a clean, dry 50 ml beaker, add 15 ml of 0.1 M NaOH, and swirl.

(2) The cyanide ion electrode and the single junction reference electrode are placed in the solution and the resulting millivolt reading recorded. The reading should be taken after the meter has stabilized. Both the samples and standards should be stirred while the readings are being taken.

Calibration and Standards

Obtain the millivolt readings from each of the cyanide standards. Note that the use of the concentrated standards (0.1 M and 0.01 M) is not recommended since they may badly corrode the electrodes.

Plot the millivolt readings as a function of cyanide ion concentrations of the standards on semilog paper. The cyanide ion concentrations in $\mu\text{g/ml}$ is plotted on the log axis.

Calculations

The millivolt readings from the analysis of the sample are converted to $\mu\text{g/ml}$ of cyanide radical (CN) of solution using the calibration curve.

The μg content of the sample is multiplied by the sample volume (15 ml) to obtain the total μg cyanide in the sample.

Convert the volume of air sampled to standard conditions of 25 degrees C and 760 mmHg:

$$VS = V \times P/760 \times 298/(T+273)$$

where:

VS = volume of air in liters at 25 degrees C
and 760 mmHg

V = volume of air in liters as measured

P = barometric pressure in mmHg

T = temperature of air in degrees C

The concentration of cyanide in the air sampled can be expressed in μg cyanide/liter or mg cyanide/cu m.

$$\text{mg/cu m} = \mu\text{g/liter}$$

$$\text{mg/cu m} = \text{total } \mu\text{g cyanide/VS}$$

The concentration of cyanide can also be expressed in ppm, defined as μ liters of component/liter of air.

$$\begin{aligned} \text{ppm} &= \mu\text{liters cyanide/VS} \\ &= [R/\text{MW}] [\mu\text{g cyanide/VS}] \\ &= 0.94 \times \mu\text{g cyanide/VS} \end{aligned}$$

where:

$$R = 24.45 \text{ liters/mole at } 25 \text{ C, } 760 \text{ mm Hg.}$$

$$\text{MW} = 26 \text{ (for CN), } 27 \text{ (for HCN).}$$

XI. APPENDIX III

HYDROGEN CYANIDE MONITORS

Whenever the possibility exists that high concentrations of hydrogen cyanide may be released or created as a result of leaks, accidents, etc, it is essential that HCN monitoring devices be installed and that these devices give immediate warning of concentrations likely to be hazardous to life. It is difficult to define the limiting circumstances when such devices may be required; if reasonable doubt exists, the decision should be made by a qualified industrial hygienist. Monitoring devices may be based upon several operating principles, and at least one is currently available commercially. In the design or purchase of a HCN monitoring device the following criteria should be considered.

Summary of Specifications

(a) Monitoring device must sound an alarm or otherwise warn employees whenever a concentration of 25 ppm HCN is reached or exceeded.

(b) The monitoring device must have a response time of 20 seconds or less when exposed to an HCN concentration of 25 ppm.

(c) Zero drift should be less than 1% of full scale in 24 hours.

(d) Sampling rate and volume are not critical, and any sampling conditions which will meet the response criteria are adequate.

(e) The monitoring device must be accurate to within plus or minus 5 ppm when exposed only to HCN gas.

(f) Precision and repeatability must be plus or minus 2% of full scale.

(g) It is desirable that the instrument respond only to HCN, but instruments which respond to other gases not normally present in the atmosphere may be acceptable. In general, it is probable that any gas which causes a reading sufficiently high to set off the alarm will itself be present at a concentration sufficiently high to warrant corrective actions. Whenever there is a possibility that gases or vapors such as hydrogen chloride, chlorine, etc, may be present, it would be desirable to determine the response of the instrument to such gases in advance.

(h) An operating range of 0-100 ppm HCN is optimal, but other ranges may be selected to suit individual needs.

(i) The device should be capable of 7 days of continuous unattended operation.

(j) The device and alarm should be intrinsically safe for use in hazardous locations.

Discussion

The principal requirements for such monitors in addition to responding to HCN gas are that they be sufficiently rugged to withstand normal extremes of temperature, pressure, vibration, etc, and not be susceptible to plugging or interferences due to contaminants likely to be encountered in most work places. They should be so constructed that it is possible to quickly check the zero setting of the instrument and the response at 25 ppm in a rapid routine manner. It may be permissible to perform such checks by electrical means, but at least once each month

instruments should be checked at or near 25 ppm HCN using a known concentration of HCN-air mixture. For instruments relying on diffusion of the gas to a sensing electrode, it may be necessary to provide a chamber or bag into which the instrument is placed. Those instruments which incorporate an air-moving device can more readily sample gases directly from a cylinder or a plastic bag.

At least once a month, the monitoring device should be calibrated by exposure to known concentrations of HCN. Pressurized cylinders containing concentrations of HCN in nitrogen down to 25 ppm are available commercially. According to work done at the National Bureau of Standards, [253] HCN concentrations in cylinders are unstable during the first 10 days after the tanks are filled. Therefore, it is recommended that when cylinder gases are used to calibrate the monitoring device, the cylinders be allowed to sit for at least 2 weeks before use and that the HCN concentrations be verified by the analytical procedure described in Appendix II. A single calibration point at 25 ppm can be checked to determine if the instrument has maintained its calibration. If the reading differs by more than 5 ppm from the previous calibration, then several other calibration points over the useful range of the instrument should be checked and a new calibration established.

In large plants, where considerable distances between work stations exist, additional monitors may be required to ensure worker safety. Alternately, a multipoint sampling system bringing sampled air to a single instrument may be satisfactory.

XII. APPENDIX IV

MATERIAL SAFETY DATA SHEET

The following items of information which are applicable to a specific product or material containing cyanide shall be provided in the appropriate block of the Material Safety Data Sheet (MSDS).

The product designation is inserted in the block of the upper left corner of the first page to facilitate filing and retrieval. Print in upper case letters as large as possible. It should be printed to read upright with the sheet turned sideways. The product designation is that name or code designation which appears on the label, or by which the product is sold or known by employees. The relative numerical hazard ratings and key statements are those determined by the rules in Chapter V, Part B, of the NIOSH publication, An Identification System for Occupationally Hazardous Materials. The company identification may be printed in the upper right corner if desired.

(a) Section I. Product Identification

The manufacturer's name, address, and regular and emergency telephone numbers (including area code) are inserted in the appropriate blocks of Section I. The company listed should be a source of detailed backup information on the hazards of the material(s) covered by the MSDS. The listing of suppliers or wholesale distributors is discouraged. The trade name should be the product designation or common name associated with the material. The synonyms are those commonly used for the product, especially formal chemical nomenclature. Every known chemical designation

or competitor's trade name need not be listed.

(b) Section II. Hazardous Ingredients

The "materials" listed in Section II shall be those substances which are part of the hazardous product covered by the MSDS and individually meet any of the criteria defining a hazardous material. Thus, one component of a multicomponent product might be listed because of its toxicity, another component because of its flammability, while a third component could be included both for its toxicity and its reactivity. Note that a MSDS for a single component product must have the name of the material repeated in this section to avoid giving the impression that there are no hazardous ingredients.

Chemical substances should be listed according to their complete name derived from a recognized system of nomenclature. Where possible, avoid using common names and general class names such as "aromatic amine," "safety solvent," or "aliphatic hydrocarbon" when the specific name is known.

The "%" may be the approximate percentage by weight or volume (indicate basis) which each hazardous ingredient of the mixture bears to the whole mixture. This may be indicated as a range or maximum amount, ie, "10-40% vol" or "10% max wt" to avoid disclosure of trade secrets.

Toxic hazard data shall be stated in terms of concentration, mode of exposure or test, and animal used, eg, "100 ppm LC50-rat," "25 mg/kg LD50-skin-rabbit," "75 ppm LC man," or "permissible exposure from 29 CFR 1910.1000," or, if not available, from other sources of publications such as the American Conference of Governmental Industrial Hygienists or the American National Standards Institute Inc. Flashpoint, shock sensitivity

or similar descriptive data may be used to indicate flammability, reactivity, or similar hazardous properties of the material.

(c) Section III. Physical Data

The data in Section III should be for the total mixture and should include the boiling point and melting point in degrees Fahrenheit (Celsius in parentheses); vapor pressure, in millimeters of mercury; vapor density of gas or vapor (air = 1); solubility in water, in parts/hundred parts of water by weight; specific gravity (water = 1); percent volatiles (indicated if by weight or volume) at 70 degrees Fahrenheit (21.1 degrees Celsius); evaporation rate for liquids or sublimable solids, relative to butyl acetate; and appearance and odor. These data are useful for the control of toxic substances. Boiling point, vapor density, percent volatiles, vapor pressure, and evaporation are useful for designing proper ventilation equipment. This information is also useful for design and deployment of adequate fire and spill containment equipment. The appearance and odor may facilitate identification of substances stored in improperly marked containers, or when spilled.

(d) Section IV. Fire and Explosion Data

This section should contain complete fire and explosion data for the product, including flash point and autoignition temperature in degrees Fahrenheit (Celsius in parentheses); flammable limits, in percent by volume in air; suitable extinguishing media or materials; special firefighting procedures; and unusual fire and explosion hazard information. If the product presents no fire hazard, insert "NO FIRE HAZARD" on the line labeled "Extinguishing Media."

(e) Section V. Health Hazard Information

The "Health Hazard Data" should be a combined estimate of the hazard of the total product. This can be expressed as a TWA concentration, as a permissible exposure, or by some other indication of an acceptable standard. Other data are acceptable, such as lowest LD50, if multiple components are involved.

Under "Routes of Exposure," comments in each category should reflect the potential hazard from absorption by the route in question. Comments should indicate the severity of the effect and the basis for the statement if possible. The basis might be animal studies, analogy with similar products, or human experiences. Comments such as "yes" or "possible" are not helpful.

"Emergency and First Aid Procedures" should be written in lay language and should primarily represent first-aid treatment that could be provided by paramedical personnel or individuals trained in first aid.

Information in the "Notes to Physician" section should include any special medical information which would be of assistance to an attending physician including required or recommended preplacement and periodic medical examinations, diagnostic procedures, and medical management of overexposed workers.

(f) Section VI. Reactivity Data

The comments in Section VI relate to safe storage and handling of hazardous, unstable substances. It is particularly important to highlight instability or incompatibility to common substances or circumstances such as water, direct sunlight, steel or copper piping, acids, alkalies, etc. "Hazardous Decomposition Products" shall include those products released

under fire conditions. It must also include dangerous products produced by aging, such as peroxides in the case of some ethers. Where applicable, shelf life should also be indicated.

(g) Section VII. Spill or Leak Procedures

Detailed procedures for cleanup and disposal should be listed with emphasis on precautions to be taken to protect workers assigned to cleanup detail. Specific neutralizing chemicals or procedures should be described in detail. Disposal methods should be explicit including proper labeling of containers holding residues and ultimate disposal methods such as "sanitary landfill," or "incineration." Warnings such as "comply with local, state, and federal antipollution ordinances" are proper but not sufficient. Specific procedures shall be identified.

(h) Section VIII. Special Protection Information

Section VIII requires specific information. Statements such as "Yes," "No," or "If necessary" are not informative. Ventilation requirements should be specific as to type and preferred methods. Respirators shall be specified as to type and NIOSH or US Bureau of Mines approval class, ie. "Supplied air," "Organic vapor canister," "Suitable for dusts not more toxic than lead," etc. Protective equipment must be specified as to type and materials of construction.

(i) Section IX. Special Precautions

"Precautionary Statements" shall consist of the label statements selected for use on the container or placard. Additional information on any aspect of safety or health not covered in other sections should be inserted in Section IX. The lower block can contain references to published guides or in-house procedures for handling and storage.

Department of Transportation markings and classifications and other freight, handling, or storage requirements and environmental controls can be noted.

(j) Signature and Filing

Finally, the name and address of the responsible person who completed the MSDS and the date of completion are entered. This will facilitate correction of errors and identify a source of additional information.

The MSDS shall be filed in a location readily accessible to workers potentially exposed to the hazardous material. The MSDS can be used as a training aid and basis for discussion during safety meetings and training of new employees. It should assist management by directing attention to measures to ensure safe handling and use of the material. It will aid the safety and health staff in planning a safe and healthful work environment and suggesting appropriate emergency procedures and sources of help in the event of harmful exposure of employees.

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MATERIAL SAFETY DATA SHEET

I PRODUCT IDENTIFICATION		
MANUFACTURER'S NAME	REGULAR TELEPHONE NO. EMERGENCY TELEPHONE NO.	
ADDRESS		
TRADE NAME		
SYNONYMS		
II HAZARDOUS INGREDIENTS		
MATERIAL OR COMPONENT	%	HAZARD DATA
III PHYSICAL DATA		
BOILING POINT, 760 MM HG		MELTING POINT
SPECIFIC GRAVITY (H ₂ O=1)		VAPOR PRESSURE
VAPOR DENSITY (AIR=1)		SOLUBILITY IN H ₂ O, % BY WT
% VOLATILES BY VOL.		EVAPORATION RATE (BUTYL ACETATE=1)
APPEARANCE AND ODOR		

IV FIRE AND EXPLOSION DATA				
FLASH POINT (TEST METHOD)			AUTOIGNITION TEMPERATURE	
FLAMMABLE LIMITS IN AIR, % BY VOL.		LOWER		UPPER
EXTINGUISHING MEDIA				
SPECIAL FIRE FIGHTING PROCEDURES				
UNUSUAL FIRE AND EXPLOSION HAZARD				
V HEALTH HAZARD INFORMATION				
HEALTH HAZARD DATA				
ROUTES OF EXPOSURE				
INHALATION				
SKIN CONTACT				
SKIN ABSORPTION				
EYE CONTACT				
INGESTION				
EFFECTS OF OVEREXPOSURE				
ACUTE OVEREXPOSURE				
CHRONIC OVEREXPOSURE				
EMERGENCY AND FIRST AID PROCEDURES				
EYES				
SKIN				
INHALATION:				
INGESTION				
NOTES TO PHYSICIAN				

VI REACTIVITY DATA
CONDITIONS CONTRIBUTING TO INSTABILITY
INCOMPATIBILITY
HAZARDOUS DECOMPOSITION PRODUCTS
CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION
VII SPILL OR LEAK PROCEDURES
STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED
NEUTRALIZING CHEMICALS
WASTE DISPOSAL METHOD
VIII SPECIAL PROTECTION INFORMATION
VENTILATION REQUIREMENTS
SPECIFIC PERSONAL PROTECTIVE EQUIPMENT
RESPIRATORY (SPECIFY IN DETAIL)
EYE
GLOVES
OTHER CLOTHING AND EQUIPMENT

IX SPECIAL PRECAUTIONS

**PRECAUTIONARY
STATEMENTS**

**OTHER HANDLING AND
STORAGE REQUIREMENTS**

PREPARED BY

ADDRESS

DATE
