

The Design of a 4 Electrode Flow Through Cell for the Online Analysis of Thiosulfate Concentration in Solutions Containing Copper and Ammonia.

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Thiosulfate is a potential alternative lixiviant to cyanide in the recovery of gold. The addition of copper(II) ions is required in order to achieve acceptable gold leach rates, but this results in thiosulfate oxidation. The presence of copper ions also makes the determination of thiosulfate concentration by traditional techniques difficult in such solutions. A flow injection analysis (FIA) method has previously been developed utilising a purpose built electrochemical quartz crystal microbalance (EQCM) cell to measure silver mass loss as a function of thiosulfate concentration (1). The requirement of a quartz crystal and the need to regularly replenish silver on the electrode surface has resulted in the development of an alternative method which utilises a more robust analysis cell. The evaluation and development of this analysis technique is described in this paper.

This alternative method involves using two solid working electrodes, one platinum and one silver. The current measured on the silver electrode is due to the oxidation of silver to form the silver thiosulfate complex, as well as other reactions such as the reduction of copper(II). The measured current of the platinum electrode is used as an estimate to the proportion of the current that is due to the reactions other than silver oxidation. Thus, the difference in the measured current on silver and the measured current on platinum is an estimate of the current due to silver oxidation. A rotating electrochemical quartz crystal microbalance (REQCM), which is described elsewhere (2), was used to verify that this approach gives a much better estimate of the thiosulfate concentration than measuring the current of a solid silver electrode alone.

A purpose built 4 electrode flow through cell, containing the two working electrodes, a reference electrode and a counter electrode was incorporated into a FIA system. With two working electrodes a bipotentiostat can be used to measure the current of the two working electrodes while controlling the potential (170 mV versus SHE used). The response of this cell to injection of a solution containing 0.1 M thiosulfate and 0.4 M ammonia is shown in Figure I. Recording of the working electrode currents commenced at the time of sample injection. Initially the measured current on both of the working electrodes is very small. Once the injected sample reaches the cell the measured current for the silver electrode increases, reaching a maximum approximately 30 seconds after sample injection, and then decays as the sample is flushed from the cell. The measured current of the platinum electrode is observed to remain relatively unchanged, as no solution species are present in this sample that are either oxidised or reduced at 170 mV. In this instance the quantity of silver oxidised during the FIA can be simply calculated by integrating the measured current on the silver electrode with respect to time.

Figure II shows the measured currents for the silver and platinum electrodes for a sample containing 0.1 M thiosulfate, 0.4 M ammonia and 10 mM copper(II) injected into the analysis system directly after the concentrated copper + ammonia was mixed with the thiosulfate solution. In this instance, a negative current is measured on the platinum electrode due to the reduction of copper(II) to copper(I). The current due to silver oxidation is thus calculated from the difference between the measured currents of the silver and platinum electrodes, Δi . Hence the integration of Δi is a measure of the charge due to silver oxidation to form the silver thiosulfate complex. For comparison the adjusted Δi calculated for the same solution in the absence of copper(II) is also shown in Figure II. Calculation of charge from the adjusted Δi profiles gives the same measure of charge, though a slight difference in the profiles is observed.

Under the conditions adopted for the FIA system, this charge was shown to be linearly related to the thiosulfate concentration of the injected sample. This is the basis of the new analytical method for the analysis of thiosulfate in solutions used for gold leaching.

REFERENCES

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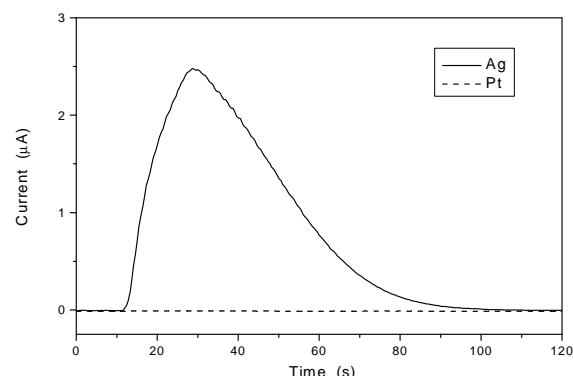


Figure I: Response of the 4 electrode cell: Injected solution contained 0.4 M NH_3 and 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$.

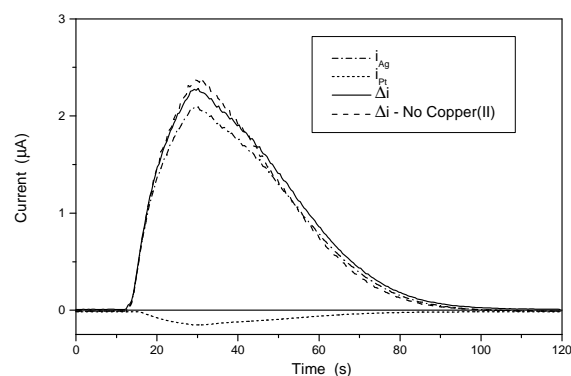


Figure II: Measured currents and adjusted Δi for a sample containing 0.4 M NH_3 , 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$, 10 mM CuSO_4 .