

Determination of Sb(V), As(V), Os(VIII), Ir(IV) & Tl(III) with iron(II) using thiazine dyes as redox indicators

K Vijaya Raju*, G Madhu Gautam & V Rama Rao

Department of Engineering Chemistry, College of Engineering,
Andhra University, Visakhapatnam 530 003

Received 20 March 1989; accepted 1 June 1989

The use of thiazine dyes as redox indicators in the determination of antimony(V), arsenic(V), osmium(VIII) iridium(IV) and thallium(III) with iron(II) in phosphoric acid medium has been investigated. The methods of determination of arsenic in some organic arsenicals and analysis of binary mixtures containing Sb(V)-As(V) employing thiazine dyes as indicators have also been suggested.

Methylene blue or thionine is the only thiazine dye that has been reported as a redox indicator in the determination of antimony(V)¹, arsenic(V)², osmium(VIII)³, iridium(IV)³ and thallium(III)⁴ with iron(II) in phosphoric acid medium. Herein we report the use of seven thiazine dyes as redox indicators in the titration of these metal ions with iron(II) in phosphoric acid medium. The methods developed have been applied to the estimation of arsenic in some organic arsenicals and for the analysis of binary Sb(V)-As(V) mixture.

Experimental

Approximately 0.025M solution of antimony(V) [from BDH, LR, sodium pyroantimonate], 0.025M solution of arsenic(V) [from E Merck, proanalysis sodium arsenate], 0.005M solution of thallium(III) [from BDH, LR, thallium(I) carbonate], 0.0025M solution of osmium(VIII) [from Johnson Matthey, osmium tetroxide], 0.01M solution of iridium(IV) [from Johnson Matthey, sodium hexachloroiridate], 0.05M and 0.01M solutions of iron(II) [from BDH, AR, ammonium iron(II) sulphate] were prepared and standardised.

Aqueous solutions (0.1g per 100 ml) of the dyes (Gurr & Co, England), Azure A (AZR A) [C.I.No:52005], Azure B (AZR B) [C.I.No:52010], Azure C (AZR C) [C.I.No:52002], Toluidine blue (TDB) [C.I.No:52040], New methylene blue (NMB) [C.I.No:52030], Thiazine blue (TAB) [C.I.No:52025] and Azure-II-eosine (AZR-II-ES) were prepared.

Hydrobromic acid (48% Riedel, distilled at

126°C), and AR grade phosphoric and hydrochloric acids were used.

General procedure

To an aliquot (2-10 ml) of the metal ion solution, enough orthophosphoric acid was added to give the required acid concentration [11-12M in Sb(V) and Tl(III); 10-11M in As(V) and 9-10M in Os(VIII) and Ir(IV)] near the equivalence point. After adding the indicator solution (0.2-0.3 ml), the reaction mixture was titrated with stirring against 0.01M iron(II) [0.05M for Sb(V) and As(V)] under CO₂ blanket. The colour change at the end point was observed to be green to pale yellow for Sb(V) and As(V) while it was from blue to colourless for the rest of the metal ions. An indicator correction of 0.10 ml of iron (II) was necessary in the titrations with 0.01M iron (II). The osmium(VIII) solution was taken in phosphoric acid, cooled in ice-water and titrated at 20-25°C because of loss due to volatilisation at higher temperature ($\geq 28^\circ\text{C}$). In the determination of antimony(V) and arsenic(V) it was necessary for the reaction medium to be about 2M in hydrochloric acid¹ and 1.5M in hydrobromic acid², respectively, in addition to (10-11M) phosphoric acid.

Determination of arsenic content in organic arsenicals

To known amounts (0.5-1.0g) of phenylarsonic acid (PAA) or p-aminobenzenearsonic acid (p-ABAA), dried at 100°C, were added sulphuric (15-20ml) and nitric acids (5-8ml) and the mixture slowly heated⁵, and then treated with 30% H₂O₂ (5-10ml) as described⁵. The reaction mixture was cooled, diluted to a known volume (100ml) and a fraction (10ml) was titrated iodometrically⁵ (standard method). Another aliquot (10ml) was analysed according to the present method and the results were comparable: arsenic content found by the standard method 36.92% in PAA and 34.34% in p-ABAA; when arsenic content obtained by the present method: 36.74%-37.10% in PAA and 34.17%-34.55% in p-ABAA.

Sequential determination of arsenic(V) and antimony(V) in a mixture

Several synthetic mixtures containing different ratios of both antimony(V) and arsenic(V) were prepared. An aliquot (10ml) of each mixture was titrated with iron(II), following the procedure

Table 1—Determination of metal ions with iron(II) using thiazine dyes as indicators

Metal ion	Range of metal ion determined, mg	Transition potential (N.H.E)*, mV \pm 5						
		AZR A	AZR B	AZR C	AZR-II-ES	TDB	TAB	NMB
Sb(V)	8-30	461	466	457	452	456	@	502
As(V)	4-18	446	436	440	450	438	430	445
Os(VIII)	1- 5	492	504	490	496	485	@	504
Ir(IV)	4-20	520	550	525	535	540	528	534
Tl(III)	2-10	518	516	511	512	515	501	518

*(N.H.E.) Normal Hydrogen Electrode

@Not found suitable

presently described for arsenic(V) [As(V) and Sb(V) get reduced to As(III) and Sb(III) respectively]. This titre corresponded to the sum of antimony(V) and arsenic(V) present in the mixture. A similar aliquot was taken in a mercury reductor⁶ (3-4M HCl medium) and the antimony(V) content determined by titrating the antimony(III) formed in the reductor against potassium bromate⁶. Antimony(V) and arsenic(V) in the range 30-120 mg and 18-70mg respectively (present in a total volume of 50ml) were determined with an accuracy of $\pm 0.6\%$.

The range of each metal ion determined is given in Table 1. The transition potential of each indicator, determined adopting the method of Belcher *et al.*⁷, have also been included in Table 1. The colour transitions of the indicators are sharp and reversible at the end-point, which correspond to the complete reduction of Sb(V), As(V), Os(VIII), Ir(IV) and Tl(III) to Sb(III), As(III), Os(IV), Ir(III) and Tl(I) respectively, while the indicators are reduced to their corresponding leuco-bases. The conditional redox potentials of the metal ion couples in 9-12M phosphoric acid medium (range used in these titrations) reported by earlier workers^{1-3,8}, are in the range of 0.74-1.10V while that of iron(III)/iron(II) couple determined by Rao and Sagi⁹ is in the range 0.400-0.390V. Therefore, any redox indicator having a transition potential in the range 0.55-0.75V may function satisfactorily in these titrations. As the standard potentials of most of the thiazine group of dyes are reported¹⁰ to be about 0.55V, the use of these indicators have been investigated in these titrations. The error in this method with each indicator has been found not to exceed $\pm 0.50\%$. The precision¹¹ has been determined for six replicate titrations of 15.50, 9.36, 2.38, 9.60 and 5.10mg of Sb(V), As(V), Os(VIII), Ir(IV) and Tl(III) respectively and the relative standard deviations are found to be in the range of 0.3-0.4%.

The advantages of the present dyes over the

earlier ones are their easy availability, more solubility in cold water and greater stability (about a year) of their aqueous solutions. Further, the detection of the end-point in most of the titrations, from blue to colourless, is facile.

In these titrations, chloride and bromide ions are found to catalyse the reductions of antimony(V) and arsenic(V). Even a large concentration of chloride ion is unsatisfactory for rapid reduction of arsenic(V), hence bromide ion (as HBr) is employed as a catalyst.

Large amounts of Mn(II), Pb(II), Sn(IV), Pd(II), Cl^- [except Cl^- in the determination of Tl(III)], SO_4^{2-} , CH_3COO^- and ClO_4^- ions do not interfere. The colours of Cr(III), Ni(II) and Co(II) do not interfere when less than 0.8, 4 and 2mg of these ions respectively are present per ml of titration mixture. W(VI) gives a white precipitate but does not interfere. NO_3^- , Cu(II), Pd(II), Pt(IV) and Ru(IV) and the colour of Ru(III) interferes.

Acknowledgement

The authors are grateful to Prof N Krishna Murthy for his encouragement.

References

- Dikshitulu L S A & Raju K V, *J Indian chem Soc*, 55 (1978) 346.
- Dikshitulu L S A & Raju K V, *Indian J Chem*, 16A (1978) 978.
- Dikshitulu L S A, Raju K V & Satyanarayana D, *J Indian chem Soc*, (1981) 415.
- Sagi S R, Ramana K V & Prakasa Raju G S, *Z Anal Chem*, 272 (1974) 208.
- The United States Pharmacopeia*, 18th Revision, 1970, 965.
- McCay L W, *Ind Eng Chem Anal Ed*, 5 (1933) 1.
- Belcher R, Nutton A & Stephen W I, *J chem Soc*, (1952) 3857.
- Sagi S R, Prakasa Raju G S & Ramana K V, *Talanta*, 22 (1975) 93.
- Rao G G & Sagi S R, *Talanta*, 9 (1962) 715.
- Bishop E, *Indicators*, (1st Edn, Pergamon Press, Oxford) 1972, 506-9.
- Dean R B & Dixon W J, *Anal Chem*, 23 (1951) 634.