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THIOUREA DETERMINATION BY TITRATION WITH PERMANGANATE IN THE PRESENCE OF OXALATE

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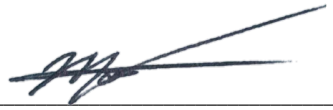
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ORIGINAL PAPER

Thiourea determination by titration with permanganate in the presence of oxalate

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Abstract

During gold and silver leaching with thiourea, the presence of the oxidizing ions Cu^{2+} and Fe^{3+} promotes thiourea oxidation, which reduces process efficiency if their concentration in the system is not adequately controlled. Therefore, several alternatives have been proposed, such as pretreatment of minerals, including flotation, acidic leaching, bioleaching, and others, to reduce the concentration of these ions and prevent the formation of stable complexes with them, using oxalate in the thiourea leaching process. However, this strategy introduces a new complication due to the interference of oxalate during thiourea quantification by permanganate titration. This work presents the effect of masking agents, such as zinc acetate and calcium chloride, on the quantification of thiourea by permanganate titration in an acidic medium. In this context, calcium chloride can mask oxalate due to the formation of CaC_2O_4, which must be filtered out before the titration.

Introduction

Thiourea (Tu) is presented as an alternative to the use of cyanide in the leaching of precious metals, such as gold and silver, from minerals due to its higher dissolution rate, up to five times faster, and its lower toxicity compared to cyanide [1]. Furthermore, their use in the recovery of these metals from electronic waste has been reported. In this context, pretreatments that involve the partial or total removal of base metals, such as copper (Cu), iron (Fe), and zinc (Zn), have been proposed to minimize unnecessary thiourea consumption resulting from the formation of complexes between these metals and thiourea. These metals are available in the system when the mineral is subjected to a fine grinding process, to sizes less than 75 µm, which increases the surface area and promotes the dissolution of these metals into the solution [2]; The presence of oxidizing ions such as Fe^{3+} and Cu^{2+} is harmful because these ions oxidize thiourea; hence, the use of organic agents has been proposed to reduce their effect, such as oxalate, which forms stable complexes with both ions and allows thiourea to be available to form complexes with gold and silver [3].

The use of calcium oxide allows the elimination of oxalates contained in sodium aluminate solutions through precipitation and absorption by causticization with lime [4]. On the other hand, oxalic acid is used to purify solutions obtained in the zinc recovery process from residual liquors of the galvanization industry [5], therefore, oxalate forms stable complexes with zinc and calcium in acidic solutions.

Thiourea quantification is crucial for monitoring the precious metal recovery process, as thiourea forms stable complexes with gold and silver. Several methods have been proposed for its determination, including ultraviolet photometry [6], electrochemical methods [7], and fluorescence and chemiluminescence [8]. These methods are recommended in the presence of low concentrations of thiourea. On the other hand, the quantification of thiourea by titration with iodate is an interesting alternative because iodate acts as an oxidizing agent and thiourea is protonated in an acidic medium, reacting with iodate to form formamidine disulfide, starch as an indicator, or recording the potential change with a platinum electrode for greater accuracy, at high Tu concentrations employed in mineral processing [9].

In 1972, a rapid and straightforward method was reported to quantify thiourea by titration with permanganate in an acidic medium, where 1 mol of thiourea reacts with 2.5 equivalents of permanganate [10]. Later, in 2007, a kinetic study of the redox reaction between thiourea and permanganate under similar conditions identified the formation of colloidal MnO_2 as an intermediate reaction. Furthermore,

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they confirmed the stoichiometric relationship between thiourea and permanganate, two moles of thiourea react with one mole of permanganate [11].

However, these studies were carried out with synthetic solutions in the presence of thiourea without evaluating the effect of oxalate on thiourea determination. The presence of oxalate can interfere with the accurate determination of thiourea, as it acts as an additional reducing agent compared to permanganate, thereby altering the quantification of thiourea. Therefore, the present work presents the effect of oxalate during the titration of thiourea with permanganate in an acidic medium with synthetic solutions at room temperature. In addition, the use of zinc acetate and calcium chloride as oxalate ion masking agents is evaluated.

Materials and methods

All solutions were prepared using deionized water and analytical-grade reagents. Potassium permanganate (Sigma-Aldrich), thiourea, oxalic acid, zinc acetate, calcium chloride, and sulfuric acid (Meyer). For the permanganate titration of thiourea, 200 µL of the solution to be analyzed is placed in a 100 mL Erlenmeyer Flask, magnetically stirred (450 rpm) with 12 mL of deionized water and 500 µL of 9 M sulfuric acid. The titrant solution (0.004 M potassium permanganate) is added by means of a micropipette (Thermo Scientific) until the endpoint is detected. Besides the self-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/Vol curve (Potential Change). The potential of the solution (ORP) was monitored (HANNA Instruments: HI5222-01), and ORP values are reported with reference to the hydrogen electrode (SHE). All tests were performed at 25 ºC, pH < 1.

To evaluate the effect of oxalate, 0.0325 M, 0.0433 M, 0.065 M, and 0.13 M oxalic acid (Ox) were used in 0.13 M thiourea solution. To mask oxalate, zinc acetate (0.2 M and 0.13 M) and calcium chloride (0.26, 0.39, and 0.52 M) were evaluated. All solutions were filtered with a 0.22 µm syringe filter before titration with permanganate, and precipitated solids were analyzed by X-ray diffraction (XRD) using an EMPYREAN diffractometer equipped with Ni filter, fine focus copper tube, and PIXcel3D detector.

Results and discussion

Determination of Tu with permanganate

Figure 1 shows the results of the determination of Tu with permanganate. There is a linear relationship between the moles of permanganate reacting with the moles of thiourea. For example, 2.62×10^{-5} mol of thiourea react with 1.39×10^{-5} mol of permanganate, i.e., a 1~ 2 ratio. This behavior can be observed from 1.31×10^{-5} to 5.24×10^{-5} mol of thiourea.

These results confirm that two moles of thiourea react with one mole of permanganate. This data will be used for subsequent analysis.

With these results, Eq. 1 proposes the relationship between thiourea and permanganate, where thiourea converts to cyanamide and elemental sulfur.

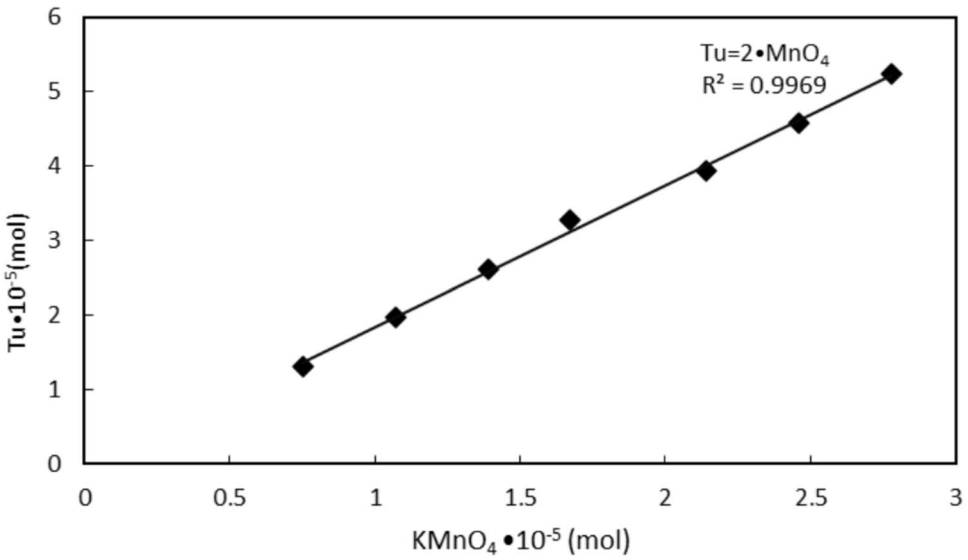


Fig. 1 Reaction between the concentration of thiourea and permanganate at different concentrations

Table 1 Determination of 0.13 M thiourea with 0.0325, 0.0433, 0.065, and 0.13 M Ox

Tu (M)	Ox (M)	Error (%)
0.13	0.0325	17
	0.0433	20
	0.065	55
	0.13	129

Table 2 Thiourea determination at 0.13 M at different concentrations of Ox (0.0325, 0.0433, 0.065, and 0.13 M) and zinc acetate (0.2 and 0.78 M)

Tu (M)	Zinc acetate (M)	Ox (M)	Error (%)
0.13	0.2	0.0325	9
		0.0433	19
		0.065	48
		0.13	57
	0.78	0.13	72

$$12\ SC(NH_2)_2 + 6\ MnO_4^- + 16\ H^+ = 12\ H_2NCN + 11\ S^0 + SO_4^{2-} + 6\ Mn^{2+} + 20H_2O \quad (1)$$

The intermediate oxidation reactions of thiourea are presented in Eqs. 2 and 3; Eq. 4 shows the reduction of permanganate in an acidic medium.

$$SC(NH_2)_2 = S^0 + 2H^- + 2e^- \quad (2)$$

$$SC(NH_2)_2 + 4\ H_2O = H_2NCN + SO_4^{2-} + 10H^+ + 8e^- \quad (3)$$

$$MnO_4^- + 8\ H^+ + 5e^- = Mn^{2+} + H_2O \quad (4)$$

Oxalic acid (Ox)

The determination of thiourea in the presence of 0.0325, 0.0433, 0.065, and 0.13 M is shown in Table 1. As permanganate concentration increases, the overestimation of thiourea increases. This is shown as a percentage error, that is, there is an error of 17, 20, 55, and 129% at 0.0325, 0.0433, 0.065, and 0.13 M Ox, respectively. This behavior is related to the stoichiometric reaction between permanganate and Ox, where permanganate acts as an oxidizing agent and Ox as a reducing agent in an acidic medium. Under these conditions, the MnO_4^- ion is reduced to Mn^{2+} and Ox is oxidized to CO_2.

Masking agents

Table 2 shows the effect of zinc acetate at a concentration of 2 M and 0.13 M of Tu, with varying Ox concentrations of 0.0325, 0.0433, 0.065, and 0.13 M. with an error of 9, 19, 48, and 57% error, that is to say that as the oxalic concentration increases the error also increases, saying that despite the presence of zinc acetate at 0.2 M it is not able to mask Ox, on the other hand if the acetate concentration is increased from 0.2 to 0.78 M with 0.13 M of Ox the error rises by 72%, this increase is related to the oxidizing power of permanganate which is capable of oxidizing acetate ions.

Figure 2a shows the quantification of 0.13 M Tu and Tu-Ox at 0.13 M (Fig. 2b), and Fig. 2c shows the quantification of the Tu-Ox-CaCl system at 0.13, 0.13 M, and 0.52 M, respectively.

When only thiourea is present in the system, the consumption of 3.25 ml MnO_4^- occurs; if Ox is added to the system, the consumption of MnO_4^- increases (7 ml), indicating a 215% overestimation of thiourea. This is related to the oxidizing power of permanganate, which oxidizes Ox in acidic medium, promoting its consumption until the abrupt change in potential occurs (Fig. 2b). Finally, in the Tu-Ox-CaCl system, the consumption of permanganate is 3.25 ml. This value is the same when only thiourea is present in solution, indicating that calcium chloride reacts with Ox and masks it due to the formation of a calcium oxalate (00–016-0379, $CaC_2O_4{\cdot}H_2O$) as a solid in the solution, and it was characterized by X-ray diffraction (XRD). Therefore, the solution must be filtered before determination with permanganate.

The ratio of oxalic acid to chloride of 1:2 and 1:3, with 0.26 and 0.39 M CaCl, has an error of 21% and 11%, respectively. However, when the concentration is 0.52 M CaCl, i.e., an Ox:CaCl ratio of 1:4, the oxalic acid is completely masked (Fig. 2c).

This methodology provides a route for quantifying Tu in the presence of oxalate, where thiourea is used as a leaching agent for the recovery of precious metals such as gold and silver, and oxalate is used to control oxidizing ions, including Cu^{2+} and Fe^{3+}, in the Tu-Au and Tu-Ag systems.

Conclusion

For thiourea determination with permanganate in acid media, 2 mol of thiourea react with 1 mol of permanganate; however, the presence of oxalate leads to overestimation. To mitigate this effect, two reagents were evaluated as potential masking agents: zinc acetate and calcium chloride. Zinc acetate does not reduce the overestimation; on the contrary,

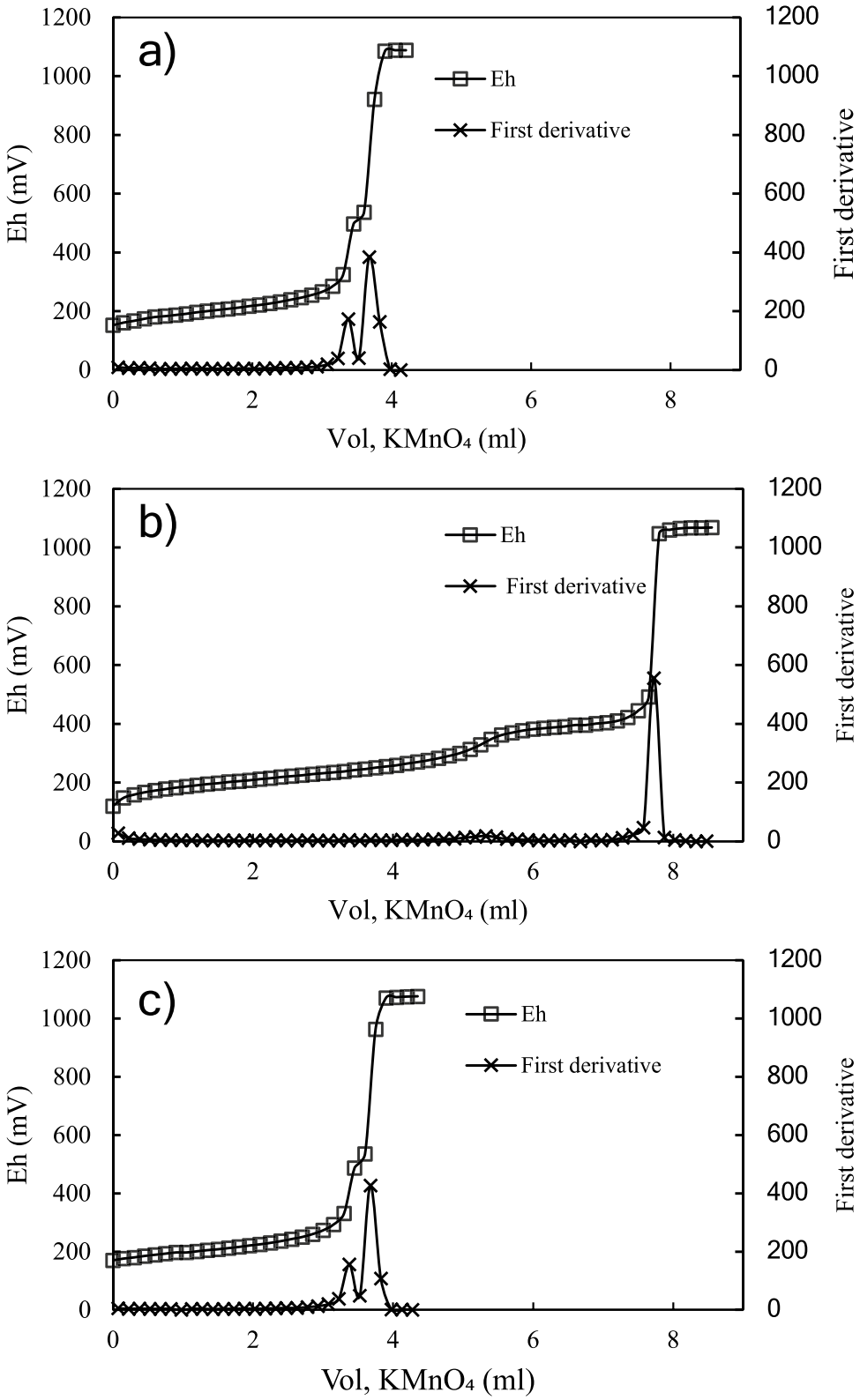


Fig. 2 Titration of thiourea at 0.13 M (**a**), 0.13 M Tu-0.13 M Ox (**b**), and Tu-Ox-CaCl with 0.13 M, 0.13 M, and 0.52 M, respectively (**c**)

this ion promotes a higher percentage of error because permanganate can oxidize acetate. Calcium chloride can mask oxalic acid due to the formation of an Ox-CaCl complex, which must be filtered before titration. The formation of this complex favors an Ox:CaCl ratio of 1:4.

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Author contributions All authors contributed to the conception and design of the study. Material preparation, data collection, and analysis were performed by Calla-Choque D. and Machorro-Reyes J. A. The first draft of the manuscript was written by Calla-Choque D., and Machorro-Reyes J. A. commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Data availability The data that support the above-presented results are available from the corresponding author upon reasonable request.

Declarations

Competing interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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