

# An amperometric method for the determination of cyanide in gold process streams and slurries

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## ABSTRACT

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A method for the determination of the concentration of cyanide based on the measurement of the diffusion current due to the oxidation of Cu to  $\text{Cu}(\text{CN})_2^-$  is described. The response is rapid and linear, and is accurate in the range of concentrations found in process streams. The response is stable and is not subject to interference from other ions present in mine solutions. This method of determination may be easily adapted to the continuous monitoring of cyanide in process streams and effluents.

## INTRODUCTION

Cyanide is widely used in the treatment of gold-bearing ores, in electroplating baths, and in chemical and pharmaceutical plants. In gold processing plants, the concentration of cyanide is usually determined by the titration of filtered slurries. The endpoint is often difficult to detect and the process of filtering the sample is slow, so that control is not effective. Since this method does not lend itself to automation, inferential control strategies, such as the continuous addition of cyanide in proportion to the bulk flow of solids, are often implemented in gold processing plants.

Cyanides are present as cyanide ions ( $\text{CN}^-$ ) and as metal complexes of widely varying stability. Cyanide compounds are classified as free cyanides (i.e., ionic cyanide,  $\text{CN}^-$ ) or as complexed metal cyanides (e.g.,  $\text{Fe}(\text{CN})_6^{4-}$  or  $\text{Zn}(\text{CN})_3^-$ ). The concentration of free cyanide in solution depends on its pH and on the content of metals capable of forming cyanide complexes. It is the concentration of free cyanide that needs to be determined in gold processing plants, since it is this species that is available for reaction with gold.

Various methods for the continuous monitoring of the cyanide concentration have been investigated. Pohlandt et al. [1] have reviewed 92 different

methods for the determination of the concentration of cyanide in process streams and effluents. A large number of these methods suffer from interference and, since process streams contain a variety of ions in solution, these methods are not, in general, applicable to the determination of free cyanide for process control purposes.

MINTEK developed the "Kegold" electrode in 1974 as a simple method for the determination of cyanide concentrations [2]. The method was based on the measurement of the potential of a silver button in contact with the solution to be measured. However, the long-term stability of the system was poor due to the build-up of materials on the electrode.

Brandt et al. [3] proposed the use of an integrated filtration/potentiometric titration system in which a measured volume of clear filtrate is automatically titrated with 0.1 *N* silver nitrate. They claimed that during 8 months of operation at the Afrikaner Leases plant a saving of over 30% in cyanide consumption was realized. The main objection to this technique is the time delay associated with the in-line filtration and the titration system which reduces the possibility of effective closed-loop control. In addition, this system is prone to blockage and mechanical failure.

In the present paper an amperometric method is described that permits a continuous, accurate determination of the concentration of cyanide in process slurries that is free from interference. Methods of analysis based on amperometry have been proposed before [4–7]. The method was first described by Baker and Morrison [4] who measured the current due to the oxidation of a silver anode in the cyanide solution. McCloskey [5] and Miller et al. [6] increased the sensitivity of the determination by using large helical silver or gold electrodes. The long-term stability of these systems was poor, and the signal decreased exponentially with time. Pihlar et al. [7] optimized the performance of this determination by better definition of the parameters affecting the hydrodynamics of the electrode system. They reported the accurate determination of amounts of less than 1 ng in volumes as small as 10  $\mu\text{l}$ . However, they also reported that certain electroactive compounds caused difficulties with the continuous mode of operation.

A method for the continuous determination of the concentration of cyanide in solution based on the measurement of the diffusion current due to the oxidation of Cu to  $\text{Cu}(\text{CN})_2^-$  is described in this paper.

## EXPERIMENTAL

A rotating-disc electrode assembly was used for the potential-sweep measurements. The electrode consisted of a copper disk with a diameter of 0.35 cm inserted in a Teflon holder. The counter electrode as made of platinum. The saturated calomel electrode (SCE) was used as a reference and all poten-

tials are referred to this electrode. The electrode was polished with 1200 grit waterpaper and less than 5  $\mu\text{m}$  alumina paste prior to each experiment.

A flow-through cell was used for the measurements in mine solutions and slurries. The cell provided ports for the copper electrode, the platinum counter electrode and the saturated calomel electrode. The cell was manufactured from perspex. The slurry or solution was pumped from a reservoir through the cell and back to the reservoir in a closed system so that the loss of cyanide as HCN gas was minimized.

The potentiostat and the linear-sweep voltameter were manufactured by MINTEK. The currents and potentials were measured by an Hewlett Packard HP 3421A data acquisition unit and recorded by an Hewlett Packard HP 9816 computer.

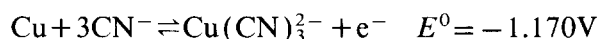
Analytical grade reagents were used. The mine solution and slurry were obtained from a Western Transvaal gold mine. All experiments were carried out at a pH of 10. A borate buffer was used in all the experiments except those using the mine solution or slurry.

The concentration of cyanide was determined titrimetrically with silver nitrate solution with potassium iodide as the indicator [9].

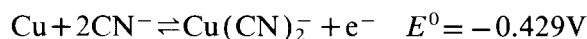
## RESULTS AND DISCUSSION

The parameters affecting the anodic oxidation of Cu in cyanide solutions were investigated so that suitable working conditions, such as the potential, could be determined. A rotating-disk electrode was used for this purpose and a series of current-voltage curves were obtained by potential-sweep voltametry for various conditions of cyanide concentration and agitation.

The results for the potential-sweep investigation of the anodic dissolution of Cu for solutions of different cyanide concentrations are shown in Fig. 1. These results show two plateaus due to diffusion currents. The first plateau, at about  $-0.40$  V (versus SCE) corresponds to the reaction:



while the second plateau, at  $-0.20$  V (versus SCE), corresponds to the reaction:



The results for these two reactions were obtained in the absence of oxygen in the solution. Also shown is the current due to the reduction of oxygen at the copper electrode in the absence of cyanide.

The strong dependence of the anodic dissolution of Cu in cyanide solutions on the agitation is shown in Fig. 2. Again, these results indicate two plateaus, due to the diffusion of cyanide to the electrode limiting the rate of reaction.

The dependence of the anodic dissolution of Cu in the limiting current region (potential  $0.0$  V versus SCE) on the concentration of cyanide in solution

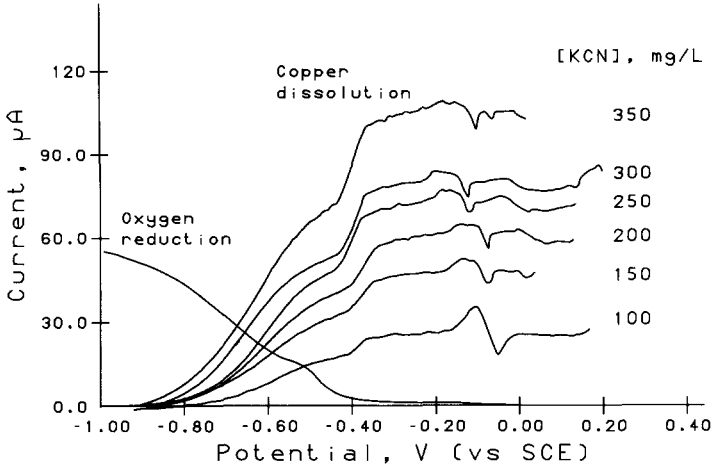


Fig. 1. Effect of cyanide concentration on the anodic dissolution copper in the absence of oxygen. Also shown is the reduction of oxygen in the absence of cyanide. Conditions: 0.165 g/l  $\text{HBO}_3$ , pH 10, 25°C.

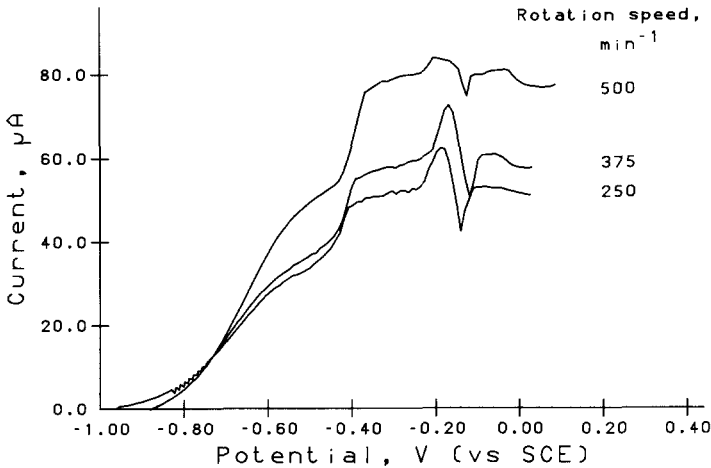


Fig. 2. Effect of disk rotation speed on the anodic dissolution of copper in the absence of oxygen. Conditions: 0.165 g/l  $\text{HBO}_3$ , pH 10, 25°C.

and on the rotation speed of the disk electrode is shown in Figs. 3 and 4, respectively. The current is proportional to the concentration of cyanide in solution and proportional to the square root of the rotation speed of the electrode. These figures indicate that, if the potential of the Cu electrode was controlled and the conditions of agitation within the cell were constant, then the current would be proportional to the concentration of cyanide in solution.

The most common problem that affects the methods for the determination

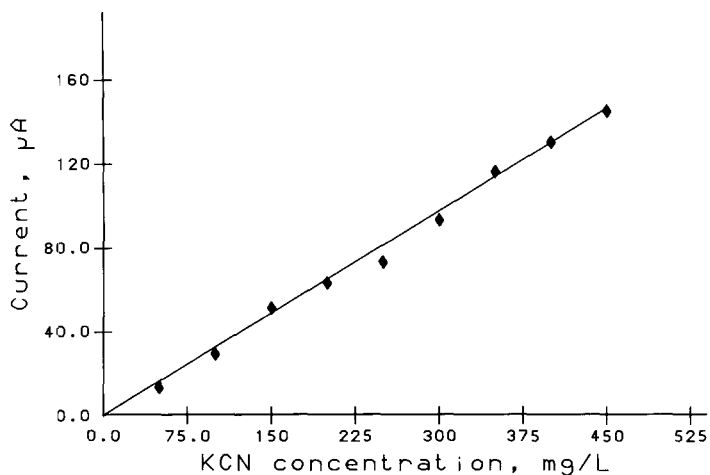


Fig. 3. Effect of the cyanide concentration on the diffusion current at 0.0 V (versus SCE). Conditions: 0.165 g/l  $\text{HBO}_3$ , pH 10, 25°C, 500  $\text{min}^{-1}$ .

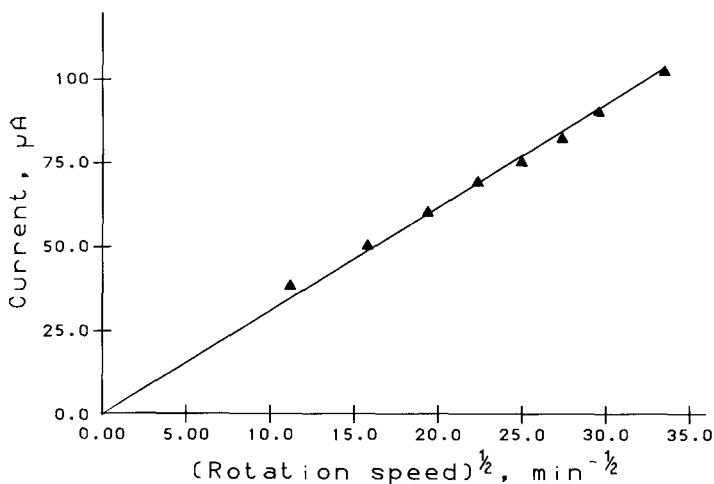


Fig. 4. Effect of the rotation speed on the diffusion current at 0.0 V (versus SCE). Conditions: 0.165 g/l  $\text{HBO}_3$ , pH 10, 25°C, 250 mg/l KCN.

of the concentration of cyanide in mine solutions and plant effluents is the presence of interfering substances such as gaseous cyanide, metal-cyanide complexes, and a variety of anions (chloride, sulphate, thiosulphate, thiocyanate, etc.). The compositions of a typical gold leach solution is shown in Table 1.

In order to implement this technique, the method must be free from interference from other ions in the solution. The amperometric determination suffers from interference caused by the presence of other electroactive ions in

TABLE 1

Composition of a typical gold leach solution (from [8])

Element	Concentration (mg/l)	Element anion	Concentration (mg/l)
Au	5.4	Ca	590
Ag	0.69	Ba	3
Cu	7	Na	310
Ni	2	K	45
Co	< 1	Si	20
Fe	1	CNS <sup>-</sup>	90
Zn	15	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	4
Pb	< 1	SO <sub>4</sub> <sup>2-</sup>	1680
Hg	0.01	Cl <sup>-</sup>	240
Al	< 1	Free CN <sup>-</sup>	92

solution. For the mine solution analysed in Table 1, these may be the metal-cyanide complexes, thiocyanate, thiosulphate, sulphate and chloride ions. Pihlar et al. [7] reported that they tested over 30 ions and compounds for interference in their system and found that only sulphide, iodide and thiocyanate were seriously interfering species.

Oxygen is commonly found in gold leach solutions. This and other oxidants, such as hydrogen peroxide, may be reduced at the copper electrode and result in a cathodic current. The cathodic current due to oxygen reduction is shown in Fig. 1. In order to eliminate the possibility of interference due to the reduction of oxygen at the anode the potential of the electrode is set between  $-0.4$  V (versus SCE) and  $0.2$  V (versus SCE), where the current due to the reduction of oxygen is low.

A potential of  $0.0$  V (versus SCE) was also chosen because at this potential the current due to the formation of copper oxide and copper sulphide (which may form coatings on the surface of the electrode) are not thermodynamically favourable.

The effect of the presence of ions other than cyanide in the solution was investigated using the rotating-disk electrode. The potential of the rotating-disk electrode was  $0.0$  V versus SCE. The current was measured in a de-oxygenated solution in the absence of the particular ion under investigation, and the current was then measured in an air-saturated solution containing the same concentration of ionic cyanide and the particular ion under investigation. The results for these experiments are shown in Table 2, which indicate that none of the ions interfere seriously with the measurement.

The stability and accuracy of the amperometric determination in real mine solutions was tested in the flow-through cell. Figure 5 illustrates the determination of the cyanide concentration in a synthetic solution and in a mine solution over a number of days. The mine solution was obtained by filtering the

TABLE 2

Effect of different ions in solution on the measured current

Ion	Concentration (mg/l)	Current without addition ( $\mu\text{A}$ )	Current with addition ( $\mu\text{A}$ )
$\text{Fe}(\text{CN})_6^{4-}$	100 Fe	110	106
$\text{Ni}(\text{CN})_4^{2-}$	100 Ni	118	114
$\text{Zn}(\text{CN})_4^{2-}$	37 Zn	48	42
$\text{Cl}^-$	100	131	124
$\text{SO}_4^{2-}$	2000	131	124
$\text{SCN}^-$	100	131	130
$\text{S}_2\text{O}_3^{2-}$	100	131	132

Note: The currents measured in the absence of additional ions were measured in the de-oxygenated solutions, while those in the presence of the additional ions were measured in solutions that were saturated with oxygen (7.1 mg/l  $\text{O}_2$ ).

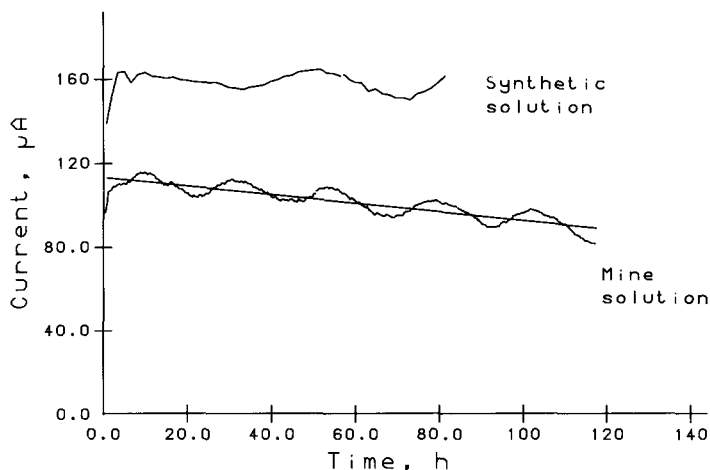


Fig. 5. Diffusion current for the anodic dissolution of copper in the flow-through cell for mine solution and synthetic solution. Conditions: ambient temperature, pH 10; synthetic solution: 300 mg/l KCN, 3.2 g/l NaCl, 3.1 g/l  $\text{HBO}_3$ ; mine solution: 231 mg/l KCN.

slurry that was fed to the leach circuit (i.e., the slurry from the thickener underflow).

The current due to the oxidation of Cu in the mine solution shows cyclic behaviour, with a period of about 24 h. This is probably due to the daily variation in temperature, of about  $5^\circ\text{C}$  in the cell reservoir. In addition, this curve shows a decline in the measured current of about 21% over the period of the test. This is due to a decrease in the concentration of cyanide in solution due to precipitation. The cyanide concentration at the beginning of the test was 231 mg/l KCN (measured by titration) and at the end of the test it was 195 mg/l KCN, representing a drop of about 15%. Discussion with plant person-

nel indicated that such precipitation is also experienced in the plant from which this solution was obtained.

A test was carried out to determine the transient response of the system, and at the same time to calibrate the cell. Equal amounts of cyanide were added to the cell reservoir, and the transient response was recorded. These results are shown in Fig. 6, and the calibration curve obtained from it is shown in Fig. 7.

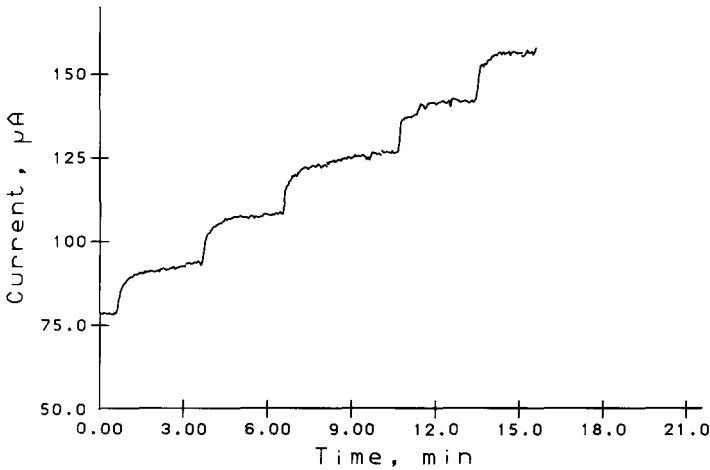


Fig. 6. Transient response for the cell for a series of step changes in the cyanide concentration in the mine solution. KCN initially 195 mg/l, 39 mg/l KCN added at each step. Conditions: pH 10, ambient temperature.

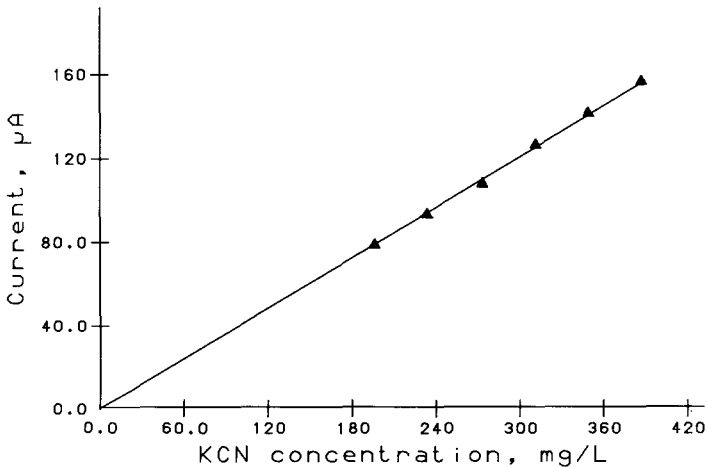


Fig. 7. Calibration curve for the flow-through cell in a mine solution for the results shown in Fig. 6.



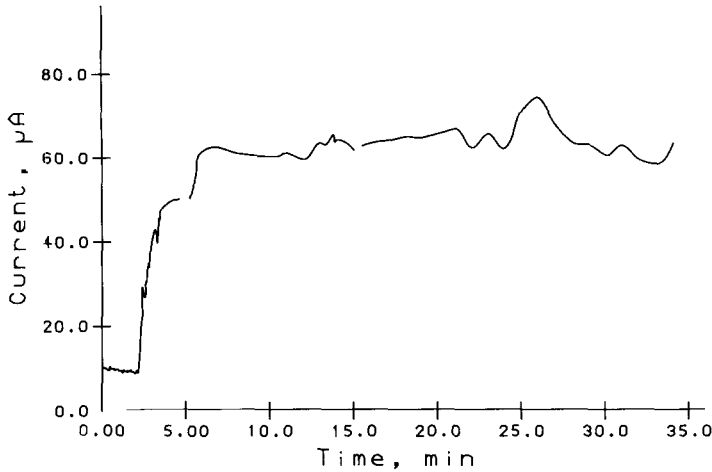


Fig. 8. Transient response of the flow-through cell for a step change in the cyanide concentration in a mine slurry. Conditions: 320 mg/l KCN, pH 10, ambient temperature.

Figure 6 indicates that the response of the electrode is rapid, with a time constant of about 1 min. Figure 7 shows that the response of the system to the concentration of cyanide is linear. These results are very well correlated. The slope of the line at the 99% confidence level is  $0.401 \pm 0.003$ .

The response of the amperometric system to a step change in the cyanide concentration in a mine slurry is shown in Fig. 8. The response time in the slurry is little slower than in the mine solution, and is about 2.5 min. The current is stable, indicating that it is possible to use this method of analysis directly in the slurry without having to filter it prior to measurement. This means that this system will not be subject to failure due to blockage of the filtration system.

These results indicate that an amperometric determination of cyanide in a mine slurry is possible. The system that is envisaged is one in which a small stream of slurry is pumped from the leach tank or pachuca through the cell and back to the leach tank. The agitation in the cell is controlled by the constant flow given by the pump, so that the only variable affecting the measurement is the concentration of cyanide in solution. The instrumentation for the cell consists of a potentiostat, and possibly a temperature-compensating circuit.

The direct measurement of the concentration of cyanide may then be used to control the addition of cyanide on a continuous basis using a closed-loop control system.

## CONCLUSIONS

An amperometric method for the direct determination of the concentration

of cyanide in mine solutions and slurries is described. This system provides reliable linear response to the concentration of free cyanide in solution. The response is free from interference, and is rapid, enabling effective process control.

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