

Results obtained for the electrochemical quantification in five different pharmaceutical formulations existing in the Portuguese market are presented in Table 1.

**Tabel 1. Pharmaceutical formulations containing fluoxetine\***

Name	Laboratory	Fluoxetine(mg/cap)	N° of samples
Prozac	El Lilly	21.58 ± 3.82	4
Prozac	El Lilly	19.15 ± 2.50	4
Prozac	El Lilly	19.80 ± 1.08	4
Prozac	El Lilly	20.39 ± 0.69	3
Tuneluz	Baldacci	18.58 ± 1.35	2
Psipax	Laborterapia S.A.	21.83 ± 0.58	2
Digassim	Vitória	19.96 ± 1.16	2
Nodepe	Eurolabor	20.37 ± 1.83	3

\* All formulations refer to 20 mg of Fluoxetine per capsule.

## CONCLUSIONS

The electroanalytical method is convenient for the study of the reduction mechanism of fluoxetine. It can be used for its quantification in commonly used pharmaceutical drugs and for the determination of therapeutic doses in biological fluids when coupling high performance liquid chromatography (HPLC) with electrochemical detection.

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## THIOUREA DEGRADATION AND ITS CONTROL

### -AN ELECTROCHEMICAL STUDY

L. M. Abrantes\* and Y. Z. Zhang\*\*

\*CECUL, Faculdade de Ciências, Universidade de Lisboa

\*\*ICAT, Faculdade de Ciências, Universidade de Lisboa  
1700 Lisboa *Codex*, PORTUGAL

### Abstract

Thiourea is a promising non-cyanide lixiviant for gold hydrometallurgy. However, its high consumption due to degradation has hindered thiourea from commercial application. Thiourea oxidation is discussed and the role of sodium sulphite as a reductant in controlling the degradation of thiourea is investigated.

**Key Words:** Thiourea; degradation; noble metals; gold; cyclic voltammetry

### Introduction

Thiourea  $(\text{NH}_2)_2\text{C}=\text{S}$  is considered as one of the most promising non-cyanide reagents for gold ores leaching[1-4]. Despite high rates of metal extraction, insensitivity to impurity interferences and non-toxicity [4-10], the commercial adoption of the process has been hindered by excessive consumption, due to chemical degradation thiourea via formamidine disulphide (RSSR) (where  $\text{R}=(\text{NH}_2)(\text{NH})\text{C}$ ) and subsequent elemental sulphur formation:



Gold leaching by thiourea is usually conducted in acidic ferric solutions which have potentials higher than that of reaction (1), giving rise to a fast reduction to formamidine disulphide. The case of more moderate oxidants, such as  $\text{H}_2\text{O}_2$ , can reduce the consumption of the lixiviant but is not economically attractive (lower gold dissolution rates and higher reagent costs).

The degradation is consequence of its weak functional bond -C=S [11] and depends on the solution potential, thiourea concentration and temperature, but unfortunately, the available thermodynamical data and the process chemistry are not well understood. This paper is intended to discuss the reasons causing thiourea oxidation and the way to control reaction.

**Experimental**

Reagent grade chemicals and Millipore water were used.

Voltammetric measurements were carried out at room temperature and were performed with a Wenking LB 75L Potentiostat and a Wenking VSG 83 Waveform generator (Bank Elektronik). A three electrode glass cell was used. The working electrode (vitreous carbon, gold, platinum and silver) were polished on 1.0 μm aluminium oxide. A platinum sheet was used as counter electrode and a saturated calomel electrode as the reference electrode, respectively.

The pH and the potential of the thiourea solution system were measured using a pH electrode (INGOLD, 405-S7/120 combination pH) and a redox electrode (INGOLD, Ag,AgCl/KCl 4mol/dm<sup>3</sup>, Pt 4805 S7/120 combination redox potential electrode) connected to a Micro-pH 2002 meter.

**Results and Discussions**

Cyclic voltammetry was used to characterise the electrochemical thiourea degradation and a typical curve is shown in figure 1.

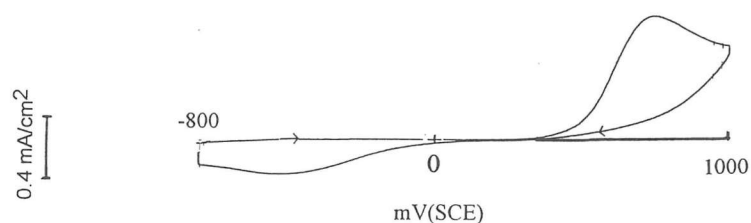


Fig. 1 Cyclic voltammogram for thiourea oxidation on a vitreous carbon electrode. (solution: 0.40 M Na<sub>2</sub>SO<sub>4</sub> + 0.010 M thiourea, pH 0.95; v=50mV/s)

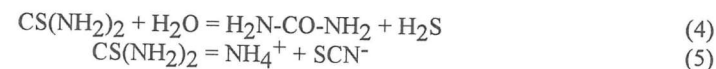
Analysis of the behaviour of several sweep rates has revealed that the oxidation of thiourea at 750 mV vs. SCE is an irreversible process.

The decreasing of the peak potentials and current densities on consecutive sweeping, indicates coating of the surface of electrode; it was observed that potentials over 0.4 V

produce darkening of the gold electrode which is believed to be S<sup>0</sup> formation according to reaction (3). The following experimental parameters were studied:

**1. Solution pH**

The influence of pH on the peak potentials has shown that the oxidation of thiourea is takes place easily at low potentials, at solution pH<1.5 or pH>2.0 due to the contribution of by-side hydrolysis (reaction 4) or acid dissociation (reaction 5); hence, the optimum pH for the lowest thiourea oxidation should be pH 1.5-2.0.



**2. Effect of Noble Metals (Pt, Au, Ag) on Thiourea Degradation**

Since thiourea is used to the leaching of precious metals, the cyclic voltammograms were recorded using Pt, Au and Ag working electrodes as shown in figure 2.

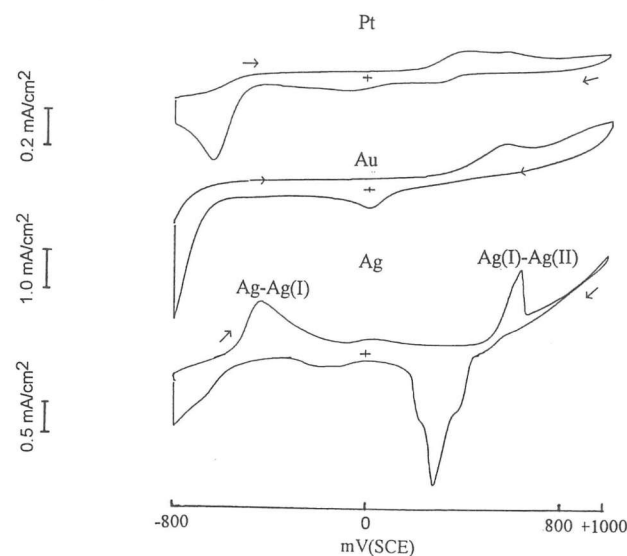


Fig.2 Cyclic voltammograms of thiourea oxidation with different electrodes. (solution: 0.40 M Na<sub>2</sub>SO<sub>4</sub> + 0.010 M thiourea, pH 0.95; v=50mV/s)

The oxidation peak potentials (table 1) clearly show the catalytic effect of gold and platinum on thiourea degradation.

TABLE 1

The Oxidation Peak Potentials of Thiourea Degradation Using Different Working Electrodes

Electrode	Vitreous carbon	Pt	Au	Ag
$E_{p}^{OX}, mV \text{ vs. SCE}$	750	383-603	500	700

### 3. Solution Media

A comparison of thiourea cyclic voltammetric characteristics was made for sulphate and chloride media, table 2, and no noticeable effect of the solution media on the thiourea oxidation has been detected.

TABLE 2

The Peak Potentials of Thiourea Anodic Sweeps in Sulphate and Chloride Solutions

Electrode	$E_{p}^{OX}(mV \text{ vs. SCE})$	
Vitreous carbon	750(sulphate)	780(chloride)
Gold	571(sulphate)	546(chloride)

### 4. Presence of Sodium Sulphite as a Reductant

A comparison of the oxidation reactions of thiourea, reductant sulphite and thiourea+sulphite systems was made. As can be seen in figure 3, the presence of reductant controls the degradation of thiourea.

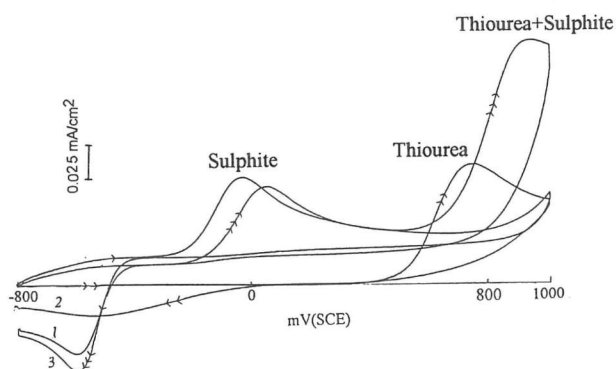


Fig.3 The cyclic voltammograms for the oxidation reactions of 1-thiourea (0.01 M) and 3-(0.01 M thiourea+0.01 M sulphite) systems (n=1)

### Conclusions

The degradation of thiourea is an irreversible process which is catalysed by noble metals. The optimum pH for the lowest thiourea degradation is about pH 1.5-2.0 and the oxidation increases with the lixiviant concentration. Apparently the solution media (sulphate, chloride) has no influence on the degradation process. The use of suitable reductants, such as sodium sulphite, can provide a practical way of controlling the thiourea oxidation and consequently of reducing the high reagent consumption when employed as leaching agent for gold ores treatment.

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