confirmed as I-5, II-5, II-7-trihydroxy-I-7, I-4', II-4'-tri-*O*-methyl [I-3', II-8]biflavone by comparison of ^{1}H nmr data of its acetate and methyl ether with those of the authentic samples.

The dried and powdered leaves of *T. gigantea* on similar treatment led to the isolation and characterisation of the same biflavones, *viz.* amentoflavone, I-7-mono-*O*-methylamentoflavone, hinokiflavone, I-7, II-7-di-*O*-methylamentoflavone, I-7, I-4', II-4'-tri-*O*-methylamentoflavone. These compounds were identified by m.p., m.m.p., R_f, characteristic fluorescence in uv light, ^{1}H nmr and finally by comparison with reference samples.

References

1. T. Sawada, *J. Pharm. Soc. Jpn.*, 1958, **78**, 1023.
2. L. Horhammer, H. Wagner and H. Reinhardt, *Naturwissenschaften*, 1965, **52**, 161.
3. H. Mivra and N. Kawano, *J. Pharm. Soc. Jpn.*, 1968, **88**, 1489.
4. N. Ilyas, M. Ilyas, W. Rahman, M. Okigawa and N. Kawano, *Phytochemistry*, 1978, **17**, 987.
5. W. Baker, A. C. M. Finch, W. D. Ollis and K W. Robinson, *J. Chem. Soc.*, 1963, 1477.

Amperometric Determination of Trace Amounts of Gallium(III), Indium(III) and Thallium(I) using Xylenol Orange

RIYAZ AHMAD and K. S. PITRE*

Department of Chemistry, University of Sagar, Sagar-470 003

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IN continuation of the previous work[1-3] on the amperometric determination of trace amounts of rare earths and some transition elements using xylenol orange, the present paper deals with the use of the same reagent for the trace determination of Ga^{III}, In^{III} and Tl^{I}. The titration procedure has been supplemented by spectral studies.

Experimental

All the chemicals were of AnalaR grade. Solutions of Ga^{III}, In^{III} and Tl^{I} were prepared by dissolving metal nitrates in double-distilled water and standardised[4]. The solution of xylenol orange was prepared by dissolving a requisite quantity of the reagent in double-distilled water. Amperometric titrations were performed on a manually operated polarograph with a multiflex galvanometer (sensitivity 8.1×10^{-9} A/div) used to measure the current. A d.m.e. and a saturated calomel electrode were used as an indicator and reference electrode, respectively. The capillary used for the d.m e. had a m value of 2.373 3 mgs^{-1}, at a drop time of 3.0 s in air-free 1 *M* KCl at 41 cm effective height of mercury column ($m^{2/3}\,t^{1/6}=2.316\ mg^{2/3}\,s^{-1/2}$). The amperometric titrations were performed at $70\pm1°$, maintained on a thermostat. Below this temperature the polarogram of xylenol orange was not well defined and the diffusion current was not proportional to the xylenol orange concentration. A Elico LI-120 digital pH meter was used to measure pH.

Voltammogram of xylenol orange: Xylenol orange gave a well defined two-step reduction wave[5] in 0.3 *M* KCl, pH = 4.0+0.02, μ=0.3 and at $70\pm1°$. The polarograms of xylenol orange at its different concentrations were recorded and it was observed that the diffusion current for the second wave is proportional to its concentration. The plateau potential for the second step is at −1.10 V vs S.C.E.

Procedure for amperometric titrations: Solutions containing known amounts of xylenol orange in 0.3 *M* KCl as supporting electrolyte were prepared and pH of the solutions was adjusted to 4.0 ± 0.02 using acetate buffer. The temperature of each set was maintained at $70\pm1°$ in a thermostat during the course of pH measurements and amperometric titrations. The plateau potential, −1.10 V vs S.C.E., was fixed on a potentiometer. Standard solution of the metal ions were added dropwise from a semimicro burette. The current was noted on a multiflax galvanometer.

TABLE 1—AMPEROMETRIC DETERMINATION OF Ga^{III}, In^{III} AND Tl^{I} WITH XYLENOL ORANGE

Plateau potential = −1.10 V vs S.C.E., μ=0.3 (KCl), pH = 4.0+0 02, Temp. = $70\pm1°$

Concn. ×10⁴	Ga^{III} (mg) Taken/ (Found)	% Error	In^{III} (mg) Taken/ (Found)	% Error	Tl^{I} (mg) Taken/ (Found)	% Error
1.0	0 0697 (0.0696)	−0.15	0.1148 (0.1140)	−0.73	0.2043 (0.2058)	+0.73
2.5	0.1742 (0.1754)	+0.68	0.2870 (0.2882)	+0.41	0.5107 (0.5119)	+0.23
5.0	0.3485 (0.3440)	−1.29	0.5440 (0.5470)	+0.55	1.0215 (1.0180)	−0.34
7.5	0.5127 (0.5139)	+0.23	0.8610 (0.8638)	+0.32	1.5311 (1.5350)	+0.25
10.0	0.6972 (0.6951)	−0.31	1.1480 (1.1468)	−0.10	2.0437 (2.0390)	−0.23
15.0	1.0457 (1.0478)	+0.20	1.7220 (1.7243)	+0.13	3.0652 (3.0601)	−0.16

Results and Discussion

On ploting galvanometer deflection, after necessary volume correction, against titrant volume a L-shaped curve was obtained The end-point indicated metal to xylenol orange ratio of 1 : 1 which was in good agreement with the results reported in the literature[6,7] and with results of spectrophotometric study. Results are presented in Table 1.

Effect of diverse ions : The titrations were not hampered by the presence of a hundred-fold excess ofthe following ions : NH_4^+, Na^I, K^{II}, Ag^I, Mg^{II}, Ba^{II}, Mo^{VI}, chloride, chlorate, nitrate, acetate and sulphate. Small amounts of Ni^{II}, Cu^{II}, Cd^{II}, Fe^{III}, Sb^{III}, Pb^I, carbonate, phosphate and some associated metal ions and rare earth ions seriously interfered.

The results (Table 1) reveal that xylenol orange is a good amperometric reagent for the trace determination of each of Ga^{III}, In^{III} and Tl^I. Amounts as low as 0.0600 mg/10 ml of Ga^{III}, 0.1142 mg/10 ml of In^{III} and 0.2040 mg/10 ml of Tl^I could be successfully determined by this procedure with an error of less than $\pm 1.30\%$.

References

1. S. C Lavale and K. S. Pitre, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 341.
2. S. C. Lavale and K. S Pitre, *Madhya Bharti, J. Sagar Univ.*, 1980, **25-28** 53.
3. S. C. Lavale and K. S. Pitre, *Proc. Natl. Acad. Sci., India Sect A*, 1982, **52**, 351.
4. F. J. Welcher, 'The Analytical Use of Ethylenediaminetetraacetic Acid", Van Nostrand, New York, 1957, pp. 174-81.
5. I. P. Saraswat and C. L. Sharma, *Indian J. Chem., Sect. A*, 1980, **19**, 961.
6. R. N. Nayan, *Indian J. Chem , Sect. A*, 1981, **28**, 382.
7. K. N. Munshi and A. K. Dey, *Mikrochim. Acta*, 1968, **5**, 1059.