

#### IV. ENVIRONMENTAL DATA

##### Sampling and Analytical Methods

Cyanide compounds may be dispersed in workroom air as gaseous HCN or as an aerosol consisting of small particles of the salt being used. Many air sampling methods do not differentiate between gaseous and particulate cyanides, inasmuch as collection takes place in alkaline solutions which efficiently absorb most cyanide compounds. Thereafter, the analytical method selected determines cyanide radical content, and it is impossible to say what fraction of the total was attributable to any particular compound. In order to differentiate between HCN gas and other cyanide compounds, it is necessary to first remove particulates by passing the air through an efficient filter, then absorb HCN from the stream by passage through an alkaline absorbing solution. The filtered cyanides can subsequently be leached from the filter by treatment with alkaline solution, and the same analytical technique applied to both portions of the sample.

The presence of small quantities of cyanide in water was of concern long before relatively recent ecologic considerations led to an awareness that many other substances were toxic at trace concentrations. As a result, there exists substantial literature dealing with the qualitative and quantitative detection of cyanides in air and water, with at least one method (the titrimetric estimation of cyanide with silver nitrate published by Liebig [156] in 1851) still in use today, more than a century after its origination. [6,7] Almost all the methods proposed for the analysis of water or other materials have been, or can be, applied to the analysis of cyanides in air, for most air methods ultimately involve the determination of cyanide ion in solution.

The frequent use of cyanide compounds for suicidal or homicidal purposes has also led to the development of numerous means for analyzing body tissues or fluids for cyanide content, and concern with chronic exposure to low levels of hydrogen cyanide resulting from occupational exposure or cigarette smoking has similarly led to the development of sensitive methods for determining cyanide or thiocyanate levels in blood, saliva, or breath.

It is not possible to completely review all published methods for determining amounts of hydrogen cyanide and cyanide salts, because there are several hundred literature references. Only a fraction of these analytical methods have been applied to air analysis. A good summary of such methods can be obtained from several comprehensive reviews and compendia. [157-164] The review of Bark and Higson [159] is particularly thorough and is recommended as a survey of methods in use before 1963.

Most analytical methods for cyanide ion depend upon the formation of a colored compound or, in some cases, the attenuation of a color formed by other compounds. Many of the color reactions require the presence of the cupric ion, which forms cupric cyanide with hydrocyanic acid. This salt is easily reduced to the cuprous state and is used to oxidize a number of organic compounds to colored substances which may be detected visually or by spectrophotometric measurement. Some of the more commonly used organic compounds are benzidine [160,165], phenolphthalein [163, 166-169], and o-tolidine. [161] Another widely used color reaction [170,171] is based on the oxidation of hemoglobin to methemoglobin, which reacts with cyanide to form cyanmethemoglobin. This compound has a characteristic red color and a characteristic absorption spectrum. Several methods rely on the

displacement of an acidic anion by cyanide, with the consequent production of a strong acid which thereafter affects some acid-base indicator. Examples are the so-called Congo red-silver nitrate test, [160] in which a silver cyanide complex is formed along with nitric acid which thereafter causes the indicator Congo red to turn blue. A similar reaction occurs with mercuric chloride [160, 163,172], with release of hydrochloric acid, causing the indicator methyl orange to become red. [165] Cyanides can also be made to form complex thiocyanates [160] or ferricyanides with the production of such familiar colors as prussian blue. [160,163,173]

One of the most widely used colorimetric methods is the so-called pyridine-pyrazolone method, an example of the Konig synthesis for pyridine dyes, first published by Aldridge [174] in 1944 (using pyridine and benzidine) and subsequently modified by various authors. [78,175-181] In this method, cyanides are converted to cyanogen bromide or cyanogen chloride, which then reacts with pyridine to form a glutaconic aldehyde. Next, a primary aromatic amine reacts with the aldehyde to yield a colored Schiff's base. In the original procedure of Aldridge, the aromatic amine used was benzidine, but the more frequently used modification of Epstein [179] involves the reaction of cyanogen chloride with pyridine and 1-phenyl-3-methyl-5-pyrazolone, in the presence of bis-(1-phenyl-3-methyl-5-pyrazolone).

Other colorimetric methods which have been described include those based on demasking palladium chelates, [159,182] on the formation of a complex with tris-(1,10-phenanthroline)-iron(II) triiodide, [183] or on reaction with picric acid [160,165,184] and numerous other substances. A fluorometric procedure was also suggested, [185] using the reagent quinone monoxime benzene sulfonate ester.

The basic titrimetric method first published by Liebig [156] has been modified many times, so that even today it is one of the standard methods widely used for water analysis. [186,187] The most common modification consists of adding the silver-sensitive indicator, para-dimethylamino-benzylidene rhodanine, which turns from a yellow to a salmon color with a small excess of silver ion.

Numerous other techniques have been used to determine cyanide, including electrometric techniques such as polarography [188-190], voltammetry [191], amperometry [192,193], coulometry [194] potentiometry [195] and others. [196,197] The most recently introduced and probably most useful in its application to air analysis, is the electrometric technique relying on specific ion electrodes, or ion selective electrodes which respond only to cyanide ion concentrations. [198-205]

Cohen et al [92] used the specific ion electrode to measure total cyanide, as collected in 10 ml of 0.1N NaOH, and reported results as low as 0.006 mg/cu m in various areas of a plating shop.

Several gas chromatographic procedures have also been described, [161, 206-208] though such procedures have not in general been favored for air analysis to date.

A novel approach to determining cyanide levels has been described by Danek and Boltz [209] involving indirect atomic absorption spectrometric analysis. In the first of two methods, the complex dicyano-bis-(1,10-phenanthroline)-iron(II) is formed and then extracted into chloroform. The chloroform is evaporated and the residue is taken up in ethanol. The ethanol solution is aspirated directly into the flame, and iron equivalent

to a known amount of cyanide is then determined. The second method is based on precipitating silver cyanide, then determining the excess silver ion in the supernatant by atomic absorption spectrometry.

In place of titrimetric techniques, several investigators have described methods in which turbidity resulting from the formation of silver cyanide, or the reduction in turbidity due to the formation of a cyanide complex with silver iodide, are measured. [210,211]

The methods which have been used for air analysis are generally modifications of the methods just described. Most frequently, papers or other absorbants have been impregnated with various combinations of chemicals so that a color change results from exposure to air containing hydrogen cyanide. [160,161,163,166, 172,173,212-214] Such testing must be considered qualitative or semiquantitative at best, although some procedures call for considerable care to be exercised and yield results that may be adequate for evaluation of concentrations in air under some circumstances.

All such procedures must be considered unsuited to the estimation of particulate cyanide compounds unless steps are taken to ensure that all particles collected on the filter are dissolved and can react with the color-forming or otherwise acting reagent.

In 1944, Lester [171] described a quantitative method in which methemoglobin was used as the color-forming agent and subsequently published a paper [215] describing a portable analyzer which enabled the determinations to be made in the field. Phenolphthalein reagent was first described by Robbie and Leinfelder [167] in 1945 and thereafter was used as the basis for a field sampling instrument described by White. [169] A similar device was also devised by Gisclard et al. [168]

Church and Campbell [216] used the ferric thiocyanate method, and described an improvement in the colorimetric estimation of cyanides by this means. The Aldridge method [174] was first applied to air sampling by Saltzman [175], who recommended certain improvements in the procedure and, in addition, described a method of preparing standard gas concentrations of hydrogen cyanide. Saltzman collected the gas in 5% sodium hydroxide in a midget impinger.

A quantitative cyanide method in which samples were collected in 0.1 N sodium hydroxide with the subsequent formation of ferric thiocyanate was used by Zhdanov [217] as an approved method in the USSR. In later Russian publications, [218,219] the formation of glutaconic aldehyde dianilide was described as an improvement on previous methods. A Romanian method for cyanide [220] in air and biologic samples made use of the pyridine-benzidine reaction. A similar method by Hungarian authors [176] elected to use the pyridine-pyrazolone method. Truhaut et al [221] also used the pyridine-benzidine method and applied it to air and biological analyses. The American Industrial Hygiene Association [222] recommended collection of hydrogen cyanide in sodium hydroxide, followed by analysis using the pyridine-pyrazolone method. Hanson et al [161] described several methods, including the use of pyridine-p-toluidine after collection in 1 M sodium hydroxide solution, a gas chromatograph method, and the use of indicator tubes and test papers. As stated earlier, many methods rely upon collection in sodium hydroxide solution, and although frequently described as HCN methods, they are in reality total cyanide methods.

Tada [223] is one of the few authors to recommend the use of the benzidine-pyridine reaction specifically for air sampling, as well as a method using picric acid.

Forensic analyses generally used for cyanides are described in books by Thienes and Haley [157], Stolman [224], Curry (Guatelli), [160] and Sunderman and Sunderman (Free and Free) [225], while specific methods for biologic sample analyses include the use of methemoglobin as a reagent [170], a specific ion electrode method [198], and a blood method using microdiffusion [77], first used by Conway. [226] A respired air method based on the pyridine-pyrazolone reagent [227], as well as more general methods applicable to biologic samples using this same reagent are also used. [220,228] The rationale used in making a forensic diagnosis of cyanide poisoning have also received some attention. [21,229]

Many of the methods listed have also been used for water and waste water analyses, and currently the methods most favored appear to be colorimetric, using some version of the pyridine-pyrazolone method, or modifications of the titrimetric determination with silver nitrate. [177,178,186,187] Specific ion electrodes [198], and picric acid [184] have also been used. Recently, an opto-acoustic infrared absorption technique as well as the titrimetric method utilizing silver nitrate have been used in the analysis of HCN in automobile exhaust. [6,7]

Virtually every method used for cyanide analyses is subject to some interferences, usually due to the presence of certain metals which may form complexes, other anions, particularly sulfide, and a host of oxidizing and reducing agents. It is, therefore, frequently necessary to isolate the cyanide by some means, most frequently by a distillation from strongly acid

solution, where all but the most tightly bound metal complexes are dissociated to release hydrogen cyanide which is then absorbed in alkaline solution.

The recommended sampling and analytical method for the cyanides covered by this document is essentially that of the standard NIOSH method for cyanide in air as published in the NIOSH Manual of Analytical Methods. [203] HCN is collected in an impinger containing 0.1 M NaOH and the sample is analyzed directly, using an ion specific (cyanide) electrode. When alkali metal cyanides or alkaline earth metal cyanides are also to be analyzed, they are collected on a pre-filter prior to the impinger. They are then leached off the filter with base and analyzed by the cyanide electrode. These methods are detailed in Appendices I and II.

#### Continuous Monitoring of HCN in Air

Whenever pure HCN is manufactured, used, or stored in reaction vessels, cylinders, and other containers, accidental leakage or spillage may occur, giving rise to potentially lethal concentrations of the gas. Because of the lethality of the gas, combined with its poor warning qualities, it is essential to monitor the airborne HCN in areas where leakage might occur to prevent loss of life. Air sampling by any of the methods previously described, with considerable time lapse between sampling and reporting of results, is inadequate and cannot be relied upon to prevent disaster. Most of the sampling and analytical methods described could be the basis for a monitoring device for HCN, but in practice relatively few devices are commercially available.



One currently (1976) available monitoring device [230] uses amperometry, the sensing device being two electrodes in an electrolyte flowing through a porous glass cell. The instrument relies on diffusion into the cell, where contact with the measuring electrode generates a current proportional to the concentration of gas present. The instrument which covers the 0-50 ppm range, with a half-scale reading of 10 ppm, is lightweight, rugged, stable, low in cost, and permits 2 weeks of continuous operation. An alarm circuit is also available for this instrument.

### Control of Exposure

Operational equipment, procedures, and work practices should be designed to prevent the dispersal of dusts or mists of cyanide salts or the escape of HCN gas into the atmosphere of the working environment. The airborne concentration must be kept within the limits of the recommended standards. When the necessary control is not ensured by operational conditions and work practices, mechanical ventilation is required.

Ventilation should be provided in all areas where release of any inorganic cyanide dust or mist or of hydrogen cyanide gas into the atmosphere is known or possible. The ventilation system must ensure that the cyanide is removed or is diluted to concentrations below the standards recommended in Chapter I. General ventilation may be adequate in some circumstances; however, control by ventilation can be achieved best by use of local exhaust ventilation at the source of emission. [63,90] In employing exhaust ventilation for such control, the design principles given in Industrial Ventilation - Manual of Recommended Practices [231] and Fundamentals Governing the Design and Operation of Local Exhaust Systems

[232] should be followed. High ventilation rate systems for the rapid dilution or removal of HCN gas and aerosols may be useful in some areas.

Control of the hazard of potential release of hydrogen cyanide from cyanide salts requires constant care and attention to good work practices. The cyanide salts should be kept well apart from, and protected from contact with, acids, moisture, or elevated concentrations of carbon dioxide. [30,233] Even weak acids contacting cyanide salts will result in the rapid evolution of hydrogen cyanide. Moisture alone releases hydrogen cyanide slowly from sodium or potassium cyanide and rapidly from calcium cyanide. Normal atmospheric concentrations of carbon dioxide in the presence of moisture generate a sufficient concentration of hydrogen ions that the rate of evolution of hydrogen cyanide from cyanide salts may become dangerous in closed or poorly ventilated spaces. High concentrations of carbon dioxide from fire extinguishers, process gases, and combustion gas can seriously accelerate the release of HCN from the cyanide salts. Special care must be exercised to protect calcium cyanide from moisture and carbon dioxide because of its particularly rapid rate of reaction with these environmental factors.

## V. DEVELOPMENT OF STANDARD

### Basis for Previous Standards

In 1948, the American Conference of Governmental Industrial Hygienists [234] adopted a Threshold Limit Value (TLV) for HCN as a time-weighted average (TWA) of 10 ppm (approximately 11 mg/cu m as HCN). This TLV of 10 ppm was considered by the ACGIH to contain a two-fold margin of safety against mild symptoms and a seven or eight-fold margin against lethal effects according to the 1971 Documentation of the Threshold Limit Values. [235]

In this documentation [235], the ACGIH cited Henderson and Haggard [149] as reporting that 20-40 ppm of HCN caused slight symptoms. Henderson and Haggard, however, credited these values to numerous review authors and to Flury and Zernik. [118] It turns out that all these reviews derived their data from the 1931 publication of Flury and Zernik. In turn, Flury and Zernik credited the values to the works of Lehmann and Hess (please see discussion in Chapter III).

The ACGIH [235] further cited the HCN air levels of Grabois [150] as being of the order of 10 ppm. Actually, Grabois reported concentrations ranging from less than 1 to 17 ppm and reported only two areas in one of the five plants sampled which had levels over 8.6 ppm. These high levels were 17.0 and 13.9 ppm. The median HCN levels for each operational area sampled at the five apricot kernel processing plants were as follows: comminuting, 5.0 ppm; cooking, 2.5 ppm; debittering bath, 3.3 ppm; and general workroom air, 1.0 ppm. Perhaps a better statement would be that no ill effects were found at levels up to 5 ppm.

The present federal standard for HCN is also 10 ppm HCN, or 11 mg HCN/cu m, as a time weighted average (29 CFR 1910.1000, which has been published in 39 FR 23541, June 27, 1974, as amended) and is based upon the 1962 ACGIH Threshold Limit Value. Thirteen other countries and six states in the United States have set standards for HCN. These standards are presented in Table XIV-8.

The American Conference of Governmental Industrial Hygienists [236] based their selection of an alkali cyanide TLV as a TWA of 5 mg/cu m (as CN) on the work of Elkins [91], in which air concentrations above 5 ppm (as HCN) were stated to cause nasal irritation and ulceration of the septum.

The present Federal standard for alkali cyanides is 5 mg/cu m (as CN) as a time-weighted average (29 CFR 1910.1000, which has been published in 39 FR 23541, June 27, 1974, as amended) and is based upon the 1968 ACGIH threshold limit value. Nine other countries and five states in the United States have set standards for inorganic cyanide. These standards are presented in Table XIV-9.

#### Basis for Recommended Environmental Standard

Cyanide is well known as an acute, fast acting poison which can be described as insidious in that its toxic action at high concentrations is so rapid that its odor has no value as a warning. [2] At lower concentrations the sense of smell may provide forewarning. For HCN, the primary routes of entry from occupational exposure are inhalation and absorption through the skin. [29,39,107,118,147,233,237] Absorption by either route is apparently rapid. [147]

Direct exposure to cyanide salts in the workplace has occurred via inhalation of the aerosol [26,63,81,88,91,95,145] and absorption through the skin. [26,50,88,95,96,147] In addition, inhalation [3,29,238,239] and skin absorption [29,63,238,239] have been mentioned by others as the primary routes of entry for cyanide salts. Despite the fact that ingestion has been the classic route of entry for the cyanide used for attempts of homicide, [19,101,240] suicide, [19,51,101-106,240,241,242,243,244] and in accidental poisoning [51,96,102] in the general population, ingestion can be considered to be of secondary importance as a route of entry for occupational exposure.

Although Wolfsie and Shaffer [107] have stated that gaseous HCN is normally, in itself, not irritating to cutaneous or respiratory tissue, Hamilton and Hardy [145] noted that low level exposures to HCN vapors produce a blotchy eruption on the face; Williams [39] stated that in fumigation a concentration of 6-10 g/cu m produces a sensation of warmth over the entire body, followed by a reddening of the skin.

Skin contact with solutions of cyanide salts can cause itching, discoloration, or corrosion [26,94-96,154,155], which is most likely due to the alkalinity of the solution. [28,96,154] The irritant response is characterized by a discoloration or rash of a non-uniform nature which may itch or burn. [26,48,94-96,146] Such lesions have been caused by cyanide solutions as dilute as 0.5% KCN. [94] Skin contact with aqueous cyanide solutions for long periods have caused caustic burns. [48,96] These cases were generally fatal. [48,96]

Besides systemic toxicity and skin irritation, cyanide salt aerosols cause upper respiratory irritation. This has been investigated as a

response to inorganic cyanide inhalation in three separate studies. [90,91,92] The study by Barsky [90] did not include air concentrations but described the nature and incidence of the response in a copper-plating plant with poor housekeeping. Elkins [91] stated that nasal irritation and ulceration of the septum were found in an electroplating room where the concentration of cyanide, expressed as HCN, did not greatly exceed 5 ppm, (about 5 mg CN/cu m). Cohen et al [92] found no ill effects in a group of 15 electroplaters exposed to breathing zone concentrations of 0.006 mg/cu m of CN.

It appears to be generally accepted that HCN and cyanide salts act by the same mechanism, namely, the release of the cyanide ion, which inhibits cytochrome oxidase and results in histotoxic anoxia. [107] Thus, it may be presumed by analogy that if 90 ppm of HCN is fatal, 96 mg/cu m of CN, derived from cyanide salts, may be also. Extending this analogy to threshold levels, presumably 11 mg/cu m of CN would be equivalent to the current Federal standard of 10 ppm of HCN and restriction of exposures to 11 mg/cu m of CN would protect against acute toxicity from cyanide salts. However, taking into account the irritant effects observed from exposure to cyanide salts, [90,91] the current Federal standard of 5 mg/cu m of CN as an 8-hour time-weighted average appears to be too high in that it allows substantial excesses above that concentration for short periods of time. Therefore, NIOSH recommends that the current value of 5 mg/cu m of CN be retained, but that its basis be changed from an 8-hour time-weighted average to a 10-minute ceiling. This action should provide the employee with adequate protection from the systemic effects of cyanide and prevent the erosional effects produced by the alkalinity associated with the cyanide salts.

A review of the cases involving exposure to cyanide reveals that they fall into three general categories. First are those cases in which there was an acute or subacute exposure followed immediately by an acute illness. [11,13,20,26, 27,42,48,51,87,88,94,101,240] Secondly, there are those cases involving a chronic, or prolonged, low-level exposure followed by a chronic or slowly developing malaise. [17,25-27, 63,81,90,91,95,99,146] In at least two of these cases, [26,27] it is uncertain whether the coexisting long-term low-level exposure or the infrequent acute or subacute exposures were responsible for the signs and symptoms noted.

The third category is represented by those cases involving an acute exposure and a delayed chronic response occurring or worsening after the cessation of exposure. [26,109] The first of these two papers [26] concerns workers who had received a mixture of acute and chronic exposures, with effects which worsened after cessation of the exposures. The second study [109] involved 13 fumigators who also received a mixture of acute and chronic exposures, with at least one severe nonlethal acute exposure. These men exhibited a high incidence of delayed signs of effect by CN some time after their acute episodes, but less marked than those induced by the acute exposure. The author [109] suggested that damage due to cyanide may not be entirely reversible. It appears that the case for a chronic effect from an acute exposure is very weak and a better classification would be simply acute and chronic cases. All the chronic cases may be attributed to either the anoxia resulting from the inhibition of cytochrome oxidase by cyanide or a reaction by sensitive individuals to the thiocyanate produced

in detoxication of cyanide, or by those unable to excrete thiocyanate at a sufficient rate.

Hardy et al [24] did observe increased urinary excretion of thiocyanate in a group of case hardeners who were exposed to HCN and possibly to cyanide salts. Breathing zone concentrations of HCN in those workers in controlled operations were measured and found to be 4-6 ppm of HCN or less, but neither the HCN concentrations in uncontrolled operations nor any of the exposures to cyanide salts were quantified. No symptoms were noted in those exposed to 4-6 ppm. However, these men may have been included among the 25 workers with increased thiocyanate excretions. An increase in urinary excretion of thiocyanate upon exposure to cyanide has been reported by several authors. [24,60,76,79] Hardy [24] also described two cases of severe chronic cyanide poisoning which included the appearance of enlarged thyroids and attributed these to the rare inability of these individuals to excrete thiocyanate.

Two other papers [25,110] also noted thyroid enlargements, however. El Ghawabi et al [110] noted that in 36 employees exposed to cyanides at concentrations of 4.2 to 12.4 ppm, 20 workers (56%) had slight or moderate thyroid enlargements, 4 of these were firm and slightly nodular while the remaining 16 were soft and smooth. It is generally accepted that thiocyanate competes with iodide for uptake by the thyroid gland. In his recent review on the biochemistry of thiocyanate, Wood [65] has concluded that the blood level necessary for this effect is far less than the concentration which is toxic. Maehly and Swensson [76] have suggested that smoking may produce a larger effect on urinary cyanide and the thiocyanate levels than occupational exposure to HCN at concentrations between 2 and 8



ppm. They also stated that it was difficult to give reliable limits for normal levels of cyanide and thiocyanate in the urine. However, in order to assess the hazards of occupational exposure, they considered it safe to state that nonsmokers who have greater than 400  $\mu\text{g}/100$  ml of free thiocyanate in the urine, or smokers with urinary concentrations exceeding 1 mg/100 ml, should be given repeated tests. An evaluation of working conditions was proposed if the concentrations should remain elevated upon repeated determinations. The concentration of thiocyanate in body fluids at which goiterogenic effects begin is not known and would probably vary with the individual and his dietary iodide intake.

Changes in the chemical and cellular composition of the blood of employees exposed to cyanide have been reported also. [23,82,83,110,118] Most notably, El Ghawabi et al [110] found significantly higher hemoglobin concentrations and lymphocyte counts in 36 cyanide workers exposed to concentrations ranging from 4.2 to 12.4 ppm for an average duration of 7.5 years (as a broad approximation) than in 20 controls.

Although increases in urinary thiocyanate excretion, lymphocytes, and thyroid size do occur, these deviations, at least when small, have not been related to any lesion or pathological symptom or sign. Rather, they may represent the body's adaptation in maintaining homeostasis to the stress of exposure to cyanide.

El Ghawabi et al [110] were able to construct a graph of urinary thiocyanate versus the concentration of cyanide in the air. The equation for the regression line was  $M=0.65 C$ , where M is the amount in mg of thiocyanate excreted in the urine during 24 hours and C is the concentration of cyanide in the air in ppm. Using this equation and the

value of 1400 ml for total daily urine output, the 400  $\mu\text{g}/100$  ml concentration of thiocyanate in the urine suggested as the upper limit of normal for non-smokers by Maehly and Swensson [76] corresponds to an occupational exposure level of 8.6 ppm of cyanides (presumably expressed as HCN).

As discussed in Chapter III, there are no substantial studies in the scientific literature demonstrating major lesions which result from long-term occupational exposure to HCN at 10 ppm. The epidemiologic study by El Ghawabi et al [110] showing an increase in the subjective symptoms of headache, weakness, changes in taste and smell, irritation of the throat, vomiting, effort dyspnea, lachrymation, abdominal colic, precordial pain, and nervous instability among cyanide workers exposed for an average of 7.5 years (as a broad approximation) at concentrations ranging from 4.2 to 12.4 ppm, as well as the papers by Colle, [83] Radojicic, [79] Saia et al, [22] Sato et al, [84] Heymans and Masoin, [112] and Chaumont, [82] leads NIOSH to recommend that employee exposure to HCN be controlled so as not to exceed 5 mg/cu m of air expressed as CN (4.7 ppm), determined as a ceiling concentration based on a 10-minute sampling period.

Many of the previously enumerated symptoms are not unique to cyanide intoxication and can be caused by a wide range of other chemical and physical stressors. However, this cyanide syndrome, or set of subjective symptoms, appears to be sufficiently well documented as characteristic of exposure to low concentrations of cyanide to warrant its being considered an indicator of impairment of worker health and well-being.

It is recognized that many workers are exposed to cyanides in concentrations considerably below the recommended occupational limits.

Under these conditions, it should not be necessary to comply with many of the provisions of the recommended standards. However, concern for worker health and well-being requires that protective measures be instituted below the enforceable limits to ensure that exposures do not exceed the standard. For this reason, occupational exposures to HCN and cyanide salts have been defined as exposure above one-half their recommended ceiling values, thereby delineating those work situations which do not require the installation of unnecessary controls and the expenditure of health resources for environmental and medical monitoring and associated recordkeeping. These occupational exposure values have been chosen on the basis of professional judgment rather than on quantitative data that delineate nonhazardous areas from areas in which a hazard may exist. However, because of nonrespiratory hazards such as those resulting from skin or eye contact or from ingestion, it is recommended that appropriate work practices and protective measures be required regardless of concentrations of HCN or other cyanide compounds in the air.

## VI. WORK PRACTICES

Good work practices are of major importance for the prevention and control of exposures in the use of HCN and of cyanide salts. The effectiveness of other control measures is enhanced by, or even dependent on, adherence to good work practices. [30,245] Because the danger arises from the cyanide radical common to both HCN and the cyanide salts, the recommended work practices must apply to all forms, melts, and solutions of these cyanides, unless exceptions or special requirements are specifically mentioned.

Because of the special importance of work practices in the safe handling of cyanide compounds, the employer must take the necessary steps to ensure that each employee:

(1) receives adequate instruction and training in safe work procedures, in the proper use of all operational equipment and protective devices, and in all emergency procedures;

(2) is periodically given additional periods of training and instruction to maintain a high level of awareness and competence in safe work practices;

(3) engages in periodic drills or tests pertinent to emergency situations relating to cyanide compounds, fires, and explosions;

(4) receives periodic drills or quizzes regarding location, purpose, and use of emergency equipment and supplies;

(5) is provided with necessary tools, equipment, and personal protective clothing or devices;

(6) is given the supervision necessary to assure that all safety requirements and practices are followed;

(7) is instructed to shower before removing any respirator or gas-tight suit if prior contact with HCN liquid has occurred or is suspected;

(8) reports to the proper authority all equipment failures and signs and symptoms of illness.

Only properly trained and authorized persons should be permitted in areas where HCN is manufactured, transferred, stored, used, or generated, or in areas where there is a likelihood of exposure to cyanide salts as solids or solutions. Workmen and supervisors should be alert to exclude any unauthorized persons. Such areas should be clearly identified by appropriate posted warnings.

All employees should be thoroughly trained in first aid and other emergency procedures. Any person showing evidence of HCN intoxication should be removed immediately from exposure and given first aid while medical aid is summoned. [2]

The specific procedures used in humans overexposed to HCN and the excellent results obtained have been reviewed by Chen et al, [101] Wolfsie and Shaffer, [107] and Wolfsie. [100]

Approved-type, self-contained breathing apparatus with a full facepiece should be worn by any employee entering or working in an area of known or suspected life threatening concentrations of HCN. [2,239,246]

Gas-tight suits should be worn by persons entering or working in any area of known or suspected life threatening concentrations of HCN. Such suits must be impervious to HCN. [2,3,247,248]

Gas masks with canisters should never be relied upon for protection when entering areas or spaces where the airborne concentration of HCN is unknown.

Clothing contaminated by HCN should be removed as soon as possible and laundered before it is worn again. [2,249]

A worker whose clothing has absorbed HCN liquid or gas should not remove his respiratory protective device immediately on leaving the exposure area or while removing his contaminated clothing. Absorbed HCN which may be released from the contaminated garment may be sufficient to be hazardous to the individual. [249]

Employees working with any cyanide salts (cast forms, pellets, and/or powder) should wear work garments covering the arms, legs and body fully to the neck to minimize the degree of contact of cyanide dusts with the skin surfaces. The body garment must be kept buttoned or otherwise kept closed during periods of potential exposure. Gloves should be worn to protect the hands from contact with gaseous, liquid, dust, or solid forms of cyanide compounds while handling cyanides or tools or equipment whose surfaces may be contaminated with cyanide. [30]

Employees working with solutions of cyanide salts should wear personal protective garments and equipment appropriate to prevent contact of the solution with their skin and/or eyes. Gloves of rubber or other material impervious to the cyanide solutions should be worn while working with the solutions or with any tools or surfaces wetted with cyanide solutions. Aprons or other body garments of material impervious to cyanide solutions should be worn while making, mixing or transferring such solutions. Full body protective clothing should be worn in circumstances where splashes or spills are likely or when other factors make such protection necessary to prevent contact of the cyanide solutions with the skin. [30,250]

Gloves, protective clothing, and regular work clothing should be changed at least daily. All such items should be thoroughly washed between uses. When the interior surfaces of any such garments become contaminated with cyanide solids or solutions during the workday, they should be changed for clean garments.

If work clothing becomes wet with cyanide solution, it must be removed immediately and the worker must shower and thoroughly wash the affected area of the body. Wetted or splashed clothing must be washed and dried before it is worn again. [30]

Boots, shoes or overshoes made of material impervious to cyanide solutions should be worn by employees working with such solutions or in areas where spills of such solutions are likely. [30] The trouser leg should be worn outside the top of the footwear to prevent any entrapment of solution in the footwear.

Chemical safety goggles should be worn in all circumstances where there is danger of mists or splashes of cyanide solution coming into contact with the eyes. Full-length plastic faceshields with forehead protection should be worn for protection of the face. If cyanide solution or solid does get into the eye of an employee, he should immediately flush the eye with a copious flow of water for at least 15 minutes and obtain medical attention as soon as possible. Eye-flush fountains or other means for obtaining a copious and gentle flow of water suitable for flushing the eyes must be provided and readily accessible in all areas where cyanide solutions are used. [30,251]

All protective and process equipment must be inspected frequently and maintained in good and safe operating condition. Storage tanks should be thoroughly cleaned, inspected, and conditioned before use. In the unloading of HCN liquid from tank cars or tanks of motor trucks, instructions of the supplier should be carefully followed. All connections and lines should be inspected and secure before the flow of HCN is turned on. Warning signs should be posted fore and aft of the tank car or truck and in a perimeter around the area. Storage tanks should be vented and have provision for destruction or safe dissipation of the vented gas. Cylinders of HCN should be stored in cool areas and away from combustible material, open flames, or other possible sources of ignition. Only responsible, authorized persons should have access to the storage area.

All areas where any cyanide salts are stored should be adequately ventilated to maintain the airborne cyanide concentration below the recommended standards. In many instances, natural ventilation may be adequate, but mechanical ventilation must be used where necessary. [30,63,90] For storage, cyanide salts in solid or solution forms should be in sealed or tightly covered containers in an area remote from any acids or acid vapors. The containers should be protected from moisture. No hooks should be used in handling containers of cyanide salts.

No employee should work alone in an area or space of possible hazard from HCN. [2,239,246] Another employee should be in attendance and contact (preferably sight contact) in a safe area or at a distance so as not to be affected by an emergency situation at the site of the first employee. The second employee ("buddy") should be alert and equipped to summon help and render aid, if needed.



The employee should carefully and precisely follow all operational procedures specified for the handling of HCN in containers, transfer operations, or other equipment. Suppliers' and manufacturers' instructions should be carefully followed. [2]

When HCN is used for fumigation purposes, the space should be sealed to prevent the gas from leaking into surrounding spaces or areas. Warning signs should be posted and guards placed to keep unauthorized persons at a safe distance. All laws, regulations, ordinances, and codes applicable should be followed. Only licensed fumigators should do such work. [246]

Open containers of any solid cyanide salts or of solutions of cyanide salts should be limited to those necessary for operational requirements and procedures. Such open containers must be used only in adequately ventilated spaces so that the recommended standards for the airborne concentration of cyanide are not exceeded. Good practice dictates that, in so far as practical, covers be provided for such containers and used whenever possible.

Solutions of cyanides should be maintained as basic as practical to prevent any evolution of hydrogen cyanide. When weakly basic or neutral solutions are used, ventilation must be provided sufficient to prevent accumulation of the HCN evolved from exceeding the recommended standard for HCN in the work room air. When the addition of an acid to a cyanide solution may be necessary, the process should be fully enclosed and ventilated. Respiratory protection should be provided for all workers potentially exposed to any release of hydrogen cyanide.

Fused salt baths containing cyanide salts should be provided with local exhaust ventilation. Care should be exercised in the operation of

such baths to avoid spills and splashes. Addition of salts should be made carefully, using a shovel or special tool. The area about the bath should be regularly cleaned to prevent accumulation and encrustation of cyanide salts on adjacent areas. Workers at fused salt baths should wear safety goggles with side shields.

Local exhaust ventilation must be used for all operations emitting dusts or mists of cyanide salts. [80,232]

Tanks and other equipment which must be entered for inspection, maintenance or repair, should be drained as completely as possible and then filled with water and agitated. After 15 minutes, they should be drained again and refilled for another 15 minutes, then drained again. The tanks should then be inspected for residue and encrustation of cyanides. These should be broken loose mechanically or by the force of a water stream and flushed away. The tank should then be purged with fresh air, followed by testing for the absence of cyanide in the air before anyone enters. Entering workmen should wear protective clothing. Approved type respiratory protective devices should be available for use, if needed. [30]

HCN liquid should not be transferred from one cylinder to another or from an applicator back into a cylinder.

Waste solutions of HCN should be destroyed by either (1) alkaline chlorination or (2) alkaline reaction with ferrous sulfate. [2]

Cyanide waste solutions and cyanide-contaminated rinse or wash waters should be treated to destroy the cyanide before being discarded. Treatment of cyanide waste is achieved by oxidation of the cyanide in alkaline solution by addition of chlorine or other oxidizing agents. [30,252]

Transfer lines should be thoroughly drained and flushed after each use for transfer of HCN.

In the event of spills of HCN liquid, the area should be cleared of all persons except emergency personnel properly trained and equipped to deal with the emergency. The area should be roped off and warning signs posted to exclude all other employees until tests show that the atmospheric concentrations of HCN are below the recommended standard. [2]

Spills of cyanide solids or solutions should be cleaned up immediately. Spills of NaCN or KCN solids may be shoveled carefully into containers, with care being taken that cyanide dust is not dispersed into the air. The residue after shoveling, or small spills, may be removed by dry vacuuming or flushing with a liberal quantity of water.

Spills of  $\text{Ca}(\text{CN})_2$  solids should be cleaned up by shoveling the bulk of the spill carefully into dry containers, followed by dry vacuuming of the spill area to remove any residual cyanide solids. Water should not be used in the cleanup of  $\text{Ca}(\text{CN})_2$  spills unless it has been alkalinized.

Respiratory protection (see Chapter I, Section 6) should be worn by workers while cleaning up spills of cyanide salts. Caution: Filter-type respirators alone do not provide adequate protection in the case of  $\text{Ca}(\text{CN})_2$  spills. Spills of cyanide solution should be washed away with water and with the same precautions stated in the preceding paragraph.

Water from the flushing or cleaning of cyanide spills or cyanide contaminated equipment should be treated as cyanide waste solution. These solutions should not be washed or emptied into a drain system which may contain or receive acid wastes.

When in the judgment of a professional industrial hygienist, the airborne cyanide concentration is likely to be excessive, continuous monitoring should be performed. Areas of potential exposure to HCN gas should be routinely monitored to ensure that concentrations of the gas in the air remain within the recommended standards. Automatic and recording monitoring systems will be desirable in certain areas. [2,247,249]

Each plant must establish an emergency plan and program. The workers and the emergency teams should be thoroughly informed and trained in their responsibilities and actions in emergencies. Emergency stations equipped with first-aid supplies and equipment, a suitable number of approved-type respiratory protective devices, protective garments, and other special equipment as needed should be established and maintained readily accessible to areas wherein cyanide emergencies may be anticipated or may occur. [30,239] A program should be established for the frequent and regular inspection and maintenance of all protective and safety equipment.

Employees should observe good personal hygiene, including showering and changing clothes at the end of a workshift. They should wash well before eating. Eating and smoking should be permitted only in uncontaminated areas designated for these purposes. Food, candy, tobacco, or other items intended for ingestion or oral contact should not be taken (or carried in garment pockets) into an area of cyanide exposure or use because of the potential for contamination. Any such items taken into a cyanide area should be regarded as contaminated and should be discarded.