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Titrimetric Determination of Iodide, Hexacyanoferrate(II), Thiourea, Cationic Surfactants, and of Picrate with a Picrate Ion-Selective Electrode

By

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With 5 Figures

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Several ion-selective electrodes have been used as indicator electrodes in potentiometric precipitation titrations[1–14]. In this paper, methods are described for the semiautomatic potentiometric precipitation titration of iodide, hexacyanoferrate(II), and sulfide with silver nitrate, in the presence of picrate and thiourea, and of mixtures of sulfide-thiourea with silver nitrate, in the presence of picrate ions. The method is based on the formation of insoluble silver salts of the anions and of insoluble complexes of silver-thiourea-picrate, $[Ag(CSN_2H_4)_2]$ $(C_6H_2N_3O_7)$ or $[Ag(CSN_2H_4)]$ $(C_6H_2N_3O_7)$. Methods are also proposed for the semiautomatic potentiometric precipitation titration of cationic surfactants (quaternary ammonium compounds) with sodium picrate and of picrate ions with tetraphenylarsonium chloride. All titrations are monitored with a picrate-selective electrode in conjunction with a double-junction reference electrode.

The semiautomatic methods are sensitive, rapid, accurate and simple. Iodide in the range 0.2—10 μmol, hexacyanoferrate(II) in the range 0.2—20 μmol, sulfide-thiourea mixtures containing sulfide in the range 0.02—0.15 mmol and thiourea in the range 0.08—0.50 mmol, and cetyltrimethylammonium bromide, cetylpyridinium chloride, didodecyldimethylammonium bromide and picrate in the range 0.02—0.2 mmol were determined with average errors and relative standard deviations of 1—2%.

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Experimental

Instrumentation

The electrodes and the recording system were the same as previously reported[10].

Reagents

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

Picric acid solutions were prepared by accurately weighing the appropriate amounts of air dried picric acid (Fluka, purum, standardized against standard sodium hydroxide solution), dissolving them in water in volumetric flasks and diluting to the mark.

Sodium picrate stock solution, 0.1000 *M*, was prepared by neutralizing a suitable picric acid solution with NaOH to a pH of about 6. More dilute standard solutions were prepared by serial dilution. All picrate solutions were stored in amber bottles.

Thiourea stock solution, 0.01000 *M*, was prepared by dissolving 0.7612 g of thiourea (Merck >99.5%) in water and diluting to 1 l. The strength of this solution was checked iodometrically. More dilute standard thiourea solutions were prepared by dilution.

Sodium iodide stock solution, 0.1000 *M*, was prepared by dissolving dried NaI (Merck) in water. The strength of this solution was checked argentometrically. More dilute standard iodide solutions were prepared by dilution.

Potassium hexacyanoferrate(II) stock solution, 0.1000 *M*, was prepared by dissolving dried substance (Merck) in water. The strength of this solution was checked by titration with $KMnO_4$. More dilute standard solutions were prepared by dilution.

Sodium sulfide stock solution, 0.0500 *M*, was prepared by dissolving $Na_2S \cdot 9H_2O$ (Merck) in oxygen-free water. The solution was standardized iodometrically just before use. More dilute standard solutions were prepared just before use by dilution with oxygen-free water.

Cetylpyridinium chloride (CPCl), 0.0100 *M*, was prepared by dissolving pure substance (Merck) in water containing 5% isopropanol.

Hexadecyltrimethylammonium bromide (HTABr), 0.0100 *M*, was prepared by dissolving pure substance (Merck) in water containing 5% isopropanol.

Didodecyldimethylammonium bromide (DDABr), 0.0100 *M*, was prepared by dissolving substance (Eastman Kodak) in water containing 15% isopropanol.

Isopropanol was added to prevent crystallization and foaming. Such concentrations of isopropanol do not influence the electrode response.

The purity of the cationic surfactants tested was checked by titration with silver nitrate for the determination of their chloride (Mohr method) or bromide (Fajans method) content.

Tetraphenylarsonium chloride (Ph_4AsCl), $2.500 \times 10^{-2} M$, was prepared by dissolving pure substance (Merck) in water. The strength of this solution was checked by a gravimetric[11] and a titrimetric method[1], the titrimetric method being the method of choice.

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

Procedures

Semiautomatic titration of iodide, Method 1. (For the range 10^{-4}—$10^{-3} M$ iodide, with $4.00 \times 10^{-3} M$ $AgNO_3$.) Pipet into a 50-ml beaker a 10.00-ml aliquot of the sample, 10.00 ml of $1.0 \times 10^{-3} M$ picric acid solution and 5.00 ml of $1.0 \times 10^{-2} M$ thiourea solution, start the stirrer, and after the potential is stabilized (~ 1 min), start simultaneously the buret and the recorder to obtain the titration curve. For the highest accuracy, calibrate the recorder for each titration, using the buret reading.

Method 2. (For the range 10^{-5}—$10^{-4} M$ iodide, with $1.00 \times 10^{-3} M$ $AgNO_3$.) Pipet into a 50-ml beaker a 20.00-ml aliquot of the sample, 4.00 ml of $1.0 \times 10^{-3} M$ picric acid solution and 3.00 ml of $1.0 \times 10^{-2} M$ thiourea solution and continue as in method 1 from the point of starting the stirrer.

Semiautomatic titration of hexacyanoferrate(II), Method 1. (For the range 10^{-4}—$10^{-3} M$ hexacyanoferrate(II), with $2.500 \times 10^{-2} M$ $AgNO_3$.) Pipet into a 50-ml beaker a 20.00-ml aliquot of the sample, 1.00 ml of $2.5 \times 10^{-2} M$ picric acid solution and 5.00 ml of $1.0 \times 10^{-3} M$ thiourea solution and continue as in the titration of iodide (method 1) from the point of starting the stirrer.

Method 2. (For the range 10^{-5}—$10^{-4} M$ hexacyanoferrate(II), with $2.500 \times 10^{-3} M$ $AgNO_3$.) Pipet into a 50-ml beaker a 20.00-ml aliquot of the sample, 3.00 ml of $2.5 \times 10^{-3} M$ picric acid solution and 1.00 ml of $1.0 \times 10^{-2} M$ thiourea solution and continue as in the titration of iodide (method 1) from the point of starting the stirrer.

Semiautomatic differential titration of sulfide-thiourea mixtures. (For the range 5×10^{-4}—$3.8 \times 10^{-3} M$ sulfide and 1.9×10^{-3}—$1.2 \times 10^{-2} M$ thiourea, with $0.1000 M$ $AgNO_3$.) Pipet into a 100-ml beaker a 40.00-ml aliquot of the sample and 7.00 ml of $0.10 M$ sodium picrate solution and continue as in the titration of iodide (method 1) from the point of starting the stirrer.

Semiautomatic titration of cationic surfactants. (For the range 6.7×10^{-4}—$6.7 \times 10^{-3} M$, with $2.500 \times 10^{-2} M$ sodium picrate solution.) Pipet into a 50-ml beaker a 30.00-ml aliquot of the sample and continue as in the titration of iodide (method 1) from the point of starting the stirrer.

Semiautomatic titration of picrate. (For the range 10^{-3}—$10^{-2} M$, with $2.500 \times 10^{-2} M$ $\mathrm{Ph_4AsCl}$ solution.) Pipet into a 50-ml beaker a 20.00-ml aliquot of the sample and continue as in the titration of iodide (method 1) from the point of starting the stirrer.

Clean the beaker and the reference electrode with acetone after each titration and wash the picrate electrode with sufficient water. Dry them by suction.

All titrations were performed at ambient temperature (27 ± 1°). MPI operational amplifiers (McKee-Pedersen Instruments, Danville, Calif.) were used for the differentiating circuit.

Results and Discussion

In the titration of iodide and hexacyanoferrate(II) with standard silver nitrate in the presence of picrate and thiourea, the insoluble salts AgI and $\mathrm{Ag_4[Fe(CN)_6]}$ are precipitated first. During these precipitation reactions the picrate concentration remains practically constant and the electrode potential is stable (Fig. 1). At the equivalence point there is a sharp increase in the electrode potential

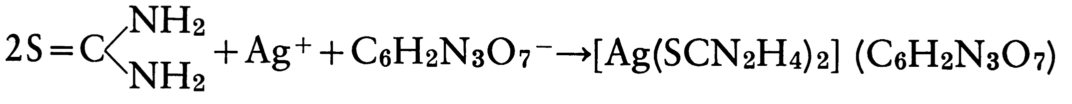
Table I. Semiautomatic Potentiometric Titration of Iodide and Hexacyanoferrate(II) with Silver Nitrate

Iodide, μmol		Error, %	Hexacyanoferrate(II), μmol		Error, %
Taken	Found*		Taken	Found**	
0.200	0.204	+2.0	0.200	0.194	−3.0
0.800	0.768	−4.0	0.800	0.808	+1.0
1.40	1.31	−6.4	1.40	1.43	+2.1
1.70	1.66	−2.4	2.00	2.04	+2.0
		Av. 3.7			Av. 2.0
1.00	0.97	−3.0	2.00	1.99	−0.5
3.00	3.01	+0.3	8.00	8.08	+1.0
5.00	5.00	—	14.00	14.1	+0.7
10.00	10.02	+0.2	20.00	20.1	+0.5
		Av. 0.9			Av. 0.7

* Single measurements.

** Average of 2 measurements.

caused by a picrate concentration decrease because of the following precipitation reaction:



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

This sharp change in potential facilitates the location of the end-point and makes it more precise.

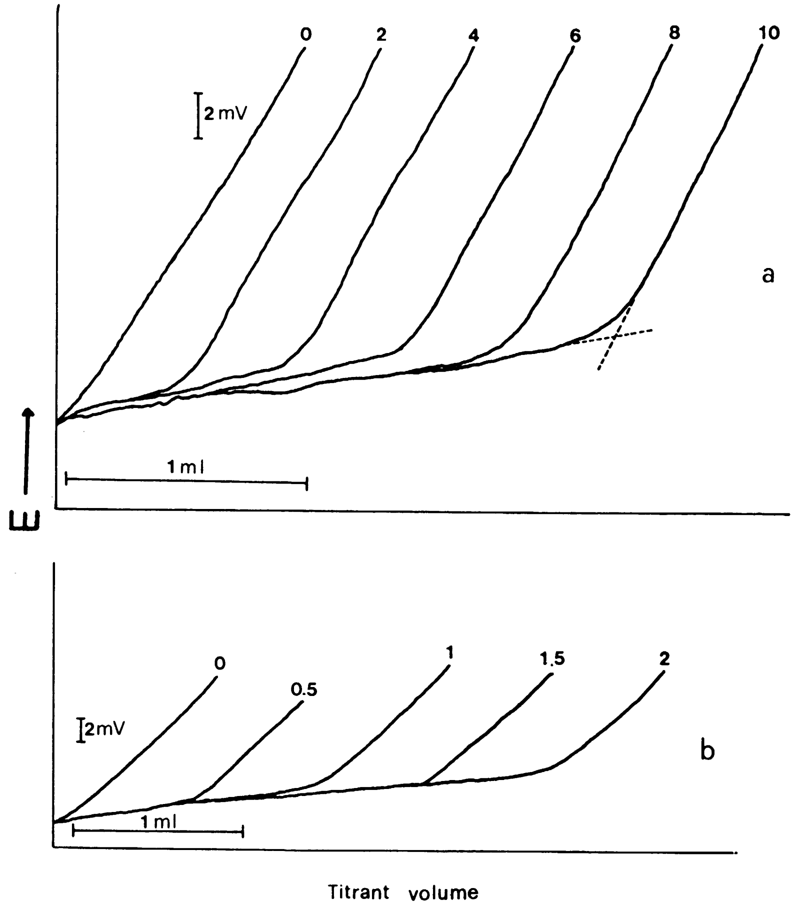


Fig. 1. Recorded curves for the semiautomatic potentiometric titration of a) 0—10 μmol Iodide with 4×10^{-3} M $AgNO_3$, and b) 0—2 μmol of hexacyanoferrate(II) with 2.5×10^{-3} M $AgNO_3$, in the presence of picrate and thiourea

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 solutions and is subtracted from the titrant volume in each titration. The concentration of the indicator (mixture of thiourea and picrate) was a compromise to avoid coprecipitation before the equivalence point and obtain small blanks.

Analysis of aqueous iodide and hexacyanoferrate(II) solutions of known concentrations gave the results presented in Table I.

The proposed method for the determination of iodide and hexacyanoferrate(II) ions can also be used for the determination of other anions forming insoluble silver salts. In many cases, the method permits the differentiating titration of binary mixtures containing such an anion and thiourea. Fig. 2 shows, as an example, the titration curve of a mixture containing sulfide ions and thiourea. Sulfide is precipitated first as Ag_2S, and then thiourea, first as $[Ag(SCN_2H_4)_2](C_6H_2N_3O_7)$, and subsequently as $[Ag(SCN_2H_4)](C_6H_2N_3O_7)$.

Analysis of aqueous solutions of known concentrations of sulfide and thiourea gave the results shown in Table II. The relative standard deviation was 1.4%, 0.9%, and 0.7% for a sample containing 0.08 mmol of sulfide and 0.30 mmol of thiourea (for the first and second equivalence point), respectively ($n=4$).

Table II. Semiautomatic Potentiometric Titration of Sulfide-Thiourea Mixtures with Silver Nitrate

Taken, mmol		Found, mmol		Error, %	
Sulfide	Thiourea	Sulfide*	Thiourea**	Sulfide	Thiourea
0.149	0.500	0.149	0.514	—	+2.8
0.0398	0.400	0.0414	0.402	+4.0	+0.5
0.0797	0.300	0.0793	0.300	−0.5	—
0.0398	0.150	0.0395	0.141	−0.8	−6.0
0.120	0.150	0.115	0.146	−4.2	−2.7
0.0199	0.0750	0.0208	0.0731	+4.5	−2.5
				Av. 2.3	Av. 2.4

* Single measurements.

** Calculations based on the first equivalence point for thiourea. The second equivalence point gave comparable results.

During the titration of cationic surfactants with picrate, it was noticed that the cationic surfactants influence the response of the picrate electrode. A calibration curve for the cation HTA^+ was constructed and it was found that the response can be expressed by the Nernst equation:

$$E = E^0 + S\log[HTA^+] \qquad (2)$$

The slope S was 65 mV in the range 10^{-4}—$10^{-3}M$ HTA^+, at 25°, and 10 mV in the range 10^{-3}—$10^{-2}M$. These observations agree with data in the literature[15] where ion-selective electrodes have been used for critical micelle concentration (CMC) determination. A similar response was observed for DDA^+. The slope was 86 mV (supernernstian) for the cation CP^+ in the range 10^{-4}—10^{-3} *M*.

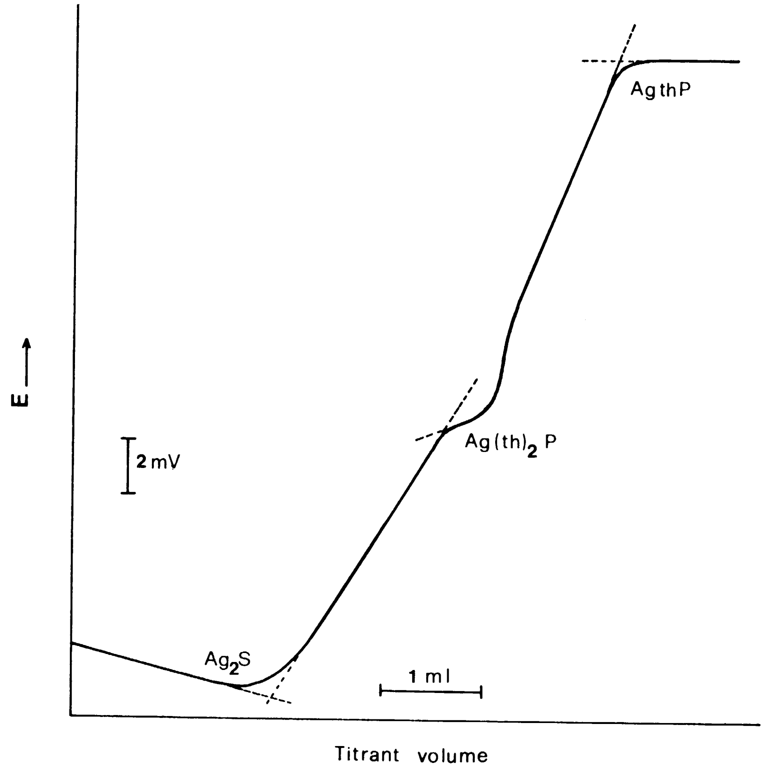


Fig. 2. Recorded curve for the semiautomatic potentiometric titration of a mixture containing 0.12 mmol of sulfide and 0.40 mmol of thiourea with 0.1000 *M* $AgNO_3$, in the presence of picrate ions

Table III. Semiautomatic Potentiometric Titration of Cetylpyridinium Chloride with Sodium Picrate

Cetylpyridinium Chloride, mmol		
Taken	Found*	Error, %
0.0200	0.0189	−5.6
0.0500	0.0500	—
0.0800	0.0806	+0.8
0.110	0.110	—
0.140	0.140	—
0.170	0.171	+0.6
0.200	0.201	+0.5
		Av. 1.1

* Average of 2 measurements.

A typical titration curve in the titration of CP^+ along with the first and second derivative curves are shown in Fig. 3. The differentiating circuit used is shown in Fig. 4. Similar curves were obtained with the other cationic surfactants.

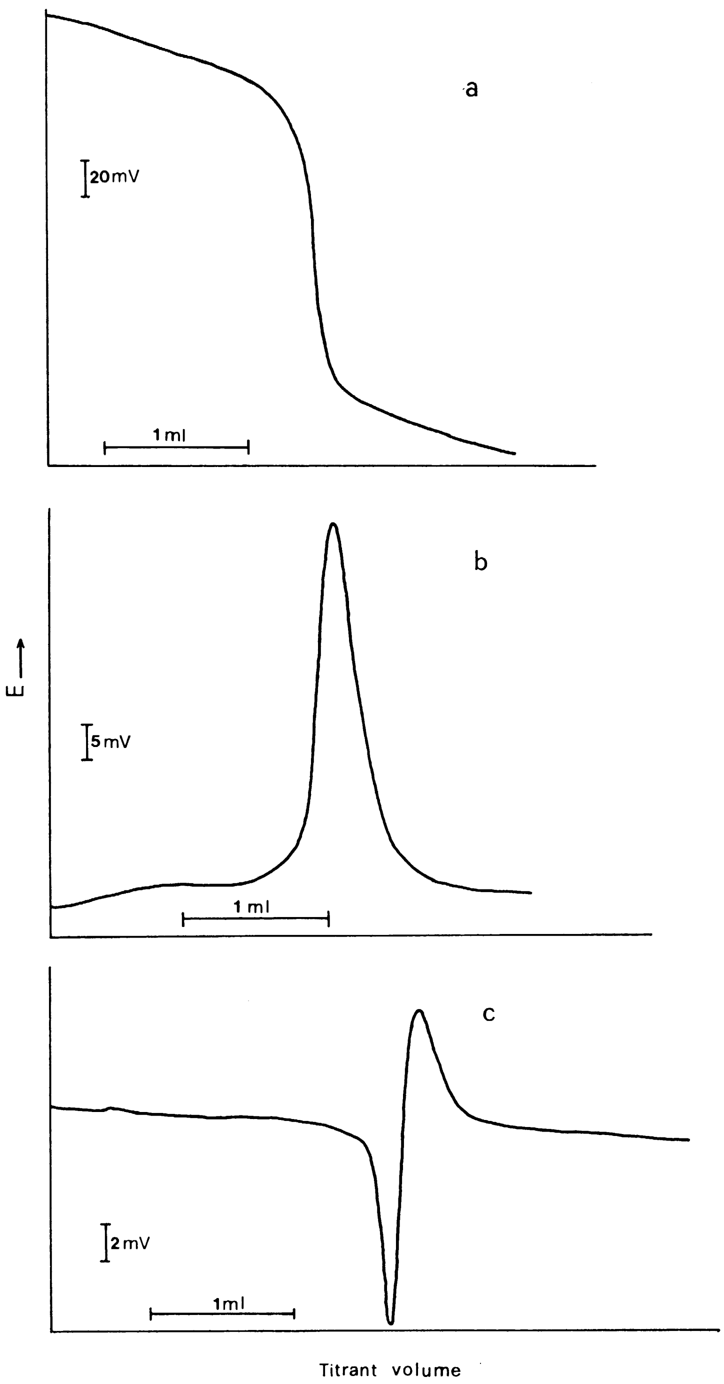


Fig. 3. (a) Recorded curve for the semiautomatic potentiometric titration of 0.05 mmol CP^+ with 2.5×10^{-2} M sodium picrate. (b) First derivative curve. (c) Second derivative curve

In the titration of cationic surfactants, there is a small blank which remains practically constant over a large concentration range.

The blank is larger with the derivative curves. The most accurate results are obtained when the titration curve or the first derivative curve is used. The blank can be eliminated by carrying out the titration manually.

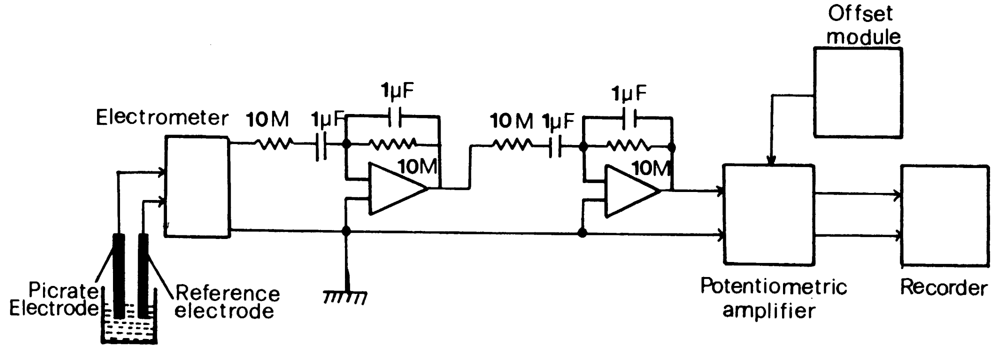


Fig. 4. Electronic differentiating circuit for the first and second derivative curves

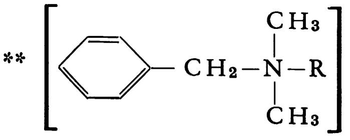
Analysis of aqueous CP^+ solutions of known concentrations gave the results shown in Table III. Similar results were obtained for the other two surfactants. The relative standard deviation was 0.20% for a sample containing 0.100 mmol of CP^+ ($n=4$). The method cannot differentiate between quaternary ammonium compounds present in mixtures.

The method was applied to the determination of quaternary ammonium compounds in two commonly used pharmaceutical preparations. The results are presented in Table IV.

Table IV. Semiautomatic Potentiometric Titration of Quaternary Ammonium Compounds in Pharmaceutical Preparations with Sodium Picrate

Pharmaceutical preparation	g/100 ml	
	Found	Labelled
Cetrimide*	19.5	20
Benzalkonium chloride**	9.7	10

* $R(CH_3)_3NBr$, $R=C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$ [16,17].

** 

Cl, $R=C_8H_{17}-C_{18}H_{37}$ [16,17].

The picrate electrode exhibits near Nernstian response to Ph_4As^+ and to other bulky quaternary ammonium compounds such as tetrapentylammonium(TPA^+). It is not clear if the response is direct or indirect, because all these cations form insoluble picrate salts.

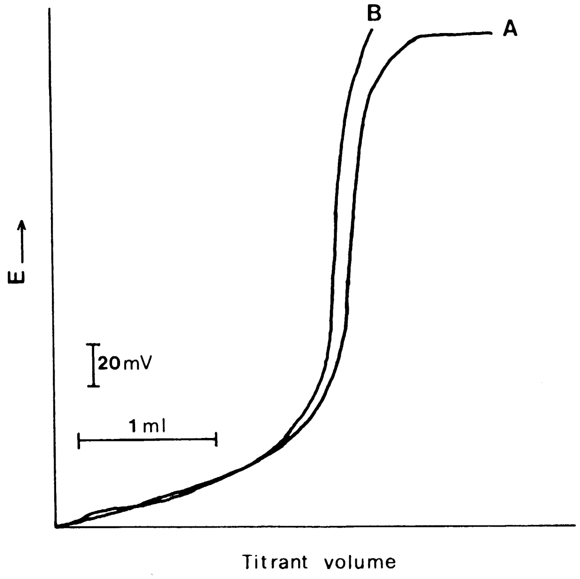


Fig. 5. Recorded (A) and theoretical (B) curves for the semiautomatic potentiometric titration of 0.05 mmol of picrate with 2.5×10^{-2} *M* Ph_4AsCl

A typical titration curve for the titration of picrate with Ph_4AsCl and the corresponding theoretical titration curve are shown in Fig. 5. After the equivalence point, the picrate concentration is calculated

Table V. Comparison of Semiautomatic Potentiometric and Neutralization Method for the Titration of Commercial Picric Acid

Sample	% Picric acid	
	Potentiometric titration with Ph_4AsCl	Titration with NaOH[18]
Fluka purum	100.6	100.3
	100.2	100.6
	100.1	100.2
	$\overline{X}$ = 100.3	100.4
Merck p. a.	100.4	100.6
	100.2	100.6
	100.7	100.6
	$\overline{X}$ = 100.4	100.6
Kahlbaum	99.0	100.2
	100.4	100.3
	99.8	100.0
	$\overline{X}$ = 99.7	100.2

from the solubility product of tetraphenylarsonium picrate (2.9×10^{-10}, as calculated with the picrate electrode). There is a small blank. The optimum pH range for the titration is 5—7. Ions which precipitate Ph_4As^+ or interfere with the picrate electrode[10] must be absent.

Picrate in aqueous solutions of known concentrations (0.02—0.2 mmol) was determined with an average error of $\pm 1.0\%$ (the absolute error varied from -1.5% at the 0.02 mmol level to $+0.2\%$ at the 0.2 mmol level). The relative standard deviation was 0.1% for a sample containing 0.10 mmol of picrate ($n = 5$).

The method was applied to the analysis of commercial samples of picric acid (Table V). Also included are data obtained by the sodium hydroxide method[18] to serve for comparison. As can be seen, a favorable comparison was obtained between the two methods.

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Summary

Titrimetric Determination of Iodide, Hexacyanoferrate(II), Thiourea, Cationic Surfactants, and of Picrate with a Picrate Ion-Selective Electrode

Methods have been developed for the semiautomatic potentiometric precipitation titration of iodide, hexacyanoferrate(II), sulfide, and sulfide-thiourea mixtures with silver nitrate, of medically important quaternary ammonium compounds with sodium picrate, and of picrate ions with tetraphenylarsonium chloride, using a picrate ion-selective electrode. Semimicro and/or microamounts of these substances were determined with relative errors and relative standard deviations of 1—2%.

Zusammenfassung

Maßanalytische Bestimmung von Jodid, Hexacyanoferrat(II), Thioharnstoff, kationischen Schaummitteln und von Pikrat mit einer pikrationenselektiven Elektrode

Methoden zur halbautomatischen Fällungstitration von Jodid, Hexacyanoferrat(II), Sulfid und Sulfid-Thioharnstoff-Gemischen mit Silbernitrat sowie von medizinisch bedeutenden quartären Ammoniumverbindungen mit

Natriumpikrat und von Pikrationen mit Tetraphenylarsoniumchlorid unter Verwendung einer pikrationenselektiven Elektrode wurden beschrieben. Halbmikro- bzw. Mikromengen der genannten Stoffe wurden mit einem rel. Fehler und einer rel. Standardabweichung von 1—2% bestimmt.

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