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Titrimetric Determination of Thiourea and Silver With a Picrate Ion Selective Electrode

By

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With 2 Figures

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A number of ion selective liquid membrane electrodes have been described which respond selectively to anions. Several ion selective electrodes have been used as indicator electrodes in potentiometric precipitation titrations[1, 2]. In this paper, a method is described for the semiautomatic potentiometric titration of thiourea with silver nitrate and of silver with thiourea, in the presence of picrate ions, using as indicator electrode the recently described picrate ion selective electrode[3]. The method is based on the formation of insoluble complexes of silver-thiourea-picrate, $[Ag(CSN_2H_4)_2]$ $(C_6H_2N_3O_7)$ or $[Ag(CSN_2H_4)]$ $(C_6H_2N_3O_7)$, and compares favorably with other methods reported for the determination of thiourea[6–10].

The semiautomatic method is sensitive, rapid, accurate and simple. Thiourea in the range 15—1500 μg and silver in the range 200—1800 μg were determined with relative errors and relative standard deviation of about 1%.

Experimental

Instrumentation

The electrodes, the reaction cell and the recording system were the same as previously reported[3].

Reagents

All solutions were prepared with deionized twice-distilled water and reagent-grade substances, except where stated.

Thiourea, 0.01000 *M*, was prepared by dissolving 761.2 mg of thiourea (Merck, >99.8%) in water and making the volume to 1 liter. The strength of this solution was checked iodometrically. More dilute standard thiourea solutions were prepared by dilution.

The picric acid used was Fluka purum and was standardized with NaOH solution.

Since silver nitrate (Merck) is a primary standard, no effect was made to standardize the solutions.

Procedure

Semiautomatic titration of thiourea, Method 1. (For the range 10^{-4}—10^{-3} *M* thiourea, with 2.500×10^{-3} *M* $AgNO_3$.) Pipet into a 50-ml beaker a 20.00-ml aliquot of the sample and 1.00 ml of 0.025 *M* picric acid solution, start the stirrer, and after the potential is stabilized (~1 min), start simultaneously the burette and the recorder to obtain the titration curve. For the greatest accuracy, calibrate the recorder for each titration, using the buret reading.

Method 2 (for the range 10^{-5}—10^{-4} *M* thiourea, with 2.500×10^{-4} *M* $AgNO_3$) is similar except that the picric acid solution is 0.0025 *M*.

Semiautomatic titration of silver. (For the range 10^{-4}—10^{-3} *M* silver, with 5.00×10^{-3} *M* thiourea.) Pipet into a 50-ml beaker a 20.00-ml aliquot of the sample and 2.00 ml of 0.025 *M* picric acid solution and continue as in the titration of thiourea from the point of starting the stirrer.

Results and Discussion

The picrate ion selective electrode can be used as an end-point sensor in potentiometric precipitation titrations involving picrate ions. In the titration of thiourea with standard silver nitrate in the presence of picrate ions, the following precipitation reaction takes place:

$$2S=C\begin{matrix}NH_2\\NH_2\end{matrix} + Ag^+ + C_6H_2N_3O_7^- \rightarrow [Ag(SCN_2H_4)_2]\ (C_6H_2N_3O_7) \quad (1)$$

Therefore, the equivalent weight of thiourea is double the molecular weight. During reaction 1, the picrate concentration decreases resulting in a continuous increase of the electrode potential. At the equivalence point there is a sharp decrease in the slope of the titration curve (Figs. 1 and 2) because after the equivalence point the picrate

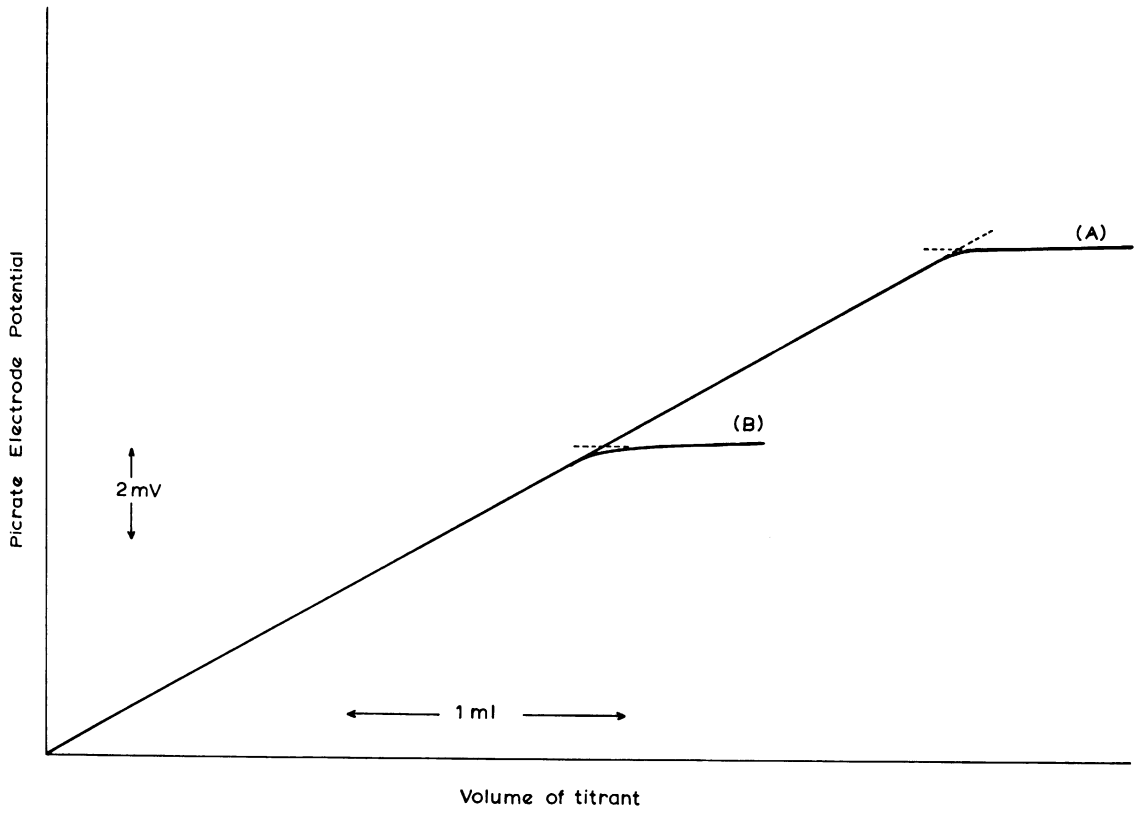

Fig. 1. Recorded curves for the semiautomatic potentiometric titration of thiourea with silver, in the presence of picrate ions. (A) 20 ml of 7.5×10^{-4} *M* thiourea titrated with 2.5×10^{-3} *M* Ag^+; (B) 20 ml of 5×10^{-5} *M* thiourea with 2.5×10^{-4} *M* Ag^+

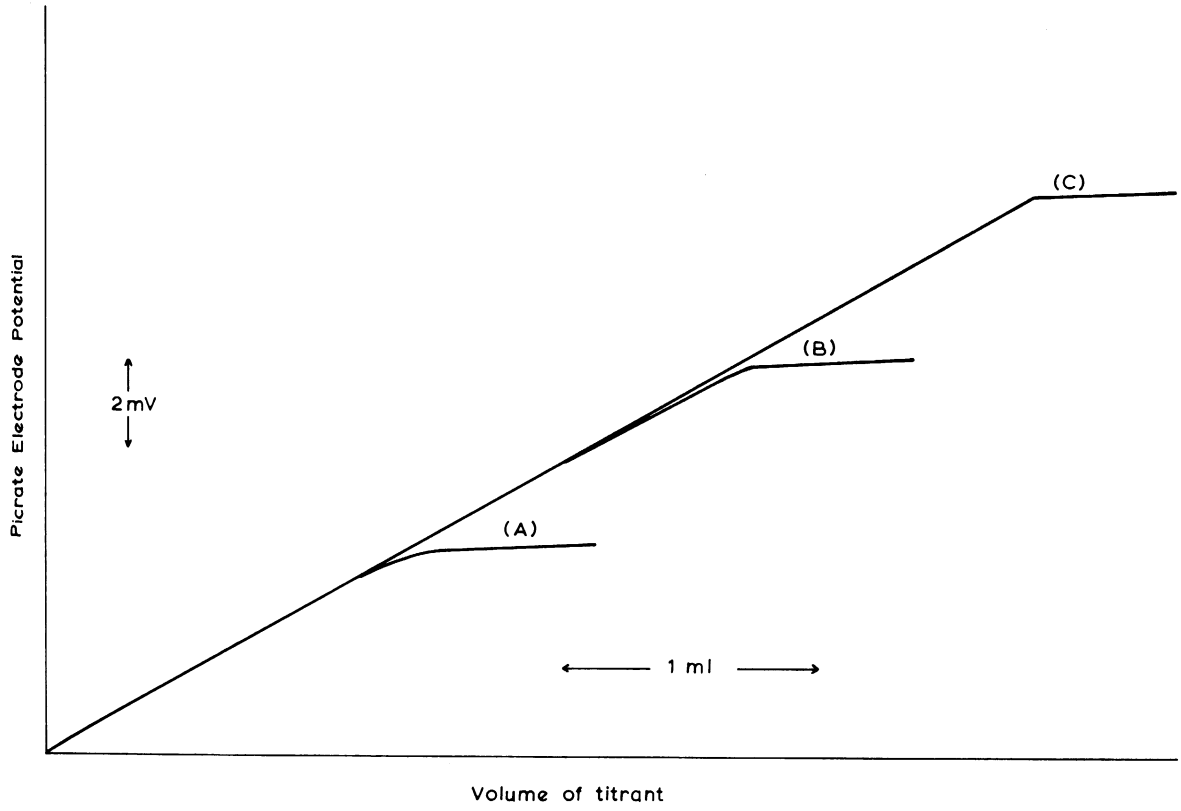

Fig. 2. Recorded curves for the semiautomatic potentiometric titration of 20 ml of silver with 5×10^{-3} *M* thiourea, in the presence of picrate ions. [Ag^+], *M*: (A) 4×10^{-4}; (B) 7×10^{-4}; (C) 1×10^{-3}

concentration remains practically constant. This sharp change in slope facilitates the location of the end-point and makes it more precise.

There is a small blank which is a function of titrant concentration, rate of addition of titrant, and experimental conditions, such as stirring, electrode geometry, etc. However, all these factors can be kept constant so that the blank remains practically constant over a large concentration range. The blank is determined by titrating standard thiourea solutions and is substracted from the titrant volume in each titration.

Analysis of aqueous thiourea solutions of known concentrations gave the results shown in Table I. The relative standard deviation

Table I. Semiautomatic Potentiometric Titration of Thiourea With Silver Nitrate

$AgNO_3$ titrant (M)	Thiourea, μg Taken	Found	Error, %
2.5×10^{-4}*	15.2	15.5	+2.0
	60.8	60.1	−1.2
	106.4	106.7	+0.3
	129.2	131.3	+1.6
			Av. 1.3
2.5×10^{-3}**	380	370	−2.5
	608	597	−1.8
	1064	1071	+0.7
	1520	1539	+1.2
			Av. 1.5

* Average of 2 measurements;
** Single measurements.

was 0.3% and 1.0% for samples containing 760 and 76 μg of thiourea respectively ($n=4$).

In the titration of silver with standard thiourea solution in the presence of picrate, it is under such conditions that during the formation of the silver-thiourea-picrate insoluble complex there is excess of silver. It has been found that the stoichiometry of the precipitation reaction corresponds to the formation of the complex $[Ag(SCN_2H_4)]$ $(C_6H_2N_3O_7)$; that is, the ratio of thiourea to silver is 1 : 1.

In previous work[3] silver nitrate in the range 10^{-3}—10^{-2} M was titrated with standard sodium picrate solution in the presence of excess thiourea. By the proposed modified procedure (by titrating silver with standard thiourea solution in the presence of excess picrate) the solubility of the precipitate is decreased and thus the titration of more dilute solutions (10^{-4}—10^{-3} M) is made possible.

The method should not be used with more dilute silver solutions because the blank becomes progressively larger and the accuracy deteriorates sharply. Under the experimental conditions, lead does not interfere with the determination of silver.

Table II. Semiautomatic Potentiometric Titration of Silver Nitrate With Thiourea

Silver, μg		Error, %
Taken	Found*	
216	217	+0.5
540	540	—
1188	1193	+0.4
1836	1822	−0.8
		Av. 0.4

* Average of 2 measurements.

Analysis of aqueous silver solutions of known concentrations gave the results shown in Table II. The relative standard deviation was 0.4% for a sample containing 1080 μg of silver ($n=4$).

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Summary

Titrimetric Determination of Thiourea and Silver With a Picrate Ion Selective Electrode

A method has been developed for the semiautomatic potentiometric titration of thiourea with silver nitrate and of silver with thiourea, in the presence of picrate ions, using a picrate ion selective electrode. Thiourea in the range 15—1500 μg and silver in the range 200—1800 μg were determined with relative errors and relative standard deviation of about 1%.

Zusammenfassung

Eine halbautomatische potentiometrische Titrationsmethode für Thioharnstoff mit Silbernitrat bzw. umgekehrt in Gegenwart von Pikrationen mit Hilfe einer selektiven Pikratelektrode wurde entwickelt. 15—1500 μg Thioharnstoff bzw. 200—1800 μg Silber wurden mit einem relativen Fehler und einer relativen Standardabweichung von etwa ±1% bestimmt.

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