



**THIOUREA DETERMINATION FOR THE PRECIOUS METALS LEACHING  
PROCESS BY IODATE TITRATION**

**DETERMINACIÓN DE TIOUREA PARA EL PROCESO DE LIXIVIACIÓN DE  
METALES PRECIOSOS POR TITULACIÓN CON YODATO**

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**Abstract**

The thiourea leaching process for precious metals recovery has been studied as an alternative process to cyanidation. The accurate and simple determination of thiourea is important to guarantee the efficiency of the process and to evaluate the thiourea consumption during the gold and silver leaching from minerals; however, there is not, until now, a trustable method to determine the thiourea concentration for the high levels used in the extractive metallurgy industry. The present work, performed at CINVESTAV Saltillo, studies thermodynamically and experimentally, the thiourea determination by iodate titration in the search of a precise technique appropriate for the high thiourea concentrations used in the leaching of precious metals. The thiourea titration by iodate in acid media permits the precise determination of high thiourea concentrations (up to 10,000 ppm). The acidification of thiourea ( $\text{CS}(\text{NH}_2)_2$ ) produces protonated thiourea ( $\text{HCS}(\text{NH}_2)_2^+$ ) which reacts with iodate to form the protonated formamidine disulfide ( $[\text{CS}(\text{NH}_2)_2]_2^{2+}$ ). The presence of oxidant ions like cupric or ferric ions can oxidize the thiourea to formamidine disulfide ( $\text{FDS}^{2+}$ ), reducing the leaching strength of the solution. The iodate titration determines only the free thiourea that is available for the leaching of precious metals, and not the metal-thiourea complexes. When zinc dust is added to the solution before the titration, zinc reduces  $\text{FDS}^{2+}$  by regenerating the thiourea.

*Keywords:* Thiourea determination; precious metals leaching; iodate titration; formamidine disulfide.

**Resumen**

El proceso de lixiviación con tiourea para la recuperación de metales preciosos se ha estudiado como un proceso alternativo a la cianuración. La determinación precisa y sencilla de la tiourea es importante para garantizar la eficiencia del proceso y evaluar el consumo de tiourea durante la lixiviación de oro y plata a partir de minerales; sin embargo, hasta ahora no existe un método confiable para determinar la concentración de tiourea para los niveles altos comúnmente utilizados en la industria de la metalurgia extractiva. El presente trabajo, realizado en CINVESTAV Saltillo, estudia termodinámica y experimentalmente la determinación de la tiourea por titulación con yodato en la búsqueda de una técnica precisa apropiada para las, altas concentraciones de tiourea utilizadas en la lixiviación de metales preciosos. La titulación de tiourea por yodato ( $\text{IO}_3^-$ ) en medios ácidos permite la determinación precisa de altas concentraciones de tiourea (hasta 10,000 ppm). La acidificación de la tiourea ( $\text{CS}(\text{NH}_2)_2$ ) produce tiourea protonada ( $\text{HCS}(\text{NH}_2)_2^+$ ) que reacciona con el yodato para formar el disulfuro de formamidina protonada ( $[\text{CS}(\text{NH}_2)_2]_2^{2+}$ ). La presencia de iones oxidantes como los iones cúpricos o férricos puede oxidar la tiourea en disulfuro de formamidina ( $\text{FDS}^{2+}$ ), disminuyendo la fuerza lixivante de la solución. La titulación con iodato determinará únicamente la tiourea libre disponible para lixiviar metales preciosos y no la tiourea que se encuentra formando complejos con otros metales. Cuando se agrega polvo de zinc a la solución antes de la titulación, reduce el  $\text{FDS}^{2+}$ , al regenerar la tiourea.

*Palabras clave:* Determinación de tiourea, lixiviación de metales preciosos, titulación con yodato, disulfuro de formamidina.

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## 1 Introduction

As thiourea is the main component of the leaching solution, it is important to quantify its concentration in order to maintain a constant leaching strength. Some methods have been proposed for low thiourea concentrations: titration with different titrant agents, spectrophotometry, Raman spectroscopy, gas chromatography, electrochemical, and others (Haurowitz *et al.*, 1950; Lisicki *et al.*, 1955; Joshi, 1957; Aravamudan *et al.*, 1964; Case *et al.*, 1967; Blagrove *et al.*, 1971; Eaton *et al.*, 1976; Calokerinos *et al.*, 1983; Krzewska *et al.*, 1984; Deschênes, 1989). Except for titration, most of these methods have the drawback of excessive cost, instrumental complexity or long analysis time. All these techniques, including titration, have been proposed and used only for low thiourea concentrations, not for the high levels needed in the precious metals leaching (around 10 g/L, 0.13 M). The titration method would be the simplest technique, but the method has not been completely understood, particularly the effect of pH on the thiourea stability, and the effect of some oxidizing species that can exist in the precious metals extraction systems. The lack of understanding the chemical of the interaction between thiourea and the titrant iodate solution, as well as the high thiourea concentrations used in these systems, impair the use of this analytical technique and makes difficult the development of the thiourea leaching process for gold and silver.

The objective of this work is to explore the iodate titration technique for thiourea analysis in the search of a simple and adequate method for high thiourea concentrations (above 0.1 M). The thermodynamic understanding of the proposed method will permit the interpretation of the obtained data at any pH, in the presence of the metallic ions usually present in the gold and silver leaching systems.

## 2 Background

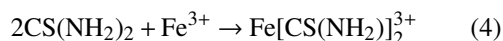
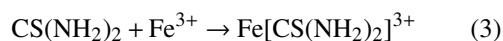
The process of gold dissolution by thiourea is complex since, besides gold oxidation, thiourea is also oxidized into formamidine disulfide, or into more oxidized products. Thiourea is an organic product (CS(NH<sub>2</sub>)<sub>2</sub>) that is used at low concentrations as additive for the electrolytic refining of copper (Oliva *et al.*, 2016; Cuevas-González *et al.*, 2018). The reaction of gold with thiourea to form the cationic complex

Au[CS(NH<sub>2</sub>)<sub>2</sub>]<sub>2</sub><sup>+</sup>, Eq. (1), has been reported since 1941, mainly with the aim of treating ores that cannot be processed by the cyanidation standard method. The oxidation potential of this equilibrium is E° = 0.38 V.



Since metallic gold (or silver) is to be oxidized, the addition of some oxidant is necessary to allow the precious metals dissolution. The most used oxidants are hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), ferric ions (Fe<sup>3+</sup>), or formamidine disulfide, which is the primary product of thiourea oxidation (FDS, [CS(NH)(NH<sub>2</sub>)<sub>2</sub>]). The instability of this FDS causes important problems of reagents consumption and it can also cause the decrease of the gold dissolution rate by precipitation of elemental sulfur on the surface particle, if FDS is further oxidized. It is therefore important to determine the concentration of both species on the system: thiourea and FDS, in order to control the precious metal leaching process.

Besides gold, some metals can form complexes with thiourea (e.g., copper). The presence of these metallic thiourea complexes can affect gold dissolution by reducing its rate, or by decomposing thiourea to elemental sulfur and causing the passivation of the precious metals. In addition to the complexing reagent thiourea, an oxidizing reagent is necessary for the oxidation of metallic gold and silver. Ferric ions are the most common oxidizing reagents used in thiourea leaching processes. Ferric ions, besides oxidizing the precious metals, oxidize thiourea into protonated formamidine disulfide (FDS<sup>2+</sup>, [CS(NH<sub>2</sub>)<sub>2</sub>]<sub>2</sub><sup>2+</sup>), Eq. (2), and can also form complexes with thiourea, Eqs. (3) and (4).



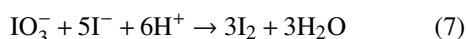
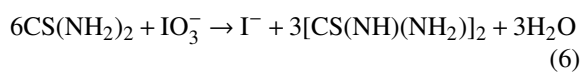
In some leaching processes, cupric ions (Cu<sup>2+</sup>) can be also present in the system; their presence is originated from the copper dissolution of the ore being processed. Cupric ions also oxidize thiourea and are reduced to cuprous ions (Cu<sup>+</sup>), which form complexes with thiourea as shown in Eq. (5).

The presence of ferric and cupric ions in the systems is detrimental to the thiourea stability and, consequently, increases the thiourea consumption.



### 2.1 Thiourea determination by iodate titration

The thiourea titration by iodate was initially proposed by Singh and Verma (1983) for low concentrations of thiourea (less than 50 mg). After the complete oxidation of thiourea by the iodate, the excess of iodate reacts with the iodide to form an intense blue complex with the starch (added as indicator), revealing the endpoint of the titration. The equilibria proposed by these researchers are presented in Eqs. (6) and (7):



In this thermodynamic-experimental work, the applicability of the thiourea-iodate equilibrium was studied with the aim of proposing a technique to determine thiourea at high concentrations and to determine the formamidine disulfide concentration. Two methods of the endpoint determination were evaluated: visual and potentiometric. The results are explained in terms of thermodynamic stability diagrams.

### 2.2 Thermodynamics

The equilibrium taking place during the titration of thiourea and their stability constants at 25 °C are presented in Table 1. These values will be used for the construction of the thermodynamic diagrams needed for the understanding of the thiourea-formamidine disulfide system, these data were added to Medusa-Hydra chemical equilibrium software for Windows (Puigdomenech, 2004); Pourbaix and species distribution diagrams were also elaborated.

## 3 Materials and methods

### 3.1 Materials

All reagents used were analytical grade (thiourea, cupric sulfate, ferric sulfate, potassium iodate, starch), and solutions were prepared with deionized water. The potassium iodate was dried by heating the sample during 30 min at 110 °C (potassium iodate decomposes at 526 °C). The starch solution was prepared with boiling water to achieve complete dissolution. This solution, used as an indicator for the visual endpoint determination, biodegrades easily, thus, it must be prepared freshly each day, or preserved with NaOH to use it for three to five days. A high precision refillable burette was used for titration. Copper and iron in solution were analyzed by atomic absorption spectroscopy (Varian SpectrAA 220FS). Sulfuric acid (0.1 M) and sodium hydroxide (0.05 M) were used to adjust pH of the solutions.

Table 1. Thermodynamic constants for the reactions of the thiourea system at 25 °C.

Reaction	E <sup>0</sup> / K	Reference
$[\text{CS}(\text{NH}_2)_2]_2^{2+} + 1\text{e}^- \leftrightarrow 2\text{CS}(\text{NH}_2)_2$	0.42 V	Preisler <i>et al.</i> (1947)
$\text{CS}(\text{NH}_2)_2 + \text{H}^+ \leftrightarrow \text{HCS}(\text{NH}_2)^+$	Log K= 1.44	Deschênes (1989)
$[\text{CS}(\text{NH})(\text{NH}_2)]_2 + 2\text{H}^+ + 2\text{e}^- \leftrightarrow 2 \text{CS}(\text{NH}_2)_2$	0.67 V	Gaspar <i>et al.</i> (1994)
$[\text{CS}(\text{NH}_2)_2]_2^{2+} \leftrightarrow [\text{CS}(\text{NH})(\text{NH}_2)]_2 + 2\text{H}^+$	Log K= -8.44	Preisler <i>et al.</i> (1947); Gaspar <i>et al.</i> (1994)
$[\text{CS}(\text{NH}_2)_2]_2^{2+} + 2\text{H}^+ + 2\text{e}^- \leftrightarrow 2 \text{HCS}(\text{NH}_2)^+$	0.50 V	Preisler <i>et al.</i> (1947); Deschênes (1989)

Table 2. Cupric and ferric ions concentrations used for the thiourea stability study (thiourea 0.13 M, pH = 2).

System	Oxidant ion	Concentration (ppm)	
T-Cu	$\text{Cu}^{2+}$	300	700
T-Fe	$\text{Fe}^{3+}$	300	700

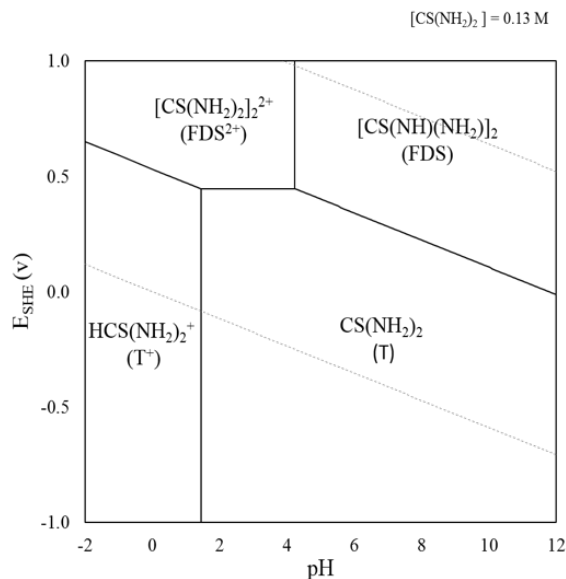
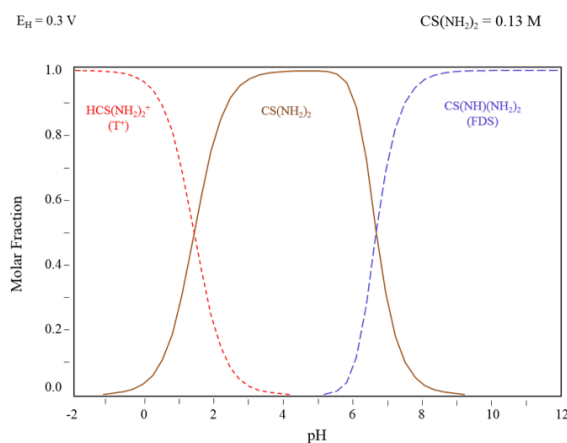
### 3.2 Methods

The experimental work is divided in two sections: the study of the pH effect on the thiourea determination by iodate titration, and the effect of cupric and ferric ions on the thiourea stability. The results are analyzed and discussed with the help of the thermodynamic diagrams elaborated.

Since thiourea can be used in acid or alkaline media, it is important to evaluate the pH effect on the stability of thiourea in the whole pH range. The thiourea determination by iodate titration was evaluated at pH 1, 5 and 10.5 (all tests at 25 °C). Besides the starch indicator for the visual determination of the endpoint, a platinum redox potential electrode was used to determine potentiometrically the endpoint of the titration by means of the first derivative of the Eh vs. Vol. curve (Potential Change). The effect of the presence of cupric and ferric ions on the thiourea analysis by iodate titration was evaluated as well. These oxidants were chosen since they can be generated in typical leaching process and they can affect the thiourea stability. The concentration of cupric and ferric ions used in the study of the thiourea stability is shown in Table 2. These tests were performed at 25 °C, pH = 2 and an initial thiourea concentration of 0.13 M (10,000 ppm).

## 4 Results and discussion

Since the main objective of this work is the understanding of the aqueous thiourea-formamidine disulfide (thiourea-FDS)-water system, the elaboration of thermodynamics diagrams of the system is essential. Fig. 1 presents the Pourbaix diagram for the thiourea-FDS system, at 25 °C and a total thiourea concentration of 0.13 M (10,000 ppm); Figs. 2 and 3 show the species distribution diagrams for the same system as a function of pH and ESHE (the solution potential with respect to the standard hydrogen electrode), respectively.

Fig. 1. Eh-pH diagram of the thiourea- $\text{H}_2\text{O}$  system for 0.13 M thiourea at 25 °C.Fig. 2. Thiourea species distribution diagram for the thiourea- $\text{H}_2\text{O}$  for 0.13 M thiourea at 25 °C.

In Figs. 1 and 2 it is observed that the molecular form of thiourea is stable in the pH range from 1.5 to 8; in acidic solutions the stable species is the protonated thiourea and in alkaline solutions the stable species is the formamidine disulfide. This behavior will undoubtedly affect the titration, depending on the pH of the thiourea solution. For the iodate titration of thiourea, 4 mL of the solution to be analyzed are placed in a 50 mL, magnetically stirred (150 rpm) beaker, together with 1 mL of starch indicator solution (2%) and 6 mL of sulfuric acid. The titrant solution (0.005 M potassium iodate) is added by means of a micro burette until the endpoint is detected. Under

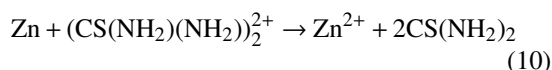
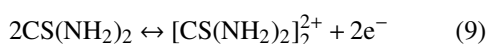
these conditions (0.005 M iodate solution and 4 mL of solution to be analyzed), the thiourea concentration ( $T_1$ ) is calculated with Eq. (8), where the numeric factor involves the molar thiourea:iodate rate (6:1) and the conversion factor from molar to mg/L.

$$T_1 \text{ (ppm)} = \text{Vol. KIO}_3 \text{ (mL)} \times \text{Molarity} \cdot \text{KIO}_3 \times 114175.05 \quad (8)$$

This iodate titration technique for determining thiourea was corroborated with different thiourea concentrations, as presented in Fig. 4, where the good correlation existing between the theoretical and experimental thiourea concentrations can be observed.

#### 4.1 Effect of pH on thiourea determination

The oxidation of thiourea produces protonated formamidine disulfide ( $\text{FDS}^{2+}$ ) in a reversible equilibrium in acid media, Eq. (9). The addition of a reducing agent as zinc powder, will cause the reduction of this formamidine disulfide to form thiourea again, as shown in Eq. (10). If a second thiourea titration is performed after the zinc addition, the thiourea quantified ( $T_2$ ) will be the initial thiourea present in the solution, plus the thiourea formed by the  $\text{FDS}^{2+}$  reduction. It is then possible to quantify the  $\text{FDS}^{2+}$  present in any solution by means of the Eq. (11). The increase in thiourea concentration after the zinc addition, compared with the initial thiourea titration, is proportional to the  $\text{FDS}^{2+}$  concentration.



$$\text{FDS}^{2+} \text{ (ppm)} = T_2 \text{ (thiourea after addition of zinc)} - T_1 \text{ (thiourea initially present)} \quad (11)$$

The use of a platinum electrode allows the precise determination of the endpoint of the titration by means of a graph. The titration curve is obtained by graphing the electrode potential versus the volume of iodate added. The volume corresponding to the sharp change in potential corresponds to the endpoint of the titration. When due to the pH of the solution the slope change is not sufficiently sharp, and consequently the titration endpoint is difficult to locate, the calculation of the first

derivative of the potential-added volume curve, can facilitate the detection by the use of a new variable: the Potential Change. The Potential Change, as indicated in Eq. (12), is then graphed against the average volume of titrant added corresponding to the value of potential being measured. The peak of this graph corresponds to the endpoint of the titration and is easier to locate, compared to the change of the slope on the original potential-added volume curve.

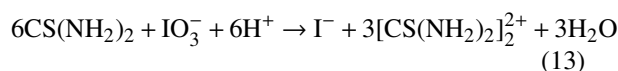
$$\text{Potential Change} = \frac{|(\text{Potential } 2 - \text{Potential } 1)|}{|(\text{Volume } 2 - \text{Volume } 1)|} \quad (12)$$

Figure 5 shows the iodate titration of synthetic solutions, 10,000 ppm thiourea, at pH 1, 5 and 10.5 (Figs. 5a, 5b and 5c respectively). In acid media (pH 1), the visual determination of the endpoint (10,018 ppm thiourea) required less than 20 min, and the change in color matched the abrupt change in slope of the Eh curve (triangles in Fig. 5a). The first derivative curve of these data ( $\times$  in Fig. 5a), calculated with Eq. (12), shows a peak at the same volume of titrant at which the change in color is detected (17.55 mL).

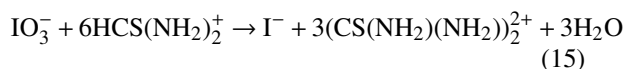
For the titration of the thiourea solution at pH 5, there is no change in color, and thus it is impossible to visually determine the endpoint of the titration. The potentiometric determination of the endpoint is not possible even when the titration is performed at the same volume rate per minute used for the first determination (around 20 min). If the titration is performed very slowly (completed in 6 h), the potentiometric detection of the endpoint permits to notice a peak of the first derivative, which coincides with the theoretical thiourea concentration with an error of less than 1% (10,047 ppm, Fig. 5b) in the analysis. This fact could be related to the change of predominant species from the unprotonated thiourea present at pH 5 to the protonated thiourea present at pH 1, as shown in Figs. 1 and 2. It is then possible to suggest that iodate reacts with protonated thiourea, and in consequence, the reaction is direct and fast at low pH values. If the titration is performed at neutral pH, the relative amount of protonated thiourea decreases. This protonated thiourea reacts with iodate, changing the equilibrium and causing the formation of more protonated thiourea to attain the equilibrium again. This newly generated protonated thiourea reacts with iodate, but at a slower rate (as the protonated thiourea is being generated). If the titration is performed slowly enough, the thiourea can be determined by the potentiometric detection of the endpoint. This is not practical for the thiourea titration, but it can support

the mechanism of iodate reacting with the protonated thiourea present at acid pH values.

The addition of sulfuric acid prior to the titration generates the appropriate conditions for the presence of protonated formamidine disulfide (FDS<sup>2+</sup>, [CS(NH<sub>2</sub>)<sub>2</sub>]<sub>2</sub><sup>2+</sup>) when the pH below 3. According with this mechanism, the equilibrium proposed is shown in Eq. (13).



The thiourea titration by iodate at pH 10.5 did not show a peak in the derivate curve, even if the titration was performed very slowly (24 h, Fig. 5c). The protonated thiourea present at alkaline pH is negligible, as it is shown in Fig. 2, and thus the iodate reaction with protonated thiourea is unnoticeable. From these results, it can be suggested that for the iodate titration of thiourea the acidification of the solution is necessary prior to titration, in order to transform thiourea into protonated thiourea, which will easily react with iodate, as shown by Eqs. (14) and (15), contrary to the mechanism proposed by Singh and Verma (1963), Eq. (6).



Based on the thermodynamic data, it may be said that at alkaline pH the unprotonated thiourea is the stable species, and that this is the reason why the iodate titration in alkaline solutions is extremely slow: the iodate reacts with the protonated thiourea, stable only at acid pH values. The thiourea leaching has also been proposed under alkaline pH; however, the leaching rate is slower than that of cyanide leaching and, for this reason, some reagents, e.g. Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and Na<sub>2</sub>SO<sub>3</sub> must be added to the process to increase the leaching rate (Zheng *et al.*, 2006). These additives prevent the irreversible decomposition of thiourea and form complexes with the dissolved precious metals (Gudkov *et al.*, 2010a; Gudkov *et al.*, 2010b).

#### 4.2 Effect of cupric and ferric ions on thiourea determination

Four tests with synthetic solutions were performed to explore the effect of the presence of cupric and ferric ions on the thiourea stability at room temperature.

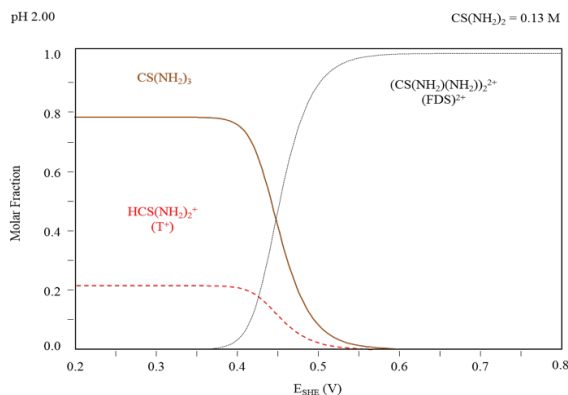


Fig. 3. Species distribution diagram for the thiourea-H<sub>2</sub>O system 0.13 M thiourea at 25 °C and pH 2.

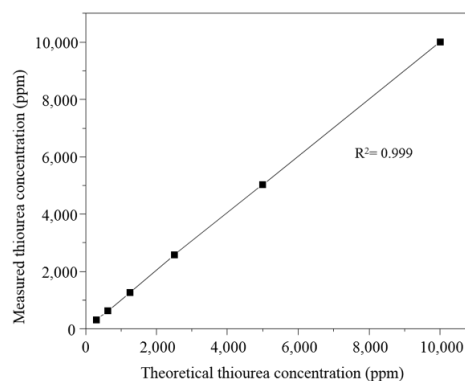


Fig. 4. Measured vs. theoretical thiourea analyses by iodate titration of synthetic thiourea solutions.

The composition of these solutions is presented in Table 2. The Eh of the thiourea solution with copper or iron ions was measured before the iodate titration. The volume of iodate solution consumed corresponds to the thiourea concentration in solution, calculated by Eq. (8). The thiourea concentration of the solution will indicate the thiourea oxidation due to the presence of the oxidant ions (cupric and ferric ions). In a second series of tests, zinc dust was added to samples of solutions (thiourea containing copper or iron ions) and these were again titrated with the same iodate solution.

As mentioned before, the thiourea can be oxidized into formamidine disulfide (FDS<sup>2+</sup>), a reversible reaction, but if the conditions are more oxidant (Eh values higher than 0.42 V, see Fig. 3) the FDS<sup>2+</sup> can react irreversibly into more oxidized sulfur species like cyanamide and elemental sulfur.

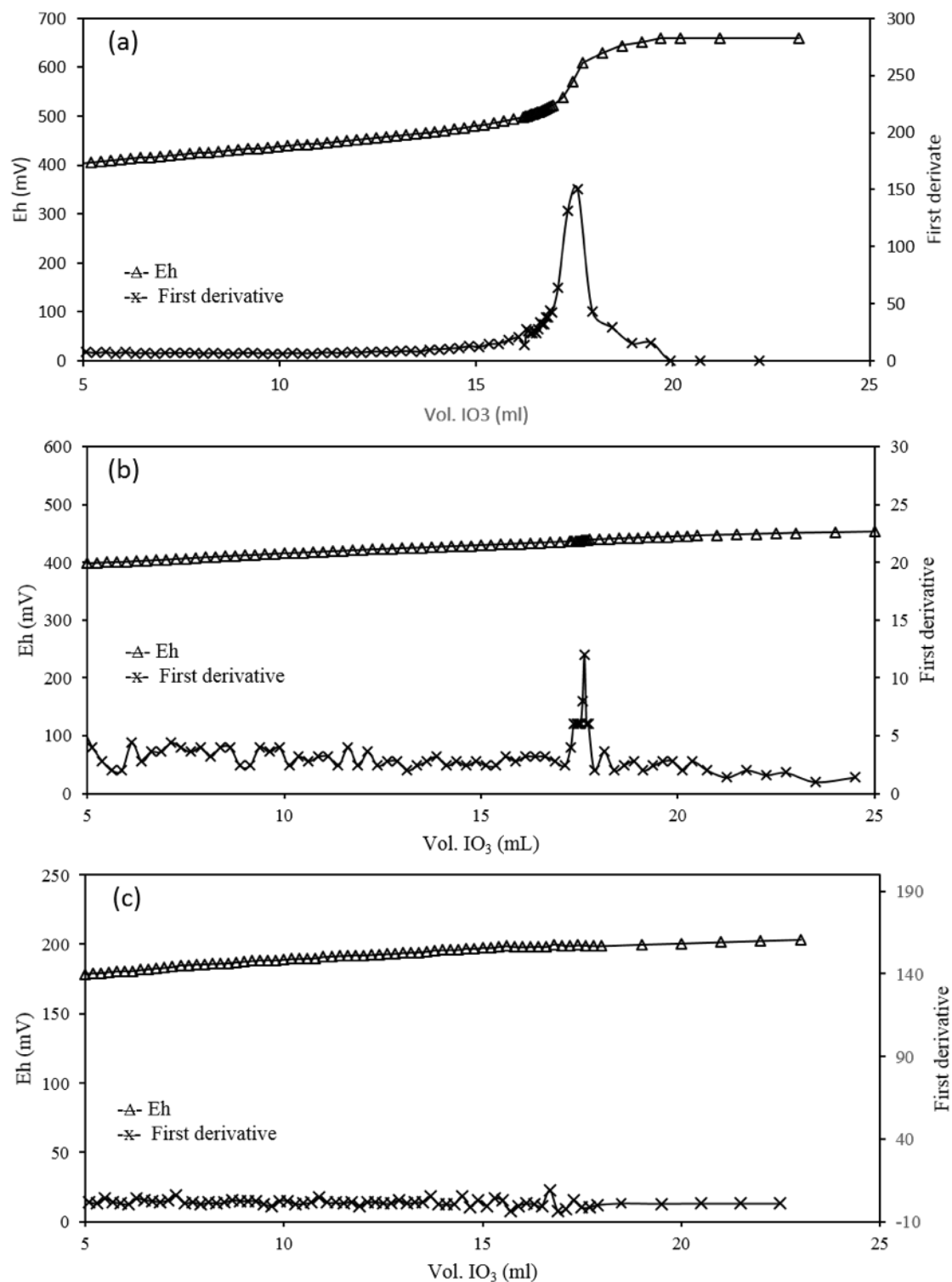


Fig. 5. Thiourea titration by iodate showing the potentiometric endpoint detection. (a) pH 1, (b) pH 5 and (c) pH 10.5. Thiourea concentration 0.13 M (10,000 ppm), and 25 °C.

Table 3. Thiourea stability in presence of cupric and ferric ions (10,000 ppm thiourea, pH 2 and 25 °C).

System		Direct titration of thiourea				Thiourea titration after zinc addition				
		Before titration		Thiourea concentration	Thiourea oxidation	Before titration		Thiourea concentration	Irreversible thiourea oxidation	
		Ion	Eh			Ion	Eh			
T-Cu	Test	(ppm)	(V)	(ppm)	(%)	(ppm)	(V)	(ppm)	(%)	
	A1	Cu <sup>2+</sup>	282.5	0.4	8,305	16.95	4.04	0.22	9,903	0.97
	A2		680.4	0.4	6,002	39.98	4.04	0.16	9,932	0.68
T-Fe	B1	Fe <sup>3+</sup>	271	0.2	9,803	1.97	201.23	0.22	9,854	1.46
	B2		590	0.21	9,384	6.16	557.72	0.24	9,575	4.25

Table 3 shows the effect of copper (Tests A1 and A2) and ferric ions (Tests B1 and B2) on the thiourea oxidation in acid media (pH 2). It can be seen in the table that cupric ions have a higher effect on the thiourea oxidation than ferric ions, as observed in the Eh values of the solutions containing these ions. These more oxidant potentials generated by the cupric ions cause the thiourea oxidation; around 17% and 40% for copper concentrations of 300 and 700 ppm, respectively. The titration of the solutions after the zinc addition permits to estimate that below 1% of the thiourea is irreversibly oxidized: almost all the thiourea is oxidized into FDS<sup>2+</sup>, and could be reduced back again into thiourea. In the case of the ferric ions, despite being a strong oxidant species, no significant oxidation of thiourea is observed, as it can be seen in the table: only 2% and 6% of the thiourea is oxidized when 300 and 700 ppm of iron are present, respectively. This occurs because the potential necessary to oxidize the thiourea (Eh 0.42 V, Fig. 3) is not reached into the solution. The irreversible thiourea oxidation when ferric ions are present is also low. It is worth mentioning that the titration with iodate quantifies free thiourea, as well as the thiourea-copper and thiourea-iron complexes. The thiourea oxidation into FDS<sup>2+</sup> is reversible; this fact implies that in a leaching process for gold and silver, this species could act as an oxidant for the precious metals, and regenerate the thiourea.

## Conclusions

The iodate titration can be used with satisfactory precision for low and high thiourea concentrations; the iodate concentration of the titrant solution should be set accordingly (the technique was evaluated for 10,000 ppm thiourea). The iodate titration of thiourea determines the thiourea in solution, and requires an acid media; therefore, it is necessary to add

sulfuric acid to the solution before the titration. The thiourea acidification produces protonated thiourea (HCS(NH<sub>2</sub>)<sub>2</sub><sup>+</sup>), which reacts with iodate to form the protonated formamidine disulfide (FDS<sup>2+</sup>). The presence of oxidant ions like cupric or ferric, coming from the leached ore, can oxidize the thiourea into formamidine disulfide (FDS<sup>2+</sup>), decreasing the leaching strength of the solution, although zinc dust addition to the solution before titration, reduce FDS<sup>2+</sup>, regenerating the thiourea. The effect of cupric ions is greater than that of ferric ions, as cupric ions could increase the redox potential of the solution above the potential of thiourea oxidation (0.42 V). When zinc dust is added to the solution before the titration, it reduces FDS<sup>2+</sup> by regenerating the thiourea. If two titrations are performed, one direct titration and a second one after zinc dust addition, it is possible to determine the concentration of FDS<sup>2+</sup> in the solution by subtracting the thiourea initially determined, from the thiourea estimated after the zinc addition.

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