COULOMETRIC TITRATION OF ANTIMONY WITH ELECTROGENERATED IODINE

by

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Electrogenerated iodine has been employed for the coulometric titration of $+3$ arsenic[1,2,3], thiosulfate[4,5], sulfide[6], and selenite[7]. The present study extends the application of coulometric titrations with iodine to the determination of $+3$ antimony.

A coulometric titration of tripositive antimony in hydrochloric acid medium with electrogenerated bromine has been described by BROWN AND SWIFT[8,2]. Using amperometric end-point detection the bromometric titration yields excellent results, but, according to our experience, it is not amenable to potentiometric e.p. indication. The iodometric titration can be performed with potentiometric, amperometric, or visual e.p. indication, and it is applicable in the presence of substances (e.g., many organic compounds) which would interfere with a bromometric titration.

EXPERIMENTAL

The optimum solution conditions for the coulometric iodometric titration of tripositive antimony are, of course, the same as for titration in the classical manner; in particular, the pH of the solution must be between about 7 and 9, and a complexing agent (e.g., tartrate ion) must be present to prevent hydrolytic precipitation of the antimony. In the coulometric titration of arsenic RAMSEY, FARRINGTON AND SWIFT[3] observed that removal of dissolved oxygen was necessary, but we found that this was unnecessary in the titration of antimony.

The supporting electrolyte consisted of a $0.1 M$ phosphate buffer of pH $= 8$ containing $0.1 M$ potassium iodide, and $0.025 M$ potassium tartrate.

The titration cell (70 ml weighing bottle) was similar to that described by MYERS AND SWIFT[9], except that magnetic stirring was used and the generator cathode (platinum wire coil) was isolated from the test solution by enclosure in a glass tube with a sintered glass bottom. The generator anode was perforated platinum foil with an area (one side) of 8.4 cm². The amperometric indicator electrodes were platinum foil with an area of 1.6 cm² each. For potentiometric e.p. detection one of these electrodes was used as indicator electrode in combination with a saturated calomel reference electrode.

The constant ($\pm$ 0.01%) electrolysis current was supplied by the regulator previously described[10], and was selected with respect to the quantity of antimony to provide titration times in the 100-500 sec range. Time was measured with a Standard Electric Time Co. Model S-10 clock (1000 sec range and $\pm$ 0.01 sec reading error), driven by the local public utility power supply whose short term frequency variation was within $\pm$0.15%.

Known quantities of antimony were taken in the form of a standard potassium antimonyl tartrate solution, whose titer was established by iodometric titration in the ordinary way. Blank titrations with the supporting electrolyte alone were performed at each current level, and the resulting small correction was deducted from the observed titration time.

Performance data

Table I summarizes the results of titrations of 6η μg to 10 mg quantities of antimony in a volume of about 5η ml, using both amperometric and potentiometric end-point detection.

TABLE I

PERFORMANCE DATA

The supporting electrolyte was a 0.1M phosphate buffer of pH = 8, containing 0.1M potassium iodide, and 0.025M potassium tartrate, and the volume was *ca.* 50 ml. Electrolysis currents ranging from 2 to 33 mA were used to yield titration times between 100 and 500 sec.

No. of trials	Sb taken μg	Sb found (av.) μg	Average deviation μg	Average error %	End-point detection
5	65.55	66.00	± 1.6	+0.7	Amp.
7	327.8	327.6	± 1.0	—0.1	,,
3	1311	1311	± 1.0	0.0	,,
4	10,450	10,530	±10	+0.8	,,
4	65.55	65.14	± 0.7	—0.6	Potent.
4	327.8	328.3	± 0.2	+0.2	,,
3	1311	1311	± 1.3	0.0	,,
4	7768	7774	± 3.0	+0.1	,,

Because the iodine-iodide couple functions with very little overpotential in either direction, whereas the antimonous-antimonic couple behaves quite irreversible, the amperometric indicator current remains very small up to the equivalence point and then increases rapidly due to depolarization of the indicator cathode by the excess iodine. Fig. 1 shows a typical amperometric titration curve. In practice generation of iodine is continued far enough to define the slope of the titration line beyond
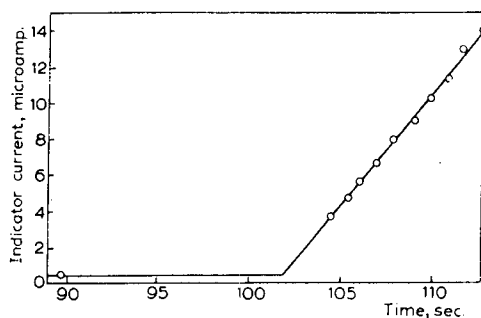

Fig. 1. Amperometric end-point detection in coulometric titration of 327.8 micrograms of antimony with a generating current of 5.151 mA, and with 0.150 V impressed across the two platinum indicator electrodes.
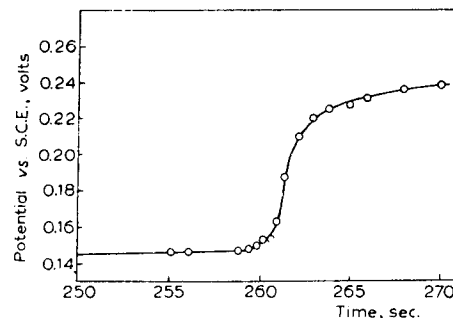
Fig. 2. Potentiometric end-point indication in coulometric titration of 1.311 mg of antimony with a generation current of 7.961 mA.

the e.p., and the latter is then determined by back extrapolation. Provided it is kept constant the voltage applied across the indicator electrodes is not very critical. A value of 150 mV was used, but equally satisfactory results doubtless could be obtained at other values in the 50 to 300 mV range.

Potentiometric e.p. detection followed the usual practice[2], and a typical titration curve is shown in Fig. 2. The titration curve displays the assymetry expected from

the assymetrical nature of the iodine-iodide half-reaction. Steady potentials are established very quickly, so that the titration can be completed rapidly simply by interrupting the generating current when the end-point potential ($+0.18$ V $vs.$ S.C.E.) is reached.

The data in Table I show that the precision (average deviation) and accuracy (average error) of both e.p. detection techniques are comparable with the intermediate quantities of antimony. However with both relatively small ($<$ 100 microgram) and relatively large ($>$ 5000 microgram) amounts of antimony potentiometric detection tends to be both more precise and more accurate than amperometric detection. Potentiometric detection is also more convenient because it permits direct titration to a reproducible signal (e.p. potential) and does not require graphical interpretation. Titration with potentiometric detection may be performed automatically with the instrument previously described[11].

A number of titrations were made to a visual starch-iodine end-point. Although fairly satisfactory (error $\pm$ 0.5%) with macro amounts of antimony (8 mg) the precision of visual indication is much poorer than the electrometric detection techniques with small quantities of antimony.

SUMMARY

A method is described for the coulometric titration of tripositive antimony with electrogenerated iodine, in a buffered solution of pH 8. The end-point can be detected either amperometrically, potentiometrically, or (less precisely) visually with starch indicator. Quantities of antimony between 0.06 and 10 mg are titratable with an average error of 0.001 to 0.01 mg.

RÉSUMÉ

Une méthode est décrite pour le dosage coulométrique de l'antimoine(III) au moyen de l'iode formé au cours du titrage, en solution tampon de pH 8. Le point final peut être déterminé soit ampérométriquement, soit potentiométriquement ou (de façon moins précise) visuellement avec l'amidon comme indicateur. Des quantités d'antimoine comprises entre 0.06 et 10 mg peuvent être titrées avec une erreur moyenne de 0.001 à 0.01 mg.

ZUSAMMENFASSUNG

Eine Methode zur coulometrischen Bestimmung von dreiwertigem Antimon mit elektrisch gebildetem Jod in einer Pufferlösung von pH 8 wird beschrieben. Der Endpunkt kann amperometrisch, potentiometrisch oder (weniger genau) optisch mit Stärke als Indikator bestimmt werden. Antimonmengen von 0.06 bis 10 mg können mit einem mittleren Fehler von 0.001 bis 0.01 mg titriert werden.

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