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STUDIES ON SOLVENT EXTRACTION OF FREE HYDROGEN CYANIDE FROM RIVER WATER

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ABSTRACT. A method for free and strongly complexed cyanide measurement in river water was developed. Recovery tests from solution with and without river water, using various solvent combinations and background control were investigated to obtain an accurate and precise extraction method for the measurement of hydrogen cyanide in Kaduna River, Nigeria. The method enhanced the determination of undissociated hydrogen cyanide and the equilibria between hydrogen cyanide, cyanide ion and complex cyanides. A small portion of the hydrogen cyanide was extracted by equilibrating the sample with methylchloroform (1,1,1-trichloroethane), methanol, hexane and 2-octanol inclusions, respectively, in the solvent matrix with 2.5 M NaOH. The extracted hydrogen cyanide is transferred into tetrasodium pyrophosphate solution and determined colorimetrically. A total cyanide concentration of 0.03 mg/L in the river water and 0.40 mg/L in an effluent water sample, respectively, were obtained by the proposed method compared to 0.020 and 0.45 mg/L from the established diffusion method. The proposed method was sensitive and reproducible in the range of 0 to 5 mgL^{-1} of hydrogen cyanide with detectable limit of about 0.01 mgL^{-1}.

KEY WORDS: Solvent extraction; Free hydrogen cyanide; River water

INTRODUCTION

Hydrogen cyanide (HCN) otherwise known as hydrocyanic or prussic acid is commercially available as a colourless gas or technical grade pale blue liquid of 95-99.5 percent purity. Soluble in both water and alcohol, it is stabilized by the addition of phosphoric acid to prevent decomposition and explosion. It is produced by synthetic catalytic processes involving the reaction of ammonia and natural gas (or methane) with or without air and as a bye-product in the production of acrylonitrile by the ammoxidation of propylene. It is released into the atmosphere from biomass burning, volcanoes and natural biogenic processes from higher plants, bacteria, algae and fungi [1].

$$NH_3(g) + CH_4(g) \rightarrow HCN(g) + 3H_2(g) \quad (1)$$

Cyanide is the primary toxic agent. It is found in the waste from metal finishing operation and mine of non-ferrous metals. It is released to the air through chemical manufacturing process industries, metal plating, and extraction of gold and silver from low grade ores. Other sources include emission from municipal solid waste incinerators, biomass burning, fossil fuel combustion including fuel emission, fumigation operation, production of coke and in cigarette smoke. In air, it is present as gaseous hydrogen cyanide with small amount in fine dust particles. Sources of cyanide in water may be from anti-caking salt run off used on roads, landfalls, agricultural and atmospheric fallout and/or washout, discharges from gold mining plants, wastewater treatment works, organic chemical industries and Iron and steel production [2-5].

Healthy individuals have small amount of cyanide in the body and concentration of 50 μg/100 kg tissue have been found in different organs. A group of people with higher risk of exposure include individuals involved in large scale processing of cassava, consumers of improperly prepared foods containing cyanogenic glucoside as in cassava, bitter almonds,

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apricot kernel seed, and also, passive smokers and fire-related inhalation victims. Death has been reported on absorption of an average of 1.4 mg HCN per kg body weight. The lowest reported oral lethal dose for human is 0.54 mg/kg body weight [6, 7].

The presence of cyanide in the body could stop the production of adenosine triphosphate (ATP) via electron transport chain; giving rise to another metabolic pathway in which ATP is synthesized through glucose degradation (glycolysis) to lactic acid. This pathway does not utilize oxygen and insufficient ATP is produced to sustain active aquatic organisms. More so, free cyanide (HCN or CN^-) is a respiration poison which inhibits cytochrome oxidase (by binding haem iron) bringing oxidative mechanism to a complete cessation with time. It also inhibits over forty enzymes and important metallo-enzymes containing iron, copper, and molybdenum. In humans, acute or severe cyanide exposure leads to cardiovascular and central nervous system disturbances, headache, weak pulse, vomitting, stupor, convulsion, coma, tracheal congestion, haemorrhage, parkinson-like syndrome and neuropsychiatric manifestation [1, 8].

Howe and Noble [9] determined total concentration rather than free cyanide spectrophotometrically and did not investigate cyanide recovery or potential analytical interference. United States Department of Health and Human Services, Public Health, Centres for occupational safety and Health (NIOSH method 6010) determined HCN by gas chromatography with visible absorption spectrometry and obtained a detection limit of 0.01 mg/Cu [10]. Broderius determined hydrogen cyanide concentration colorimetrically from linear calibration curves that related the determined HCN displacement rate (or quantity of HCN collected) to the known concentration of HCN for standard cyanide solutions [11]. Seto *et al.*, [12] applied colorimetry, ion-specific electrode and headspace gas chromatography with a nitrogen specific detector while the United States EPA determined cyanide in aqueous matrices by colorimetric, titrimetric and electrochemical methods after pretreatment to produce hydrogen cyanide and subsequent absorption in sodium hydroxide solution [13]. Most of the described methods required additional sample handling which lead to increase in free cyanide loss. Also, cyanide recovery or potential analytical interferences were not determined. The analysis of total cyanide provides information on cyanide speciation, as well as harmful effects of free hydrogen cyanide to aquatic organisms and drinking water. Sample preparation by solvent extraction using organic solvents has been done by other workers in the literature but unlike in the previous studies the choice of our solvent combination prevents emulsion formation between phases due to low viscosity and sufficiently low-density difference from the aqueous phase. The aim of this work was to develop an extraction method for total cyanide determination to minimize cyanide losses while providing an accurate and precise measurement of cyanide content in river water.

EXPERIMENTAL

Reagents and solution

All reagents were of analytical grade, unless otherwise stated. 1000 mg/L standard cyanide solution (BDH) was prepared by dissolving 1.65 g NaCN in 25 mL of 0.10 M NaOH and diluted to 1 L with distilled water. The solution was standardized by titration against $AgNO_3$ solution. Other reagents include 2 % (w/v) tetrasodium pyrophosphate solution (Fisher) and 0.25 M *p*-phenylenediamine solution (Analar) in 0.1 M HCl. The desired concentration required for the calibration of standard curves for each sample were prepared from stock solution by serial dilution and sample solution was determined by colorimetry.

Solvent extraction

Methanol-NaOH solvent matrix

Methanol in combination with 2.5 M NaOH was the first solvent matrix examined. Concerns about methanol interference with cyanide colorimetric analysis suggested evaporation of the methanol prior to distillation [14, 15]. MeOH samples were therefore evaporated overnight in an oven at 60 ^{o}C; while the other sample treated in same way was sealed mixed for 16 h. Aliquots were drawn from the sodium hydroxide portion of each sample and analyzed for total cyanide before and after distillation.

Chloroform-NaOH solvent matrix

Testing of chloroform as an extraction enhancer was performed using extraction of cyanide spiked solvent mixture. This is because sodium hydroxide-chloroform mixture is explosive. Flasks containing NaOH-chloroform mixture were left open during mixing but kept closed thereafter, due to possible volatilization that could occur during heating. Spiked samples containing 70 μgL^{-1} as KCN without water sample were prepared for 2.5 M NaOH alone and for 2.5 M NaOH-chloroform mixture, (35:15 v/v), after a 16-hour extraction in the dark. The sodium hydroxide solution was withdrawn and analysed for total cyanide.

Hexane/2-octanol-NaOH solvent matrix

Hexane and 2-octanol were examined using 2.5 M NaOH/hexane and 2.5 M NaOH-2-octanol (v/v) mixture in 50 mL centrifuge tubes, respectively. The ratio was chosen based on the recommended value for preventing fatty acid interference during distillation [16]. Sample spiked with 37 μgL^{-1} as KCN were prepared for each solvent combination, including a 2.5 M NaOH control. The tubes were sealed and covered to prevent light intrusion and rotated for 16 prior to total cyanide analysis without filtration of the sodium hydroxide phase.

Adsorption procedure [14]

The adsorbed cyanide ion on sediment and rock of river Kaduna was determined by measuring 1 g sample into a well stoppered plastic bottle and mixed with 20 mL of distilled water for 1 h at 25 ^{o}C. 10 mL 0.1 M KCN solution was added and stirred, then filtered. The pH of the filtrate measured is proportional to the cyanide concentration. The decrease of the concentration was determined relatively to null samples. The change in cyanide concentration with time was measured in buffer solutions at pH 7, 8, 9 and 10 containing KCN or cyanide as well, Cu(I) and Zn(II). This is because the river water was polluted with large amounts of amount of Cu^{+} and Zn^{2+} ions with cyanide ion. The adsorption method and HCN evaporation were done in the presence of Zn^{2+} and Cu^{+} ions taking their equilibria into consideration.

Proposed sample procedure

The temperature of bottle containing methylchloroform was adjusted to about that of the river and sample was obtained with the least possible disturbance to avoid equilibria changes between HCN, CN^{-} and complex cyanides in the system; and aeration which lead to CO_2 and HCN losses. 100 mL of river water was measured into a 150 mL separatory funnel containing 40 mL of methylchloroform followed by 5 mL 0.1 M HCl. (3 mm glass bead is added if emulsion forms). The temperature was noted and the funnel stoppered and shaken for 30 seconds. The

organic layer was separated and transferred to a 50 mL separatory funnel containing 10 mL of tetrasodium pyrophosphate solution. The aqueous layer was shaken for 30 seconds and the organic layer was separated for subsequent recovery. The aqueous layer was transferred to a 50 mL flask containing 2 mL of concentrated HCl. The funnel was rinsed with a few drops of water and stoppered tightly. The procedure was repeated with addition of measured amount of the working cyanide solution diluted to 100 mL in each case with distilled water. The temperature at which extraction were carried out was noted. 2 mL of bromine water was added and each flask was stoppered and set aside for 5 min. 4 mL arsenous acid was added to each flask to decolourise the solution as well, drops of methylchloroform present. 10 mL of freshly prepared mixed reagent (3:1 v/v) pyridine-*p*-phenylenediamine solution was added followed by dilution to mark. The solution was mixed thoroughly and left for 30 min for colour development. The absorbance was measured at 540 nm with water as reference. A blank determination was carried out on 100 mL of distilled water for each batch of sample and corrected for. Calibration graph was constructed.

Standard method [16, 17]

Solvent combinations were examined to assess the potential interference (of solvent) with the cyanide analytical technique using solutions spiked with cyanide in the absence of river water which contains cyanide. The method was used to determine recovery from river water by adding cyanide spiked solution, and treated as described by Ebbs *et al.* [14]. The solution is equivalent to a solution of hydrogen cyanide of concentration, 2700 x 2 x volume of 0.1000 1 M silver nitrate required/volume of cyanide titrated. 5 mL of the solution was diluted to 250 mL, and 20 mL of this solution was further taken and diluted to 500 mL to give a working solution equivalent to 2 mg HCN L^{-1}.

Calculation of HCN concentration

The concentration of hydrogen cyanide [17] in sample is,

$$\frac{C \times 35}{V[1-0.02(t_1-t_2)]} \quad (2)$$

where, t_1 = temperature at which the calibration graph was prepared; t_2 = temperature of sample; v = volume (mL) of organic phase; c = concentration of HCN from calibration graph (after correcting for the blank).

Effect of pH on the proposed method

Cyanide solutions containing 0.05 M diethanolamine were prepared and varying amounts of HCl were added to give pH values between 8 and 10. The total concentration of cyanide as hydrogen cyanide was 1.5 mg/L. The solutions were analyzed in triplicate by the proposed method and the pH values were determined after extraction at 25 ^{o}C. The theoretical hydrogen cyanide concentrations were calculated from the standard equation,

$$K_a = \frac{a\mathrm{H}^+ \times a\mathrm{CN}^-}{a\mathrm{HCN}} \quad (3)$$

where K_a is the dissociation constant of hydrocyanic acid (6.17 x 10^{-10} at 25 ^{o}C), *a* is the activity and pH measurements were assumed to give activity coefficient of un-ionised hydrocyanic acid which was taken as unity. $a\mathrm{CN}^-$ is the cyanide-ion activity coefficients calculated by using Debye-Huckel equation since the ionic strengths were low.

Sampling

Sampling, storage and analysis were done with caution and immediately upon sample collection according to reported method [18].

Preparation of river water prior to extraction is important for obtaining uniform, consistent result as determined by the standard deviation of the sample replicate. Extraction tests were performed on river water sample with and without cyanide under liquid nitrogen (i.e. sample homogenization) prior to extraction in 2.5 M sodium hydroxide (NaOH) since river water under liquid nitrogen increases recovery of cyanide content [3, 4]. It also improves precision measurement while simultaneously minimizing cyanide losses to volatilization. River water exposed to 2 mgL^{-1} total cyanide as $K_4Fe(CN)$ for 20 and 7 days, respectively, were extracted in 2.5 M NaOH with and without homogenization.

RESULTS AND DISCUSSION

The analysis of total cyanide ($HCN + CN^- +$ complexed cyanide) helps to provide information on cyanide speciation while the choice of solvent mixture was important for minimizing cyanide recovery during extraction without adversely affecting cyanide analysis. For example, chloroform being heavier than water with distribution coefficient of HCN in chloroform-to-HCN in water as 0.28 at 18 ^oC is very suitable for HCN extraction with a sample-to-solvent ratio of 4:1; but carbondioxide was extracted as well. The pH of 10 was maintained in the extraction procedure to prevent cyanide loss and changes in the chemical species of cyanide present in the sample. The infusion of NaOH in the solvent matrix minimized volatilization losses during extraction. Changes in pH were avoided as much as possible because of the effect on the ionization of HCN and on the dissociation of the complex cyanide with metals in water. Previous studies have shown that toxicity of cyanides to aquatic organisms is by free hydrogen cyanide and not cyanide ion, however, cyanide ion is toxicologically important because it exists in equilibrium with hydrogen cyanide [18].

$$CN^- + H_2O \leftrightarrows HCN + OH^- \quad (4)$$

Differences in sensitivity to cyanide occur between different animal species and many plant mitochondria contain electron transport chains which are insensitive to cyanide. The concentration of cytochrome oxidase in fish mitochondria does not vary with ambient temperature but the activity of the enzyme is greater in mitochondria from cold associated individuals. Thus fish are more sensitive to cyanide when acclimated to lower temperature [8].

Recovery of used solvent is necessary because methylchloroform is toxic to the bacteria responsible for the anaerobic digestion of sewage sludge and should not be discharged into a sewage system. When methylchloroform was shaken with solutions of sodium hydroxide, emulsion was not formed. After the trial of solutions of various multivalent alkaline salts, a two percent (10 mL) of tetrasodium pyrophosphate was adopted and used for this study.

Preliminary studies indicated that HCN could be stored for about 24 h in a stoppered glass vessel without significant change if the pyrophosphate extract is acidified with HCl. It was only under this condition, samples were transported to laboratory for further analysis. Calibration curve was constructed using the proposed sample procedure to obtain a straight line. This suggests that hydrogen cyanide obeys the distribution law in the system under the concentration range of 0 to 5 mg/L studied. The present method is restricted to this range where it is most reproducible and sensitive.

If the river water containing cyanide comes into interaction with air, soil or sediment the cyanide content decreases due to dilution, and HCN, a weak acid, with pK of 9.14, can be

formed in weakly alkaline solution. Cyanide ion can also adsorb on the rocks, surrounding soil or react with the organic material. The adsorbed cyanide may reappear as a polluting agent. Thus, the adsorption method was necessitated by the fact that the long-lasting damaging effect of cyanide is connected with its adsorption on soil, sediment or rocks which form the river bed and if the effect is reversible or not. The quantity of this potential pollution (adsorbed cyanide) is determined by first evaluating cyanide evaporation in buffer solutions at various pH without soil, water or sediment, within the same conditions as the sorption experiments or such conditions where HCN does not evaporate must be provided. [19].

Table 1 shows that changes in pH values on extraction are not completely avoidable and it is possible that substances other than carbon dioxide are extracted in some instances. The distribution of HCN between the phases at equilibrium was achieved within 20 min and the proportion of HCN extracted is about 3.5 % at 25 ^{o}C giving a distribution coefficient of 0.10. The amount of HCN extracted by methylchloroform decreases as the temperature falls below the room temperature.

Table 1. Effect of pH on extraction.

Sample	pH before extraction	pH after extraction
River water	7.50	7.45
	7.40	7.10
	7.10	7.10
	8.80	8.74
	8.50	8.55
	8.00	8.20
Waste water	6.56	6.70
	6.50	6.35

Determinations of hydrogen cyanide were carried out in solutions of the complex cyanides of iron which are largely undissociated, (strong complex) and in those of zinc and cadmium in which dissociation is practically complete at concentrations of 10^{-6} M and lower (weak complexes).

Cyanide reacts with many chemical elements including phenol, oleic, citrate and others, producing a wide variety of toxic cyanide-related compounds; leading to serious interferences (Table 2). The chemical break down of many of the above cyanide and cyanide-related compounds lead to formation of high concentrations of nitrate and or ammonia which may affect aquatic life. There are many other interfering ions in river water but we selected the parameters of interest peculiar to our environment and further work is envisaged.

Table 2. Interference studies.

Species	Amount added (mg/L)	Tolerable limit (mg/L)
Phenol	10	> 10
Oleic, stearic acid	1	Serious interference
Cu^{2+}, Zn^{2+}, Cd^{2+}	1	Serious interference
Tartrate, citrate	5	> 5
Fe^{2+}	100	> 150
Chloroamines	10	> 10
Ammonia	4	Serious interference

All glasswares were cleaned with chromic acid to avoid high blank values and associated erratic results. To assess the sensitivity of the proposed method, replicate determination were

carried out on standard cyanide solutions. Results obtained were standard deviations of ± 0.008 mg/L for 0.03 mg of HCN L^{-1}; ± 0.015 mg/L for 0.03 mg of HCN L^{-1} and ±0.004 mg/L for six determinations of the blank value in 1-cm cells. This suggests a limit of detection of 0.01 mg/L.

In Table 3 the effect of pH on the proposed method was evaluated by comparing calculated concentration of HCN with that found in solutions of known pH and (known) total concentration. The results show satisfactory agreement.

Table 3. Calculated and observed hydrogen cyanide concentrations at different pH values.

pH value	Ionic strength	Calculated HCN (mg/L)	HCN obtained (mg/L)
10	2×10^{-4}	0.65	0.80
9.5	5×10^{-4}	0.92	0.98
9.0	2×10^{-3}	1.34	1.30
8.5	3×10^{-3}	1.40	1.43
8.0	5×10^{-3}	1.45	1.48

In Table 4, KCN were added to samples of river water and waste water, respectively. The effect of ionic strength on the dissociation constant was ignored while allowance was made for the ionization of hydrocyanic acid. The recoveries for river water was quantitative while recoveries of hydrogen cyanide with waste water were low probably due to the presence of complexing metals in water.

Table 4. Recovery experiment for added cyanide.

Sample	pH value on cyanide addition	Addition of cyanide as potassium cyanide (mg/L)	Hydrogen cyanide found (mg/L)
River water	-	0.05	0.05
River water	7.8	1.00	0.86
Waste water	-	0.05	0.64
Waste water	7.4	1.00	0.78

Comparison with established method

The proposed method was compared with standard diffusion method [16, 17] to obtain total cyanide (free plus complex cyanide).

Table 5. Comparison with standard diffusion method [16, 17].

Sample	Total cyanide obtained (mg/L)	Hydrogen cyanide by diffusion method (mg/L)	Hydrogen cyanide obtained by proposed method (mg/L)
River water	0.03	-	0.009, 0.009, 0.007
River water	0.025	0.020	0.018, 0.016, 0.018
Effluent water sample from Peugeot Automobile plant	0.40	0.45	0.4, 0.5, 0.6

Effluents are of less interest to the toxicologist than river water as concentrations of HCN resulting from the discharge of such effluents into river cannot be evaluated accurately from the dilution ratio which affects equilibrium and pH changes by the mixing. Complex cyanides may be present in such solution but the high pH (>10) obtained with 2.5 M NaOH reduces cyanide reactions with both organic and inorganic solid [14].

From extraction point of view, the methanol-NaOH solvent matrix is not very effective due to methanol interference with cyanide to give low results. Thus, methanol must be evaporated prior to sample analysis. The chloroform-NaOH mixture can be explosive, and must be left open when mixing which could lead to loss of HCN via volatilization. Chloroform also reacts with the free cyanide and NaOH to release a gas [6]. The hexane or 2-octanol-NaOH mixture as NaOH/hexane and NaOH/2-octanol (4:1 v/v) lead to interference from fatty acids as evidenced by forming [16, 20]. Solvent extraction is time consuming and it requires the use of large volumes of generally toxic organic solvents compared to other methods. However, the three commonly used techniques namely, colorimetric, titrimetric and electrochemical, all suffer from interferences. For example, sodium thiosulfate used as an antidote to treat chemical poisoning interferes with HCN determination, while the presence of metals may suppress the transformation of cyanide to formic acid and lower its (HCN) concentration [19]. The proposed method helps in the removal of interfering substances in Table 2, coupled with minimum loss of free cyanide. Furthermore, a high distribution ratio for the solute and low distribution ratio for undesirable impurities of 0.10 was due to choice of solvents for extraction. This method further enhances the ease of recovery of cyanide content (solute) from the solvent under liquid nitrogen for subsequent analytical processing.

CONCLUSIONS

It is inconvenient to carry out the entire determination at the point of sampling because of possibility of changes in temperature, loss of carbondioxide or HCN by physical, chemical or biological means. However, by the addition of concentrated HCl to tetrasodium pyrophosphate extract in a stoppered vessel, HCN can be stored for about 24 h at 25 ^{o}C. The optimal sample extraction method of methylchloroform with 2.5 M NaOH provided reproducible results of total and free cyanide recoveries from water sample and was adopted as method of choice. The singular most important advantage of the proposed method is the prevention of emulsion formation between phases, and its convenience for field use. The ratio of HCN ion in a sample varies with pH, temperature and ionic strength, and results obtained in Tables 3-5 are lower than the literature values of 0.8 to 300 mg/L for aqueous sample [19]. Cyanide concentration in ambient air is less than 1 μg/m^3 and 10 μg/L in water [13].

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