

Spectrophotometric determination of cyanate and ammonia in water sources around a Gold Mine

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Abstract

Modern mining methods have resulted in an increasing number of hazardous inorganic compounds being discharged into the environment. Although chemical treatments are used for detoxification of these inorganic compounds, they are expensive and not sensitive enough. Speciation products which are hazardous may also be formed. This study focused on the spectrometric determination of cyanide speciation products of cyanate (CNO⁻) and ammonia (NH₃) in water samples from around a Gold Mine environment. The data for the species during sampling months were tested by analysis of variance (ANOVA) and Geometrical Principal Component Analysis. The concentration ranges of speciation products in environmental samples were 0.03 to 53.7 mg/L and 1.70 to 10.0 mg/L for CNO⁻ and NH₃ respectively. The obtained values were well above their acute levels. Cyanate and ammonia concentrations decreased with sampling distance along the stream. High levels of CNO⁻ and NH₃ concentration up the stream were attributed to conversion of CN⁻ to CNO⁻, thiocyanate (SCN⁻) to NH₃/CN⁻ to NH₃. The decrease downstream may be as a result of the dilution, as the effluent enters the stream.

Key words: cyanide speciation; water; cyanate; ammonia; spectrometry.

1. Introduction

In the last few years, research activities around gold mines involving cyanidation extraction process (Haddad and Kalambaheti, 1991) have focused mainly on monitoring levels of cyanide alone (Madungwe et al., 1991; Gurira, 2004; Zagury et al., 2004) and its reduction in mining tailings (Scott and Ingles, 1981; Akcil, 2003). Reduction for levels of cyanide is achieved by the addition of oxidants

(Khodadad et al., 2008) and complexing agents such as ferrous sulphate which acts as cyanide sinks.

Studies on speciation products of cyanide (Zagury et al., 2004), like cyanate and ammonia which evolve during extraction and detoxification have been given little attention by waste management agencies at most gold mines. The lethal concentration of

cyanate to trout is between 13 and 32 mg/L. The high toxicity of cyanate results from its inhibition of the polymerization of haemoglobin S and the sickling of drepanocytes (Akcil, 2003). Ammonia may be extremely toxic to fish if allowed to accumulate in the body. Small increases in ambient ammonia (NH_3) level result in an elevation of body NH_3 which have many deleterious (chronic) effects on fish. A variety of methods for cyanide species determination have been reported including spectrophotometric, electrochemical and chromatographic techniques (Eiger and Black, 1985; Guilloton and Karst, 1985; van Staden, 1989; Black and Schulz, 1999; Luque-Almago et al., 2003).

Cyanate is determined using the Kjeldahl nitrogen method. The method has been reported to be time consuming since it requires over 1 hour per analysis and involves boiling of concentrated acids (Black and Schulz, 1999). Guilloton and Karst (1985) reported a spectrophotometric method suitable for samples containing cyanate samples. The above method is well characterised, generally sensitive, simple and practical for many laboratories. Several procedures have been proposed for the determination of NH_4^+ (Luque-Almago et al., 2003, Ruzicka and Hausen, 1989; van Staden, 1989). Spectrophotometric methods that appear to be used almost universally are the indophenol blue method (Berthelot reaction) (Standards Methods for the Examination of Water and Wastewaters, 20th edition, 1998), the gas diffusion/acid-base indicator

reaction procedure (van Son et al., 1983), and the use of the Nessler's reagent which offer high sensitivity and has less sample preparation (Krug et al., 1979). Other methods reported include titration (Methods for the examination of waters and associated materials, 1981), potentiometric determination (Methods for the examination of waters and associated materials, 1981), selective electrodes (Schmidt et al., 1984) and carbon dioxide laser photocooustic spectroscopy (Solyom, 1982). In this paper, it was decided to illustrate the usefulness of spectrophotometric method in the determination of the levels of cyanide speciation products of CNO^- and NH_3 in water samples, such as those taken from the vicinity of gold recovery plants in which a cyanidation process is employed for the extraction of gold.

2.0 Materials and methods

2.1 Location of study area

The location of the study area is shown in Figure 1, marked as Mazowe mine. Mazowe mine is located about 50km north-west of Harare, Zimbabwe ($18^{\circ}46'S$; $32^{\circ}19'W$). The area is found in agro-ecological region 2 characterized by seasonal and reliable rainfall. Three seasons are generally recognized, namely hot wet season from mid-November to March (summer), a cold dry season from mid-April to July (winter) and hot dry season from August to mid-November (spring). The area receives an average annual rainfall of 700 to 1000 mm. The soils are reddish brown, moderately deep to deep and

well drained with an average pH of 6.2. The following is a general layout of the map in which systematic sampling was carried out over a period of 7 months (Fig. 1).

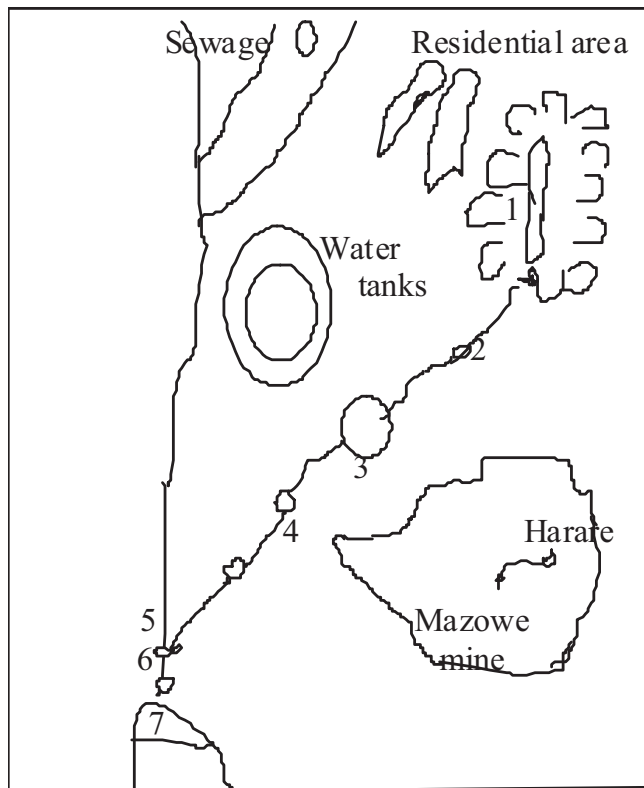


Figure 1: Map showing sampling points. 1: Slime Dam; 2: Penstock Discharge; 3: Marsh Land; 4: V-notch; 5: Intersection of streams; 6: Point along the stream; 7: A point in the dam; Map of Zimbabwe (bottom right)

2.1 Sample collection and analysis

Mining effluent and water samples were collected systematically in triplicates from the seven points marked 1 to 7 in Figure 1. The samples were collected into 1L polythene bottles which had been initially thoroughly rinsed with dilute nitric acid. The polythene bottles were

sealed immediately thereafter (Zvinowanda et al., 2008). Samples were then taken to the laboratory where they were placed in the refrigerator and analysis was done within 48 hours to minimize sample attenuation. A Perkin Elmer Lambda-2-UV-vis Spectrometer (Japan), glass cuvettes (Saarchem, S.A.), quartz cuvettes (Saarchem, S.A.) was used in the sample analysis. Chemicals used in this work were analytical reagent quality: 2-aminobenzoic acid (ABA, S.A), 32% HCl (Saarchem, S.A) and glacial acetic acid, $\text{CH}_3\text{CO}_2\text{H}$ (Saarchem, S.A). For ammonia, all the

solutions were prepared with doubly distilled water, potassium tartrate tetrahydrate (ACE, Glenvista), mercuric iodide (ACE, Glenvista), NaOH (Skylab, S.A), ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$ (ACE, Glenvista).

2.3 Synthetic Procedures

2.3.1 Cyanate

Before derivatising the sample, 40.0 mL of each sample was filtered through a 0, 45 μm Whitman filter paper to remove particulate matter followed by measurement of pH. Samples with pH above or lower than 7 were adjusted by adding few drops of either 0. 10 M HNO_3 or NaOH solutions to pH7 in order to increase the presence of NH_4^+ in the $\text{NH}_3/\text{NH}_4^+$ equilibrium (Zvinowanda et al., 2008).

Cyanate was determined as 2,4-(1H,3H)-quinazolinedione (Guilloton and Karst,1985) obtained by reacting samples with 2-aminobenzoic acid, in the presence of 32% HCl and glacial acetic acid, CH_3COOH to form quinazolinedione after cyclisation. The product 2, 4-(1H, 3H)-quinazolinedione formed, absorbed strongly in the ultraviolet region at 310 nm. The reaction mixture was found to be pH dependent and as a result the reaction was performed at pH range 1-6.

2.3.2 Ammonia

Sample filtration was as described earlier in section above. Measurement of pH and adjustment in samples and standards where necessary to $\text{pH}>9$ but <12 was done using 0. 10 M NaOH

solution and 0.10 M HNO_3 depending on the alkalinity or acidity of the sample, respectively. The method was based on the formation of an orange brown complex with ϵ_{max} at 420 nm (Krug et al.,1979). This was based on the addition of Rochele salt solution to samples or aliquots of standards. Finally, the Nessler's reagent was added and the mixture was allowed to stand for 18-20 minutes. In all cases, doubly distilled water was placed in a glass cuvette and its absorbance was adjusted to zero as measurement blank.

2.4 Statistical analysis

Principal Component Analysis (PCA) was used to show relationship between variables of different sampling points for sampled months. The results among sampling months for the two species were also subjected to one-way ANOVA to test whether there was significant variation. Microsoft Excel was used to calculate mean concentrations of samples.

3.0 Results and Discussion

3.1 Validation of analytical methods

Validation of different analytical methods by calculating recoveries after spiking pre-extracted real samples has been reported (Abbas and Ali, 2007; Zvinowanda et al., 2008; Radhey et al., 2010). In this paper, the same technique was also adopted. The recoveries of the two cyanide species were determined, after spiking the pre-extracted real samples by different concentrations as shown in Table 1.

Table 1: Recovery values (R, %) and relative standard deviation (R.S.D) (n=3) of Cyanide Species

Sampling Point	Amount added (mg/L) ±RSD		Amount recovered (mg/L) ±RSD		Recovery (%±RSD)	
	NH ₃	CNO ⁻	NH ₃	CNO ⁻	CNO ⁻	NH ₃
1	6.50±0.10	2.50±0.05	5.90±0.03	2.16±0.10	90.0±0.4	93.6±0.5
2	5.00±0.15	2.00±0.02	4.84±0.06	1.60±0.09	96.8±0.5	90.0±0.4
3	4.00±0.19	1.00±0.14	3.74±0.12	0.88±0.36	93.5±1.2	88.0±0.8
4	3.50±0.02	0.50±0.06	2.80±0.05	0.48±0.25	94.3±0.6	96.0±1.2
5	2.50±0.02	0.40±0.05	1.70±0.12	0.34±0.13	87.2±0.3	85.0±0.6
6	2.00±0.12	0.20±0.03	1.88±0.10	0.19±0.05	94.0±0.1	95.0±0.5
7	0.50±0.03	0.10±0.03	0.45±0.13	0.09±0.05	90.0±0.1	90.0±0.3

High recovery was obtained for all the species studied by the spectrophotometric methods. For this reason the methods were validated. This is supported by percentage recoveries as shown in Table 1, which ranged from 87-96% for cyanate and 85-96% for ammonia.

The spectrophotometric methods are known to provide the easy detection of cyanide species. Some authors (Guilloton and Karst, 1985; Loret and Pettine, 1985; Zvinowanda et al., 2008; Madungwe et al., 1991) have used these methods in the determination of cyanide and its species namely, free cyanide, cyanate and thiocyanate. Figures 2, 3,

5, 6, 8 and 9 show three batches of samples, which were analyzed for cyanate and ammonia from June to December 2008.

The variation of cyanate and ammonia among the seven sampling points was observed to have a similar pattern. It was observed that the concentration of the two species studied decreased from the Slime Dam (1), Penstock Discharge (2), Marsh Land (3), V-notch (4), Intersection of streams (5) up to the dam (7). This is indicative of chemical and/or biological processes leading to the decrease of these species. From Figure 2 and Figure 3, it can be seen that the concentrations of cyanate were higher

than those of ammonia for all the sampled points except on the intersection of streams, points in the stream and the dam.

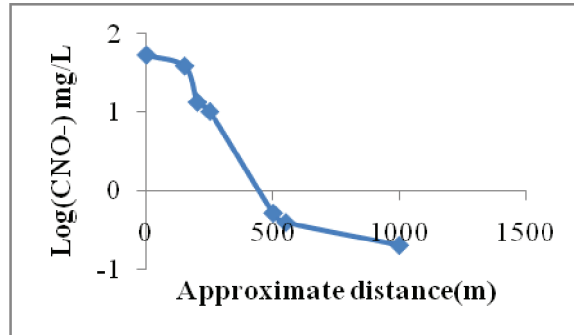


Figure 2: Cyanate ion profile along the stream receiving effluent from the gold mine in June 2008.

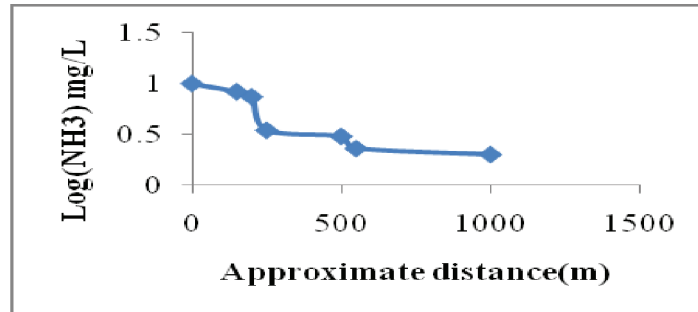


Figure 3: Ammonia gas profile along the stream receiving effluent from the gold mine in June 2008

A steep drop was also observed in both patterns, between points 2 and 3, 4 and 5 in Figure 2 and points 3 and 4 in Figure 3. This was attributed to dilutions as the effluent enters the stream from the Marsh land (4). The Slime Dam (1) which receives fresh effluent from the mine, showed the highest levels of cyanate and ammonia for all the sampled points. The high levels of cyanate may be due to speciation or microbial generation of cyanate from cyanide (Technical Report, 1994; Robert, 2004).

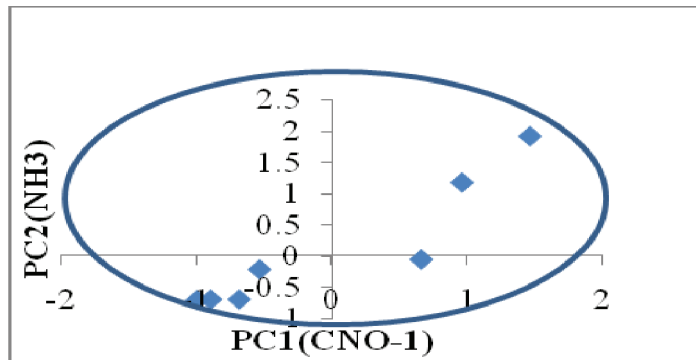


Figure 4: Scatter plots to show relationship between two variables (cyanate and ammonia) for the month of June 2008

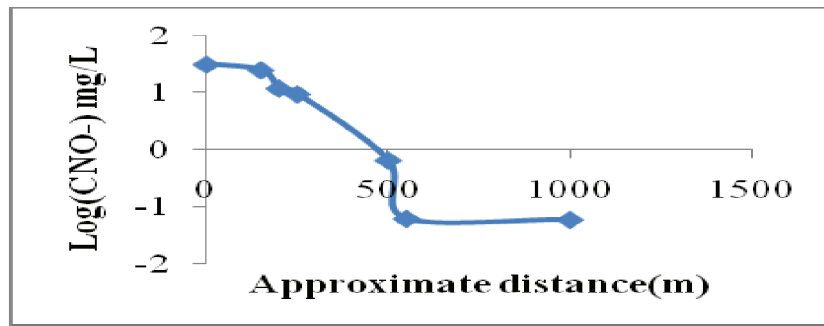


Fig. 5 Cyanate ion profile along the stream receiving effluent from the gold mine in September 2008

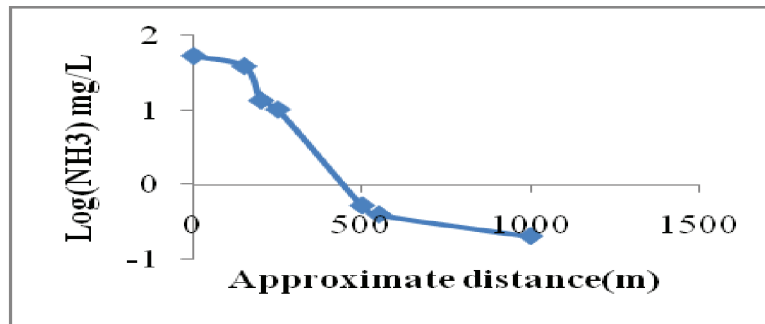


Fig. 5 Ammonia gas profile along the stream receiving effluent from the gold mine in September 2008

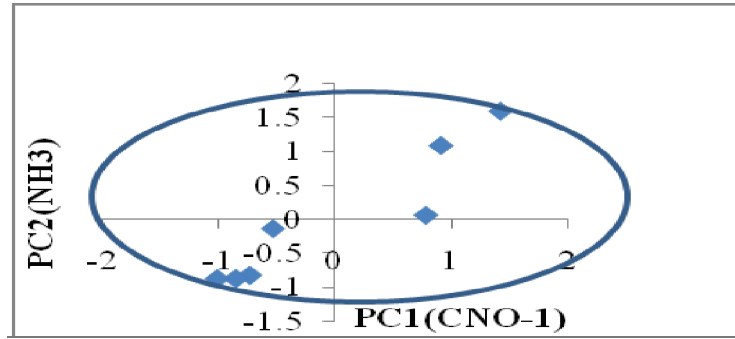


Figure 7 Scatter plots to show relationship between two variables (cyanate and ammonia) for the month of September 2008

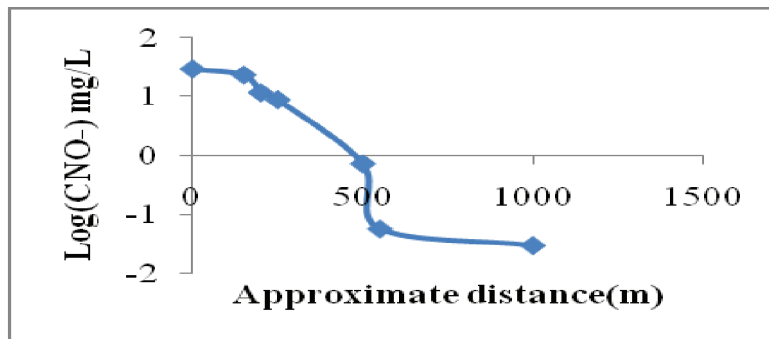


Figure 8: Cyanate ion profile along the stream receiving effluent from the gold mine in December 2008.

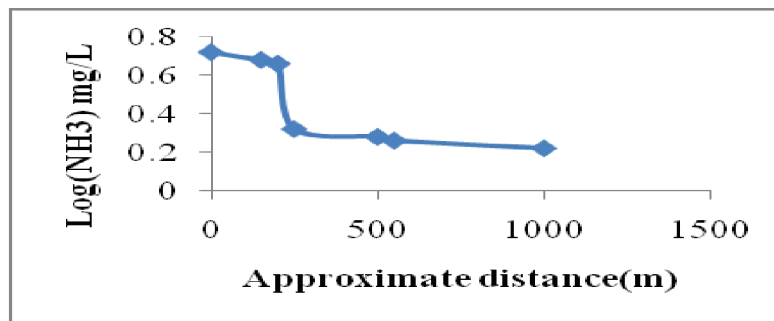
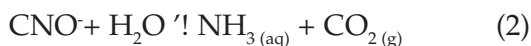


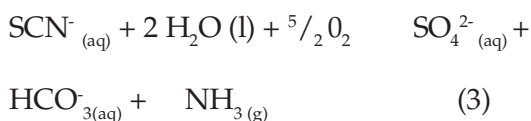
Figure 9: Ammonia gas profile along the stream receiving effluent from the gold mine in December 2008



The decrease along the stream may also be attributed to the attenuation of cyanate to ammonia:



The same pattern was also observed for ammonia, the high levels in the Slime Dam could be ascribed to oxidation of thiocyanate as shown by equation (3):



The higher levels in the Marsh Land may also be due to natural degradations (Technical Report, 1994) such as microbial generation (Equations 1 and 2) and anaerobic biodegradation:



Natural degradation process such as volatilisation allows ammonia into the atmosphere hence can also explain the general decrease observed for this species up to the dam level. Principal component analysis (Miller and Miller, 2000) was applied to the two variables measured from point 1 to 7 (Fig.4). The scatter plot shows that cyanate and ammonia are closely related hence speciation is evident. This close relationship also suggests that the sources of these species originate within the same environment.

During the month of September 2008, the same pattern was repeated as shown

in Figure 5 and Figure 6 with reference to cyanate and ammonia respectively. The levels of ammonia in Figure 6 when compared to Figure 3 were generally lower for some of the corresponding sampled points up to the dam. The lower values may be attributed to high temperatures and windy conditions whereby volatilization was very high as compared to cool temperatures in June.

Conversion of cyanide to cyanate was minimal since most cyanide was lost into the atmosphere (Zvinowanda et al., 2008). The same reasons were also proposed for lower values of ammonia. Principal component analysis was also applied, the same pattern as in Figure 4 was observed as shown below (Fig.7). The results for the month of December 2008 samples are as shown in Figure 8 and Figure 9 for cyanate and ammonia respectively. Again the same pattern was displayed; levels of cyanate were higher than those of ammonia gas. Volatilization of ammonia gas and bacteria degradation, where it is fixed by nitrogen fixing bacteria to form nitrates (Technical Report, 1994) could also be given as reasons for the lower values. This month had also the lowest levels for both species when compared to the other two months. This is not surprising since the month of December had some rains. Excessive dilution of the samples could give low values and also shorter residence times of species in the reservoirs sampled. Furthermore the speciation process, may have been slow due to reduced mining activities and cyanide ions may have been complexed with many metal ions, due to its strong affinity forming complexes

such as ferrocyanide complex with iron, $\text{Fe}(\text{CN})_6^{4-}$ (Scott and Ingles, 1981).

3.2 Analytical figures of merit

Linear calibration curves with ranges of 0.01 to 60.0 mg/L, 0.10 to 40.0 mg/L were obtained for cyanate and ammonia; respectively. The two different methods had detection limits of 0.02 and 1.00 mg/L (Eiger and Black, 1985) for cyanate and ammonia, respectively. Regression co-efficients values ranged from 0.979 to 0.998.

3.0 Conclusions

The spectrophotometric methods used in this study for the determination of cyanide species have shown that they can be used for the analysis of gold processing leach solutions. The methods had detection limits of 0.02 mg/L and 1.00 mg/L for cyanate and ammonia, respectively. Method validation by spiking pre-extracted real samples gave values of 87-96% and 85-96% recovery for cyanate and ammonia respectively; hence the procedures are suitable for the routine laboratory determination of environmental samples and provide an alternative to existing methods such as chromatography.

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