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Note

Simultaneous determination of thiourea and formamidine disulphide, using reversed-phase high-performance liquid chromatography and a UV detector

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Sulphur-containing ligands, particularly thiourea, have recently received increasing attention for possible application as lixiviants in the hydrometallurgy of gold.

Thiourea in aqueous solution reacts with certain transition metals to form stable cationic complexes. The reaction of gold dissolution in acid solutions of thiourea was given by Kazakov in 1964 as quoted by Groenewald[1]:

$$Au + 2CS(NH_2)_2 \rightarrow Au[CS(NH_2)_2]_2^+ + e^-$$

The reaction is oxidative, therefore an oxidising agent such as hydrogen peroxide or ferric iron is required. Under oxidising conditions thiourea will undergo successive oxidation reactions, forming a number of products. The first step of the oxidation process is the formation of formamidine disulphide[2,4,5,9]:

$$2CS(NH_2)_2 \underset{+2e}{\overset{-2e}{\rightleftarrows}} NH_2(NH)CS \cdot SC(NH)NH_2 + H_2$$

This is a rapid, reversible reaction with an electrode potential of +0.42 V (ref. 4).

It has been shown that formamidine disulphide (FDS) is a very active oxidant and is considered to be necessary for gold dissolution[2,4,9]:

$$2Au + 2CS(NH_2)_2 + NH_2(NH)CS \cdot SC(NH)NH_2 \xrightarrow{2H^+} 2Au[CS(NH_2)_2]_2^+$$

The second oxidation step is an irreversible reaction: the thiourea decomposes to cyanamide and elemental sulphur[3,5]:

$$CS(NH_2)_2 \rightarrow CN \cdot NH_2 + S + H_2$$

This reaction is much slower, but it is the reason for loss of reagent. It is also the source of silver loss and some operational difficulties: the elemental sulphur generated is in such a finely divided form that it covers all surfaces, and passivates the feed material[5].

FDS itself undergoes some oxidation changes. Under strong oxidising conditions it oxidises to cyanamide, hydrogen sulphide and elemental sulphur[4]:

$$NH_2(NH)CS \cdot SC(NH)NH_2 \rightarrow 2CN \cdot NH_2 + H_2S + S$$

Under mild conditions FDS decomposes to thiourea, sulphur and cyanamide:

$$NH_2(NH)CS \cdot SC(NH)NH_2 \rightarrow CS(NH_2)_2 + CN \cdot NH_2 + S$$

To avoid complications and technical difficulties, the irreversible reactions must be prevented.

The basic principle of thiourea leaching of precious metals is the selective reduction of formamidine disulphide to thiourea, maintaining the oxidized part of the initial thiourea at about 50% (ref. 5). The importance of control on the oxidation process of the thiourea is obvious; hence the need of an accurate analytical procedure to determine the thiourea and its oxidation products becomes apparent.

Investigate work, using the ability of liquid chromatography was undertaken, and an accurate, rapid and selective analytical procedure for the simultaneous determination of thiourea and formamidine disulphide has been developed. The technique offers significant benefits to the hydrometallurgical extraction of gold.

EXPERIMENTAL

Apparatus

A Waters liquid ion chromatograph was used. The equipment consisted of a Model 590 solvent delivery system, a Rheodyne fixed loop injector (20 μl), and RCM-100 radial compression system fitted with a 5-μm C_{18} separation column, a Model 481 variable wavelength/UV detector and a Model 740 data processor. A Milli-Q water purification system was used to produce reagent grade deionised water. An ultrasonic bath was used for sample degassing.

Reagents

All solutions were filtered through a 0.45-μm filter membrane and degassed prior to use. Standard stock solution of thiourea: 1000 mg/l prepared from analytical reagent grade $CS(NH_2)_2$ of purity >99%. Standard working solution of thiourea: 100 mg/l $CS(NH_2)_2$ was prepared fresh each day, by dilution of the 1000 mg/l $CS(NH_2)_2$ solution. Hydrogen peroxide solution: 30% (v/v) H_2O_2. Formamidine disulphide: 50 mg/l $NH_2(HN)CS \cdot SC(NH)NH_2$ was prepared fresh each day from the 1000 mg/l $CS(NH_2)_2$: 10 ml of the thiourea solution was transferred to 100 ml volumetric flask and 10 drops of hydrogen peroxide solution was added. The solution was diluted with water. The oxidation to FDS is completed in 3 h.

When calculating the formamidine disulphide (FDS) concentration, it was taken into consideration that 2 mol of thiourea, yield 1 mol of FDS.

Chromatographic procedure

The eluent was methanol–PIC A (5:95). Methanol was low UV chromatographic reagent and 2.5 mmol/l tetrabutylammonium hydrogen sulfate (low UV PIC A) was used.

A flow-rate of 1 cm^3/min and chart speed of 1 cm/min were selected. A detection wavelength of 214 nm was chosen.

After separation, the thiourea and the formamidine disulphide were identified from their retention times (t_R). The thiourea and FDS concentrations were calculated by the date processor, after the integration of their peak areas.

RESULTS AND DISCUSSION

In all experimental work, a 100 mg/l standard working solution of thiourea and a 50 mg/l solution of FDS were used.

Two tests under different oxidation conditions were carried out. The first test was performed using 1 ml of hydrogen peroxide. A sample of the thiourea solution was injected first. Elution at t_R 3.78 min was recorded. The second sample was injected after 10 min oxidation. Very selective separation of FDS at t_R 3.40 min and thiourea at t_R 3.77 min was achieved.

The height of the peaks changed drastically after 20 min of oxidation, thus indicating that the oxidation of thiourea to FDS is a rapid reaction. At 60 min

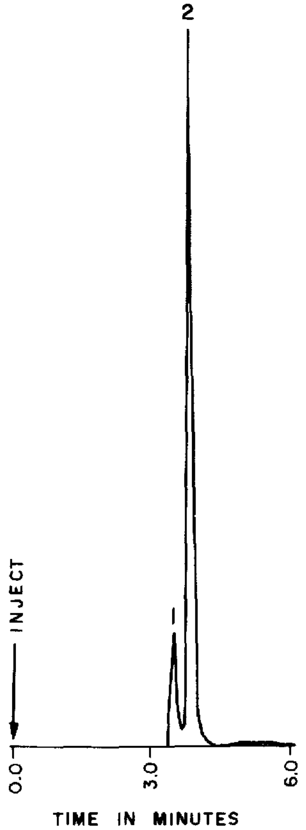


Fig. 1. Chromatogram showing the separation of (1) FDS (t_R = 3.39 min; conc. = 13.55 mg/l) and (2) thiourea (t_R = 3.77 min; conc. = 72.90 mg/l) after 10 min of oxidation (mild oxidising conditions).

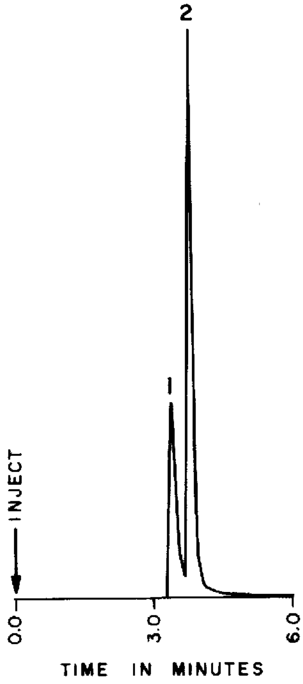
oxidation, the formation of a third peak, most probably cyanamide, was recorded at t_R 4.90. After 90 min, the oxidation of thiourea was completed.

For the second test, milder oxidation conditions were chosen. The experiment was repeated, using 10 drops of the hydrogen peroxide solution, to delay the oxidation process. The thiourea oxidation at 10 min is shown in Fig. 1. The thiourea concentration had decreased to 72.9 mg/l, while 27.1 mg/l had been converted to 13.55 mg/l FDS. After 20 min of oxidation, the concentration was 58.6 mg/l thiourea and 20.9 mg/l FDS (Fig. 2). This result was very close to the theoretical value of 20.7 mg/l FDS, calculated from the reaction:

$$2CS(NH_2)_2 \rightarrow NH_2(NH)CS \cdot SC(NH)NH_2 + 2e^-$$

After 3 h, complete oxidation of the thiourea (< 1 mg/l) was observed (Fig. 3). The oxidation to the cyanamide was delayed and limited to negligible concentration, as the oxidant content was restricted. After 4 h oxidation time, a slight decrease of the FDS concentration (43.8 mg/l) was recorded, and small increases in the thiourea and cyanamide peaks were observed (Fig. 4). This could be an indication that the decomposition of the FDS had begun, according to the reaction:

$$NH_2(NH)CS \cdot SC(NH)NH_2 \rightarrow CS(NH_2)_2 + CN \cdot NH_2 + S$$



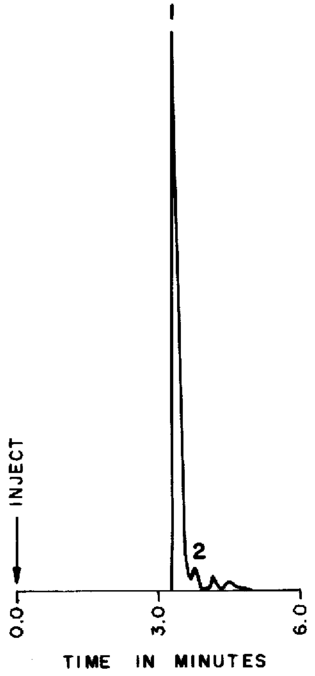
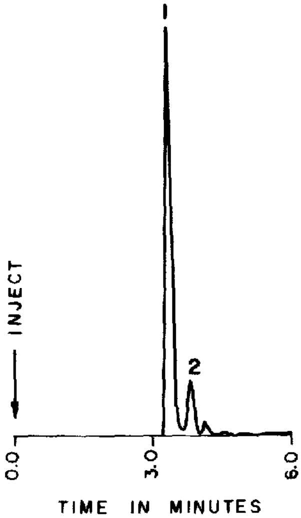


Fig. 2. Chromatogram showing the separation of (1) FDS (t_R = 3.40 min; conc. = 20.90 mg/l) and (2) thiourea (t_R = 3.78 min; conc. = 58.60 mg/l) after 20 min of oxidation (mild oxidising conditions).

Fig. 3. Chromatogram showing the elution of FDS after 3 h of oxidation (complete oxidation under mild conditions). Peaks: 1 = FDS (t_R = 3.40 min; conc. >48 mg/l); 2 = thiourea (t_R = 3.80 min; conc. <1 mg/l).



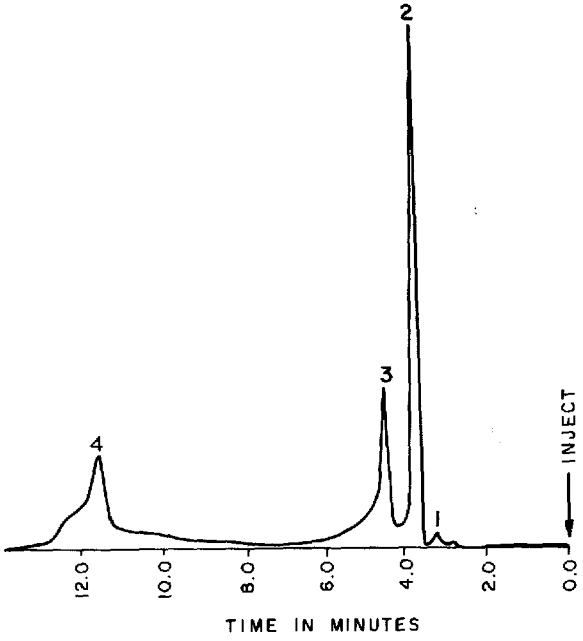


Fig. 4. Chromatogram showing the separation of (1) FDS (t_R = 3.40 min; conc. = 43.80 mg/l) and (2) thiourea (t_R = 3.78 min) after 4 h of oxidation (mild oxidising conditions).

Fig. 5. Chromatogram showing the separation of FDS and thiourea (TU) on a sample from a metallurgical plant. Peaks: 1 = FDS (t_R = 3.10 min); 2 = TU (t_R = 3.55 min); 3 = cyanamide (t_R = 4.30 min).

The applicability of reversed-phase high-performance liquid chromatography to the simultaneous determination of thiourea and FDS was tested on solutions from a metallurgical plant. Fig. 5 shows good separation of FDS (t_R 3.10 min) and thiourea (t_R 3.55 min). The peak at t_R 4.30 indicates the presence of cyanamide. The accuracy of the technique was evaluated against the well established iodimetric titration method[8], and by the standard addition procedure. Four portions of a metallurgical plant solution were measured and spiked with the equivalent of 0.0, 2.0, 4.0 and 6.0 mg/l thiourea standard solution. The peak heights recorded at t_R 3.20 min were plotted against the thiourea concentration added. The result of 84.2 mg/l thiourea obtained was in very good agreement with the 83.7 mg/l thiourea achieved by the iodimetric procedure. The statistical data for the precision and the accuracy of the technique were obtained from analysis of synthetic solutions containing 100 mg/l thiourea and 50 mg/l FDS: standard deviation (s) = 0.345 mg/l, relative mean error (R.M.E.) = 0.68% for thiourea and s = 0.244 mg/l, R.M.E. = 0.88% for FDS.

CONCLUSIONS

A selective and accurate analytical procedure for the separation and determination of thiourea and FDS is proposed. The advantages of the method to the iodimetric titration procedure are that (1) separation of thiourea and FDS is achieved in 4 min; (2) thiourea and FDS can be determined simultaneously; (3) no sample pretreatment is required; and (4) the technique is free of interferences[6,7,10]. The procedure covers a concentration range from 0.5 to 100 mg/l for thiourea and from 0.5 to 50 mg/l FDS. When dilution is employed, the concentration range can be increased further.

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