

DETERMINATION OF FREE CYANIDE AND TOTAL CYANIDE CONCENTRATIONS IN SURFACE AND UNDERGROUND WATERS IN BOGOSO AND ITS SURROUNDING AREAS IN GHANA

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ABSTRACT. Concentrations of free cyanide and total cyanide in water samples in Bogoso and its surrounding areas in Ghana have been measured in this study. Concentrations of free cyanide and total cyanide were found to be above the maximum permissible discharge limit of effluent from mining companies into natural waters set by Environmental Protection Agency, Ghana (GEPA). A comparison of the results obtained in this study with permissible levels set by US Environmental Protection Agency and the World Health Organization reveals that surface waters in the study areas are highly polluted with cyanide and it's not safe for human consumptions. This means that, the resident in and around Bogoso are at risk.

KEY WORDS: Free cyanide, Total cyanide, River Bogo, River Aprepre (River Dumasi), River Ankobra

INTRODUCTION

Cyanide is a singly charged anion containing equal atoms of carbon (C) and nitrogen (N) triply bonded together as $\text{C}\equiv\text{N}$ or CN^- . Cyanide has strong ability to attract metals. Mining companies have made huge profit from the use of cyanide in extracting gold from its ore, even from low grades of ores. Bogoso Gold Limited (BGL), have adopted the use of cyanide solution in extracting metallic gold from its ores. The ores include surface ores (iron oxides – haematite $\alpha\text{-Fe}_2\text{O}_3$ and magnetite Fe_2O_4), sulfide ores and transition ores. Effluent from BGL treatment plants contains high concentration of cyanide [1].

Cyanide is a toxic species that is found in effluents of mining companies. For example, a teaspoonful of cyanide solution containing 50 to 200 mg of cyanide ingested by an adult human being will result in his premature death. Cyanide exerts its toxic effects by forming a complex with ferric ion (Fe^{3+}) of mitochondrial cytochrome oxidase, the enzyme that catalyze the terminal step in the electron transport chain thereby preventing the use of oxygen by cells. Since cytochrome oxidase occupies a central role in the use of oxygen in all cells, its inhibition leads to the disruption of cellular respiration producing cytotoxic hypoxia [2].

The use of cyanide as an extractive technique for gold mining in Ghana has become unpopular in recent times because of cyanide spillages that the country has witnessed. Ghana has recorded about ten officially reported cyanide spillages between 1989 and 2003 [1]. Notably among them are: (i) in 1989, there was a cyanide spillage by Obenemase Mines near Konongo, which contaminated a tributary of River Oweri. River supplies about 10 gallons of water a day to the residents of Kumasi metropolis, (ii) in 1996, large quantities of cyanide solution was spilled by Teberebe Goldfields Limited into Agonaben stream, a tributary of River Bonsa causing harm to lives and aquatic organisms, (iii) Bogoso Gold Limited also spilled large volumes of cyanide solution into River Anikoko in 1991, which flows into River Bodwire. This forced many of the farmers to abandon their farms and resettle in other communities. The company constructed boreholes for some of the affected communities but in places where the boreholes were not operational, the farmers' were compelled to drink the polluted streams posing health hazard to them. The affected communities were Brakwaline, Nakaba and Anikoko.

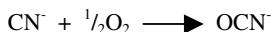
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Goldfields Ghana Limited – Tarkwa Gold Mine in 2001 and 2003 spilled large volumes of cyanide solutions into River Asuman, which serve as the source of drinking water for the people of Abekoase and its surrounding areas [1]. The mining companies maintain that cyanide breaks down quickly in the environment into less toxic forms and that the effect of cyanide spillage is transient. However, many of these less toxic forms of cyanide may persist for long periods of time, stored or bioaccumulate in aquatic plants and in human beings [3].

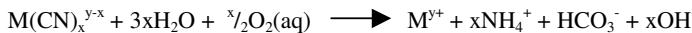
The use of cyanide compounds by mining companies, coupled with the toxic nature of cyanide compounds, cyanide spillages into nearby water bodies and limitations in current analysis and monitoring of cyanide related compounds, raises serious concerns regarding public safety and environmental protection at mine site and mining communities.

Cyanide break down quickly in surface water to form other products and the three most commonly monitored cyanide species in surface waters around the concession of mining companies are: (i) free cyanide: refers to cyanide ion and hydrogen cyanide, (ii) weak acid dissociable cyanide: refers to cyanide complexes with metals like Cd, Ni, Cu and Zn. These complexes readily break down in the environment to release the cyanide ion [4, 5], (iii) total cyanide: refers to all free cyanide, all dissociable cyanide complexes and all strong metal cyanide complexes of Fe, Au, Co and Pt. Ferrocyanide and Ferricyanide, which decompose in the presence of sunlight to release cyanide ions into the environment [5-7].

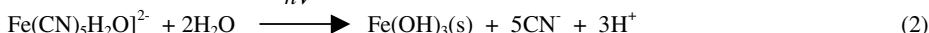
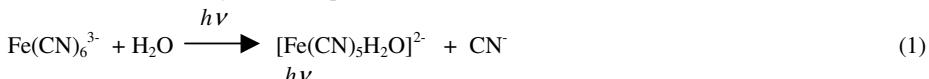
Several methods exist for treating cyanide-contaminated solutions. These include: (1) Physical methods such as dilution, the use of membranes with either electrodialysis or reverse osmosis to separate cyanide from water and hydrolysis/distillation where free cyanide hydrolyzes in water to produce aqueous hydrogen cyanide [HCN(aq)]. The HCN(aq) can then volatilize as hydrocyanic gas [HCN(g)] because [HCN(g)] has a vapour pressure of 100 kPa at 26 °C, which above that of water [8-10]. (2) Complexation methods: cyanide treatment can also be done with several complexation methods such as acidification/volatilization, metal addition, flotation and solvent extraction [5]. (3) Cyanide oxidation can be conducted using biological, catalytic, electrolytic, chemical and photolytic methods. Various species of bacteria, fungi, algae, yeasts and plants, along with their associated enzymes and amino acids, are known to oxidize cyanide naturally. The predominant mechanism of bio-oxidation is the metabolic conversion of cyanide to cyanate, OCN⁻ a species less toxic than cyanide:



Pseudomonas paucimobilis bacteria are used to metabolize cyanide in water from tailings and underground mines. This strain of bacteria can treat metal cyanide complexes including total cyanide species and strong acid dissociable cyanide species:



Anaerobic bacteria can also be used to oxidize cyanide in oxygen – starved conditions such as ground waters and stagnant tailings ponds [5-8]. Photolysis reaction liberate cyanide ions from ferro- and ferri-cyanide complexes into the environment as shown below:



Reactions 1 and 2 are referred to as photo-aquation reactions and have also been observed for cobalthexacyanide, Co(CN)₆³⁻ complexes. Combinations of reactions (1) and (2) liberate cyanide at UV – wavelengths less than 420 nm, thus posing significant health risk to human beings and aquatic organisms who consume the cyanide contaminated water body [11, 12].

It must be noted that, the above forms of cyanide in surface water are highly toxic to human beings and aquatic life if ingested. Free cyanide forms react within few hours to days with almost any other chemical they are exposed to producing a wide variety of new compounds whose toxicity may be greater or less than the free cyanide itself [6].

It is in the light of this that this study was conducted to determine the levels of free cyanide and total cyanide concentrations in surface waters within the vicinities of Bogoso Gold Limited in the Western Region of Ghana.

The main thrust of the paper is to: (i) determine the levels of free cyanide and total cyanide concentrations in surface and underground waters around the vicinities of Bogoso Gold Mine in Western Region of Ghana and (ii) determine the extent of free cyanide and total cyanide pollution in Bogoso and its surrounding areas by comparing the results obtained in this study with GEPA (Ghana Environmental Protection Agency), USEPA (US Environmental Protection Agency) and the World Health Organisation (WHO) permissible levels of free cyanide and total cyanide in surface waters.

EXPERIMENTAL

Sampling technique and description of sampling points

Judgmental sampling techniques were adopted to select the following rivers: River Aprepre, River Mansi, River Ankobra and River Asuokofi based on previous history of cyanide spillage. Random sampling technique was also used to select River Bogo. In all 288 water samples were collected from each sampling point between November 2002 and April 2003 (Table 1). The water samples from each sampling point were analyzed separately for free cyanide and total cyanide and the mean results of free and total cyanide in the water sample from each sampling point computed.

River Aprepre flows through the Dumasi and Chujah waste dumps. River Aprepre also flows into River Mansi, which finally flows into River Ankobra. River Asuokofi is a tributary of River Ankobra. Former Prestea Gold Resources (PGR) used to discharge its waste containing cyanide solution directly into River Asuokofi. Prestea Gold Resources (PGR) has folded up and has been taken over by Bogoso Gold Limited in 2002.

Table 1. Sampling sites and number of samples obtained.

Sampling point	Number of samples				Total
	Zone 1	Zone 2	Zone 3	Zone 4	
River Aprepre (River Dumasi)	8	8	8	8	32
River Mansi	8	8	8	8	32
River Ankobra	8	8	8	8	32
River Asuokofi (Upstream)	8	8	8	8	32
River Asuokofi (Downstream)	8	8	8	8	32
River Bogo (Upstream)	8	8	8	8	32
River Bogo (Downstream)	8	8	8	8	32
Borehole at Dumasi	8	8	8	8	32
Boreholes at Bogoso	8	8	8	8	32
Total	72	72	72	72	288

Analytical methods for the analysis of cyanide species

There are several methods for the analysis of cyanide species directly in a matrix or following a pretreatment. The methods include titrimetric, spectrophotometric, potentiometric, ion-selective

electrode (ISE), ion chromatography – high performance liquid chromatography (IC-HPLC), indirect AAS, gas chromatographic and infrared spectrometric. Of all these methods, titrimetric method was used in this analysis due to the fact that equipment required for the alternate methods were not available. Titrimetric method for cyanide analysis is considered to be a primary. Primary methods are highly recommended for cyanide analysis. The lower quantification level for analysis of free cyanide species in the samples is 1 mg/L and that of total cyanide is 0.10 mg/L. A lower quantification level (LQL) represents the concentration of the various cyanide species in samples that all laboratories should be able to reliably determine [12-14].

Sample collection, preparation and storage

Water samples collected from streams and rivers within the catchment area of the company into plastic bottles that have been pre-washed with detergent and distilled water, rinsed with 1:1 nitric acid and distilled water. 1.5 L of the water samples from each sampling point was collected into the bottles with identification labels fixed on them.

The presence of oxidizing agents in the samples was tested using moist potassium iodide/starch test papers. The oxidizing agents were then removed by addition of 0.1 g/L of sodium arsenite solution until the potassium iodide/starch test paper gave no blue colouration.

Similarly, using moist lead acetate paper did the test for the presence of sulfides in the samples. Sulfides in the samples were removed by adding 0.1 g/L lead carbonate solution. The solutions were all filtered immediately using suction filtration. The samples were then stored in an ice-chest and later conveyed to the laboratory for analysis. In laboratory, the samples were filtered using Whatman No. 0.45 µm filter paper. The filtered samples were stabilized by the addition of 10 % NaOH solution. The samples were stored in a refrigerator at a temperature of 4 °C for 2 days [15].

The free cyanide concentrations in the samples were determined as follows. A blank solution was titrated against standardized 0.1 M AgNO₃ solution using *p*-dimethylaminobenzalrhodanine indicator solution, until the colour of the indicator changed from canary yellow to salmon blue. The blank titre was recorded and subsequently used. 100 mL of the sample was titrated against 0.1 M AgNO₃ using 5 mL of *p*-dimethylaminobenzalrhodanine as an indicator to the end point.

The concentrations of total cyanide in the water samples were determined by distillation of the sample to which 10 mL of conc. HCl and 10 mL of 12 % w/v hydroxylamine hydrogen chloride solution has been added to generate hydrogen cyanide gas (HCN), which was absorbed into 2 M NaOH solutions. The resulting sodium hydroxide solution was further diluted to 250 mL out of which 100 mL was titrated against standardized 0.1 M AgNO₃ solution using 5 mL of *p*-dimethylaminobenzalrhodanine indicator to the salmon blue end point [15]. The concentrations of free and total cyanide in the samples were calculated as follows:

$$\text{CN mg/L} = (A - B)/100 \text{ mL} \times (250/1000) \text{ mL} \quad (3)$$

where A – samples titre volume of AgNO₃ and B – blank titre volume of AgNO₃.

Recovery and reproducibility studies

To check the sensitivity and efficiency of the method used in the chemical analysis, recovery and reproducibility studies were conducted.

In recovery studies, known certified concentrations of NaCN solutions were titrated against 0.1 M AgNO₃ and the blank as well using *p*-dimethylaminobenzalrhodanine indicator. The end point colour change was salmon blue. Table 2 shows the results of the recovery studies.

Table 2. Results of free cyanide ions recovered in the recovery studies.

Concentration, mg/L	Amount recovered, mg/L			Percentage recovered	Standard deviation
	1	2	Mean		
0.20	0.19	0.19	0.19	95	0.00
0.40	0.41	0.38	0.40	100.0	0.02
0.80	0.81	0.77	0.79	98.8	0.02
1.00	0.98	0.98	0.98	100.0	0.00

From Table 2 it can be seen that the percentage of free cyanide recovered from double distilled water is between 95 to 100 % with a standard deviation between 0.00 to 0.02. It was realized that the method used for the chemical analysis was very efficient.

To check the reproducibility of the method used, reproducibility studies were also carried out. In the reproducibility studies, double distilled water containing 1.0 mg/L of free NaCN solution was titrated against 0.1 M AgNO₃ solution using *p*-dimethylaminobenzalrhodanine after the blank titration (Table 3).

Table 3 shows that the percentage of free cyanide recovered in the reproducibility studies is 99.6 %. The lower standard deviation suggests that method employed for the analysis of free cyanide is reproducible.

Similarly, known concentrations of potassium ferrocyanide solutions were titrated against 0.1 M AgNO₃ after the blank titration using *p*-dimethylaminobenzalrhodanine indicator to the salmon blue end point. Table 3 shows the results of recovery studies.

Table 3. Reproducibility of 1.0 mg/L of free cyanide and potassium ferrocyanide solution in doubled distilled water.

Recovery of free cyanide		Recovery of potassium ferrocyanide	
Replicates	Amount recovered (mg/L)	Replicates	Amount recovered (mg/L)
1	0.974	1	1.003
2	0.969	2	1.000
3	1.014	3	0.985
4	1.002	4	0.968
5	1.010	5	0.988
6	0.988	6	0.996
7	0.991	7	0.990
8	0.994	8	0.995
9	0.995	9	0.989
10	1.021	10	0.979
Mean	0.996	Mean	0.989
Percentage recovered	99.6	Percentage recovered	98.9
Standard deviation	0.017	Standard deviation	0.010
% CV	1.706	% CV	1.011

Again to check the efficiency of the distillation processes for total cyanide, reproducibility studies were also conducted. In the reproducibility studies, double distilled water containing 1.0 mg/L of potassium ferrrocyanide solution was taken through the distillation process to generate HCN gas, which was absorbed into 2 M NaOH solution. The resulting solution was further diluted to 250 mL with double distilled water out of which 100 mL was titrated against 0.1 M AgNO₃ solution using *p*-dimethylaminobenzalrhodanine indicator to the salmon blue end point. The results are presented in Table 4.

From Table 4 it can be seen that the percentage of total cyanide recovered from double distilled water is between 95 to 98 % with standard deviation between 0.00 and 0.03. This means that the method used for the chemical analysis was very efficient.

Table 4. Results of total cyanide recovered in the recovery studies.

Concentration, mg/L	Amount recovered, mg/L			Percentage recovered	Standard deviation
	1	2	Mean		
0.50	0.48	0.50	0.49	98	0.01
1.00	0.98	0.98	0.98	98	0.00
1.50	1.45	1.51	1.48	98	0.03
2.00	1.90	1.90	1.90	95	0.00

RESULTS AND DISCUSSION

The results of mean concentrations of free cyanide and total cyanide in water samples have been presented in Table 5. For samples where the cyanide concentration exceeded the recovery values a dilution factor 10 was applied.

Table 5. Mean concentrations of free cyanide and total cyanide ions in surface waters in Bogoso and its surrounding areas.

Sampling point	Free CN ⁻ mg/L	Standard deviation	Total CN ⁻ mg/L	Standard deviation	pH
River Aprepre (River Dumasi)	0.494	0.210	7.300	0.362	7.90
River Mansi	0.256	0.210	5.85	0.491	7.85
River Ankobra	0.519	0.001	9.848	0.001	7.25
River Asuokofe - Upstream	0.930	0.001	11.40	0.001	7.92
River Asuokofe - Downstream	1.541	0.021	17.50	0.002	7.98
River Bogo - Upstream	0.198	0.001	1.358	0.003	7.50
River Bogo - Downstream	0.295	0.001	2.130	0.012	7.98
Borehole at Dumasi	0.027	0.001	0.848	0.001	5.89
Borehole at Bogoso	0.289	0.069	0.741	0.001	6.25

Table 5 shows that the concentration of free cyanide in the water samples increased from 0.027 mg/L (Borehole at Dumasi) to 1.541 mg/L (River Asuokofe – Downstream), whilst the concentration of total cyanide increased from 1.358 mg/L (River Bogo upstream) to 17.50 mg/L (Asuokofe Downstream), whilst the concentration of total cyanide increased from 0.741 mg/L (borehole at Bogoso) to 17.50 mg/L (River Asuokofe). Temperature, pH, total dissolved solids, carbon dioxide concentration and air affect the rate of decomposition of cyanide related compounds in water. That is, water samples contaminated with acid mine drainage or cation hydrolysis of dissolved ions such as iron makes the water sample acidic in nature. The acidic nature of the water from the borehole lowers the pH to 5.89, at low pH below 7.0, essentially all dissolved cyanide is present as HCN. Hydrogen cyanide readily forms a gas, which is released into the air, hence the low concentration of free cyanide values recorded for water samples obtained from boreholes in Bogoso and Dumasi in this study.

In the same vein, the pH of the water samples in the study areas increased from 5.89 to 7.98. This is responsible for the concentrations of free cyanide obtained from each sampling point in the study. That is, the relative concentration of free cyanide in water is largely controlled by the pH of the water [4].

Free cyanide and total cyanide concentrations in drinking water set by Ghana Environmental Protection Agency (GEPA), US Environmental Protection Agency (USEPA) and British Columbia Ministry of Environment (BCME) have been presented in Table 6 [20]. A water sample is said to be contaminated if its concentration is two or three times higher than the permissible or background levels of the contaminants.

Table 6. Permissible levels for free cyanide and total cyanide concentrations in drinking water.

Agencies	Parameter		
	Free cyanide (mg/L)	Total cyanide (mg/L)	pH
GEPA	0.200	1.0	6.0 - 9.0
USEPA	0.200	-	6.0 - 8.5
BCME	0.0100	0.02	6.0 - 8.5

Comparing the concentration of free cyanide in River Aprepre (River Dumasi) with the permissible levels in Table 6, it could be observed that free cyanide concentration in River Aprepre is 2.47 times polluted as compared to GEPA and USEPA permissible levels. A similar comparison with BCME permissible levels reveals that, free cyanide concentration is 49.4 times higher than the maximum levels of free cyanide in drinking water. This shows clearly that drinking water from River Aprepre by residents of Dumasi would lead to serious health problems. A similar comparison of free cyanide and total cyanide concentration in River Ankobra with GEPA guideline values reveals that, free cyanide concentration in River Ankobra is 2.595 times contaminated.

CONCLUSIONS

The rivers monitored in this study are the source of drinking water for the inhabitants in Bogoso and its surrounding areas. Therefore high levels of free and total cyanide concentration in these rivers will pose significant health risk to the residents in the study areas. This is due to the fact that cyanide is very toxic and oral ingestion and dermal contact with cyanide-contaminated water is likely to pose significant health hazard. Symptoms associated with cyanide intoxication are difficulty in breathing, headache, weakness, changes in smell and taste, throat irritation, vomiting, itching and rashes. These symptoms are common in the study areas. Though it has not been proven scientifically, the inhabitants blame the numerous unexplained deaths, which occur in the study areas to cyanide intoxication as a result of frequent cyanide spillages that occurs in the study area. Given the limitations of routine analytical techniques for measuring cyanide and weak or lack of clear enforceable standards in Ghana, mining companies spilling cyanide solutions into rivers cannot be prosecuted. Residents of mining communities are not protected in the event of cyanide spillage. The Ghana Environmental Protection Agency (GEPA) should develop enforceable standards so as to effectively monitor the levels of cyanide related compounds in Ghanaian surface waters. When such standards are prescribed, mining companies using cyanide to extract metals should endeavor to abide by this regulation. Much public education should be given to inhabitants of these communities so that they not use these cyanide polluted streams/rivers. Alternatively, mining communities whose sources drinking water has been impacted upon should be provided with another source of drinking water by government and mining companies.

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