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Improved derivatisation methods for the determination of free cyanide and cyanate in mine effluent

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Abstract

Generally, the level of cyanide in waste effluents is too high to be discharged into the environment. Consequently, treatment regimes are necessary in order to protect the environment. However, the cost of most of the treatment methods is expensive and not sensitive enough and, therefore, cannot always be justified. In this research, cyanide speciation products, free cyanide (CN^-) and cyanate (CNO^-) were determined by highly sensitive derivatisation methods followed by spectrometric analysis. Spectral scans were carried out for pure and environmental samples derivatives in order to evaluate the possibility of interfering species. For CN^- a linear range from 0.01 to 80.0 mg/L was determined. In the case of CNO^-, the linear range was between 0.02 and 80.0 mg/L. The detection limits were 0.05 and 0.20 mg/L for CN^- and CNO^-, respectively. These values are in good agreement with those reported in literature. The concentration ranges of the speciation products in environmental samples were 0.70–52.0 mg/L and 0.50–76.0 mg/L for CN^- and CNO^-, respectively. These values were well above their acute toxicity levels. Increase in cyanate levels in the effluent with time was clearly observed while the concentration of cyanide decreased. This was attributed to the oxidation of CN^- to CNO^-.

Keywords: Derivatisation method; Spectrometry; Cyanide; Cyanate; Mine effluent

1. Introduction

Cyanide is a strong ligand capable of complexing with virtually any heavy metal [1]. The complexation of cyanide with heavy metals in organs can totally inhibit all the biochemical processes which may result in human organ failure and even death. The lethal dose of cyanide to human adult is between 50 and 200 mg [2].

Cyanide waste management at most gold mining dump sites involves the monitoring of levels of cyanide and its remediation is by addition of oxidants and complexing agents such as ferrous sulphate which acts as cyanide sinks. The overall toxicity though synergistic, can also depend on the predominant species with concentration above acute toxicity range [3–9].

Different methods for the determination of cyanide and its species have been reported [8–10]. Ion pair/ion interaction chromatography (IIC) has also been used to determine free cyanide (CN^-) from leached liquor [11–14]. However the method is time consuming in sample pretreatment. For the analysis of free cyanides, Guibauilt and Kramer described the reaction of *p*-nitrobenzaldehyde (I) with cyanide in alkaline solution [10]. The method is widely used as a qualitative test since a highly coloured purple compound is formed in the presence of cyanide.

Cyanate is commonly determined using the Kjeldahl nitrogen method. This method requires over 1 h per analysis and involves boiling of concentrated acids. Prior to the development of ion chromatographic method for the analysis of cyanate, a colorimetric method was used [15,16]. This colorimetric method was shown to be unreliable for samples containing low CNO^- in the presence of high concentrations of metals or ammonia. Fagan and Haddad [17] reported an ion chromatographic method which was suitable for samples with Cl^- levels up to 100-fold higher than the CNO^-. However, rapid column deterioration was reported, thus this technique was considered very expensive for routine CNO^- analysis [18,19].

Cyanate is one such anion which is produced during protein poisoning in the body. This anion has been studied extensively in the field of biochemistry because of its toxicity.

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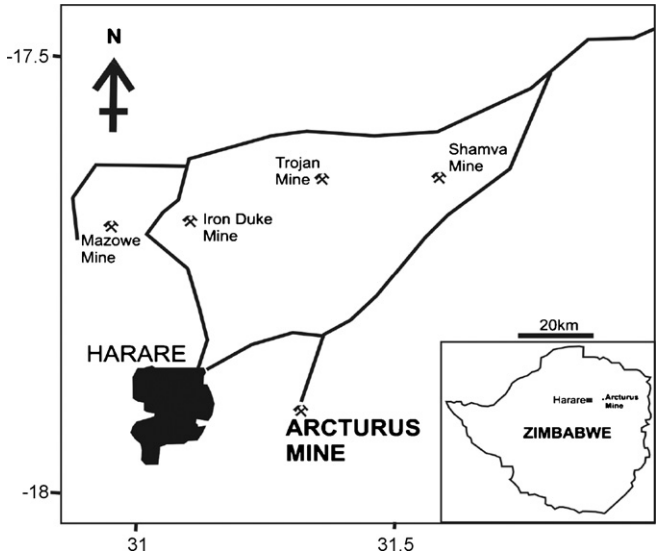

Fig. 1. Map of Zimbabwe (bottom right) and the position of Arcturus Mine (top left).

Cyanate in blood plasma has been determined by the method which involves the derivatisation of cyanate with 2-nitro-5-thiocarbamylbenzoic acid (TNB) [20]. In this paper we report the use of the derivatisation of CNO^- and 2-amino benzoic acid, followed by spectrophotometric method of analysis to determine free cyanate (CNO^-) in environmental samples [23].

2. Experimental

2.1. Location of study area

The location of the study area is shown in Fig. 1, marked as Arcturus Mine.

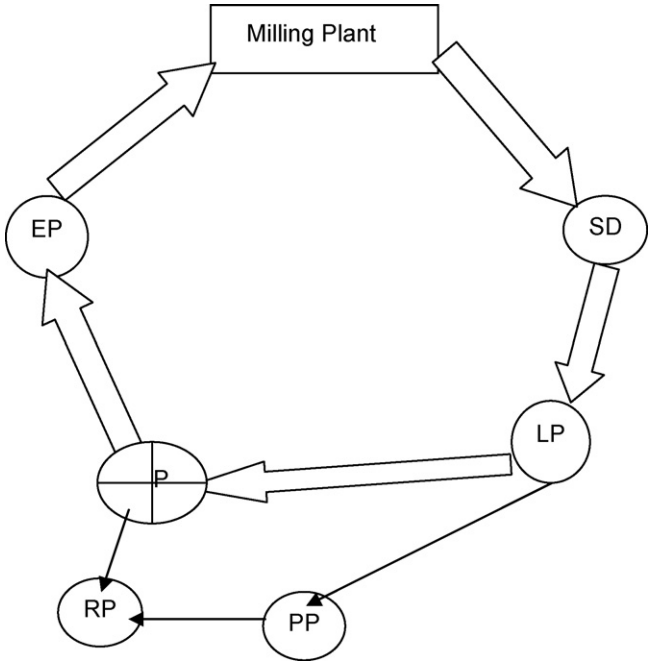

Fig. 2. Flow and seepage of effluent in reservoir ponds. SD: Slime Dam; LP: Lined Pond; PP: Panic Pond; RP: Recollection Point; EP: Evaporation Pond; P: Pump.

Arcturus Mine is located about 40 km northeast of Harare at latitude 17°46′60″S and 31°19′0″E. The mine performs both opencast and underground mining of gold ore and the gold is extracted by the cyanidation process. The effluent from the mine is technically recycled using a system of ponds for storage before pumping back most of the clarified effluent. The following is a general layout of the pond system in which the sampling was carried out over a period of 6 months (Fig. 2).

2.2. Sample collection

Effluent samples were collected randomly in triplicates from the five effluent ponds. The samples were collected in 2.0 L polythene bottles which had been initially thoroughly rinsed with dilute nitric acid and sealed immediately thereafter. Samples were then taken to the laboratory where they were placed in a refrigerator until ready for treatment and analysis. Sample treatment and analysis were carried out at the earliest time possible after collection in order to minimize sample attenuation. Sampling was carried out over a period of 5 months.

2.3. Reagents and chemicals

All reagents and chemicals used in this research were of analytical grades. *p*-Nitrobenzaldehyde (BDH) and *o*-dinitrobenzene (BDH) were used for cyanide determination. For cyanate determination, the reagents used were potassium cyanate (Saarchem, SA), 2-aminobenzoic acid (ABA, SA), 32% HCl (Saarchem, SA) and glacial acetic acid, CH_3CO_2H (Saarchem, SA).

2.4. Sample treatment

2.4.1. Free cyanide

Fifty millilitres (50.0 mL) of each sample was taken for pretreatment before analysis. The pretreatment involved filtration of the sample using 0.45 μm Whitman filter paper to remove particulate matter followed by measurement of pH and adjustment where necessary to pH range 8–9 using 0.10 M NaOH solution or 0.10 M HNO_3 depending on the alkalinity or acidity of the sample, respectively.

2.4.2. Cyanate

Sample filtration was as described earlier in Section 2.2. 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 pH 7 in order to increase the presence of NH_4^+ in the NH_3/NH_4^+ equilibrium.

2.4.2.1. Derivatisation of free cyanide. Free cyanide was derived as shown in Eq. (1). The derivatisation method was based on the formation of *o*-nitrophenylhydroxylamine anion, with characteristic blue colour with λ_{max} at 560 nm [21,22]. The method involves forming a mixture consisting of 1.0 mL of 0.01 M *o*-dinitrobenzene and *p*-nitrobenzalaldehyde, 0.10 mL of 0.50 M $NaOH_{(aq)}$ and 0.10 mL of 0.10 M of cyanide added to the mixture to initiate the reaction. The mixture was thoroughly stirred and allowed to stand for varied 15–20 min. However,