Amperometric Determinations of Metals with Chloramine T

By G. S. DESHMUKH and M. C. ESHWAR*

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Erdey and co-workers[1] reported the application of ascorbic acid for direct and indirect determination of vanadium(V) using variamine blue as indicator. An ascorbimetric method[2] was also investigated by Erdey for the determination of cerium(IV) and chromium(VI). Various workers[3-5] found the reduction of pentavalent vanadium by arsenous oxide as too slow, and the reaction was therefore catalysed by iodide :[5] Analytical determination of Ce^{4+} was carried out with arsenous oxide using osmium tetroxide or iodine monochloride as catalyst and ferroin as indicator. Lang[8] studied the reduction of chromic acid with H_3AsO_3. Various workers[9-11] investigated the reduction of vanadium(V) to vanadium(IV) by hydrazine in sulfuric acid. Bray[11] and Cuy discarded the reaction for analytical determination, due to the occurrence of a partial side reaction resulting in the formation of ammonia and hydrazoic acid. Kolthoff[12] inferred that the oxidation of hydrazine proceeds smoothly to nitrogen and water in presence of sufficient concentration of hydrochloric acid. Benrath and Ruland[13] studied the oxidation of hydrazine by ceric sulfate. A review of the literature however, revealed that the reduction of Cr^{6+} with hydrazine has not been attempted.

Earlier results from these laboratories reported the utility of chloramine T in the oxidation of ascorbic acid,[14] arsenious oxide[16] and hydrazine sulfate[15] amperometrically at the rotating platinum wire micro-electrode. Following this, an investigation on the possibility of reducing V^{5+}, Ce^{4+} and Cr^{6+} by the

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* Present address: Planning & Development Division, Fertiliser Corporation of India Ltd., Sindri.

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above reductants, and titrating the excess reductant with chloramine T was taken up.

Experimental

Reagents and Apparatus. — Stock solution of vanadium(V) was prepared by dissolving an accurately weighed amount of vanadium pentoxide (E. Merck) in sodium carbonate (AnalaR) and the solution was made slightly acidic with hydrochloric acid. The vanadium content of this solution was checked by the method of Willard and Young.[17] Ceric sulfate solution was obtained by the usual method and the strength of this solution was determined with a standard solution of ferrous ammonium sulfate. A decinormal solution of potassium dichromate was prepared from a pure E. Merck (G. R.) sample. Approximately decinormal solutions of ascorbic acid and hydrazine sulfate were obtained from pure samples, while that of arsenious oxide was prepared as suggested by Pierce and Haenisch[18] and standardised amperometrically with chloramine T.[14-16]

A solution of chloramine T, approximately N/10, was prepared from a pure sample and standardised iodometrically with sodium thiosulfate. Iodine monochloride solution was 0.005 M. A sodium citrate-citric acid buffer (pH ~5.8), prepared by mixing 3 vol. of 0.5 M sodium citrate, 1 vol. of 0.5 M citric acid and 1 vol. of water, was used to control the pH of the reaction mixture. A simple form of amperometric unit, with an impressed potential of +0.3 volt vs. S. C. E., was used.

Determination of Vanadium

The reduction of V^{5+} to V^{4+} with hydrazine sulfate was found to be smooth, resulting in the formation of nitrogen and water. The possibility of the side reaction reported[10,11] was overcome by using hydrochloric acid instead of sulfuric acid, for acidifying the vanadium solution. Ascorbic acid also was found to reduce V^{5+} to V^{4+} quantitatively, with the formation of dehydroascorbic acid and water. In strongly acidic solutions, the reduction of vanadium(V) by arsenous oxide required more than 24 hr. for completion. However, iodine monochloride was found to catalyse the reaction, and it was also observed that the reaction was accelerated with an increase in the concentration of the catalyst. It was seen that the reaction required 10~15 min. for completion, when 1.0 ml. of iodine monochloride (0.005 M) was added. Accordingly, all the experiments with arsenous oxide were carried out using 1.0 ml. iodine monochloride as catalyst. For titration of excess hydrazine sulfate, 0.25 ml. of iodine monochloride was added as catalyst. The amount of iodine monochloride added to catalyse the reduction of vanadate by arsenous oxide, also served for titration of excess arsenous oxide. The reduction is found to be quantitative with each reductant under the above operating conditions according to:

$$2VO_3^- + C_6H_8O_6 + 6H^+ \rightarrow 2VO^{2+} + C_6H_6O_6 + 4H_2O \quad (1)$$

$$4VO_3^- + As_2O_3 + 12H^+ \rightarrow 4VO^{2+} + As_2O_5 + 6H_2O \quad (2)$$

$$4VO_3^- + N_2H_4 + 12H^+ \rightarrow 4VO^{2+} + N_2 + 8H_2O \quad (3)$$

$$\left.\begin{array}{l}\text{Hence, 1.0 ml. of}\\ \quad NC_6H_8O_6\text{, or}\\ \quad NAs_2O_3\text{, or}\\ \quad NN_2H_4\cdot H_2SO_4\end{array}\right\}\equiv 0.05094\text{ g. of vanadium}$$

Determination of Cerium

Tetravalent cerium was reduced quantitatively to trivalent state by ascorbic acid with the formation of dehydroascorbic acid and water, whereas the reduction with arsenous oxide was rather slow. The latter reaction was found to be accelerated by the addition of 0.25 ml. (5 drops) of iodine monochloride (0.005 M), which also served for titration of excess arsenous oxide with chloramine T. The procedure with hydrazine under similar conditions presented certain difficulties, detrimental to its utility as an analytical tool and could not therefore be pursued at the present stage. Ascorbic acid and arsenious oxide were, however, suitable for the quantitative determination of cerium.

$$2Ce(SO_4)_2 + C_6H_8O_6 \rightarrow Ce_2(SO_4)_3 + C_6H_6O_6 + H_2SO_4 \quad (4)$$

$$4Ce(SO_4)_2 + As_2O_3 + 2H_2O \rightarrow 2Ce_2(SO_4)_3 + As_2O_5 + H_2SO_4 \quad (5)$$

$$\left.\begin{array}{l}\text{Hence, 1.0 ml. of}\\ \quad NC_6H_8O_6\text{, or}\\ \quad NAs_2O_3\end{array}\right\}\equiv 0.1401\text{ g. of cerium}$$

Determination of Chromium

Reduction of Cr^{6+} to Cr^{3+} was complete with all the three reductants viz., ascorbic acid, arsenous oxide and hydrazine sulfate. The reaction products presumably are dehydroascorbic acid, arsenic pentoxide and nitrogen respectively. Whereas the titration of excess ascorbic acid was carried out in presence of citrate buffer only, that of excess arsenite and

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[17] H. H. Willard and P. Young, *Ind. Eng. Chem., Anal. Ed.*, **6**, 48 (1934).

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TABLE I. DETERMINATION OF VANADIUM

With $C_6H_8O_6$			With As_2O_3			With $N_2H_4 \cdot H_2SO_4$		
Amount of V			Amount of V			Amount of V		
Taken mg.	Found mg.	Error %	Taken mg.	Found mg.	Error %	Taken mg.	Found mg.	Error %
5.266	5.257	−0.17	5.098	5.126	+0.55	2.463	2.477	+0.57
3.949	3.944	−0.13	4.078	4.093	+0.37	2.155	2.138	−0.79
2.633	2.646	+0.49	3.059	3.068	+0.29	1.847	1.842	−0.27
1.975	1.955	−1.01	2.549	2.565	+0.63	1.478	1.489	+0.74
1.317	1.313	−0.30	2.039	2.053	+0.69	1.232	1.217	−1.22
1.054	1.055	+0.095	1.529	1.527	−0.13	1.109	1.119	+0.90

TABLE II. DETERMINATION OF CERIUM

With $C_6H_8O_6$			With As_2O_3		
Amount of Ce			Amount of Ce		
Taken mg.	Found mg.	Error %	Taken mg.	Found mg.	Error %
34.34	34.24	−0.29	17.17	17.14	−0.17
25.75	25.80	+0.19	12.88	12.88	Nil
17.17	17.10	−0.41	8.586	8.634	+0.56
12.87	12.83	−0.31	6.869	6.889	+0.29
8.584	8.592	+0.093	6.010	5.984	−0.43
6.868	6.926	+0.84	5.152	5.182	+0.58

TABLE III. DETERMINATION OF CHROMIUM

With $C_6H_8O_6$			With As_2O_3			With $N_2H_4 \cdot H_2SO_4$		
Amount of Cr			Amount of Cr			Amount of Cr		
Taken mg.	Found mg.	Error %	Taken mg.	Found mg.	Error %	Taken mg.	Found mg.	Error %
3.472	3.447	−0.72	3.472	3.485	+0.37	3.472	3.477	+0.14
2.604	2.622	+0.69	2.604	2.575	−1.11	2.604	2.610	+0.23
1.736	1.711	−1.44	1.736	1.738	+0.11	1.736	1.741	+0.29
1.519	1.526	+0.46	1.302	1.296	−0.46	1.302	1.304	+0.15
1.302	1.295	−0.54	1.040	1.037	−0.29	1.128	1.125	−0.27
1.042	1.054	+1.15	0.8680	0.8638	−0.48	0.9548	0.9468	−0.83

hydrazine required iodine monochloride to catalyse the oxidation. The quantitative reduction proceeds as follows:

$$K_2Cr_2O_7 + 3C_6H_8O_6 \rightarrow 2KCrO_2 + 3C_6H_6O_6 + 3H_2O \tag{6}$$

$$2K_2Cr_2O_7 + 3As_2O_3 \rightarrow 4KCrO_2 + 3As_2O_5 \tag{7}$$

$$2K_2Cr_2O_7 + 3N_2H_4 \rightarrow 4KCrO_2 + 3N_2 + 6H_2O \tag{8}$$

$$\left.\begin{array}{l}\text{Hence, 1.0 ml. of}\\ NC_6H_8O_6\text{, or}\\ NAs_2O_3\text{, or}\\ NN_2H_4 \cdot H_2SO_4\end{array}\right\} \equiv 0.01734\text{ g. of chromium}$$

Procedure.—An aliquot of VO_3^-, Ce^{4+} or $Cr_2O_7^{2-}$ solution was taken in a 150 ml. Pyrex beaker, to which an appropriate quantity of the reductant viz., ascorbic acid, arsenous oxide and hydrazine sulfate was added. One milliliter of iodine monochloride (0.005 M) was added for accelerating vanadium(V)-arsenic(III) reaction, and 0.25 ml. for that of cerium(IV)-arsenic(III) reaction. For titration of excess arsenous oxide in $Cr_2O_7^{2-}$ determination and of excess hydrazine sulfate (in VO_3^-, $Cr_2O_7^{2-}$ determinations), 0.25 ml. (5 drops) of iodine monochloride was added as catalyst. In each case, 10∼15 ml. of sodium citrate-citric acid buffer (pH ∼5.8) was introduced to maintain an overall pH of 4.3∼4.9. The contents were diluted approximately to 50 ml. and titrated amperometrically with chloramine T at a potential of +0.3 volt vs. S. C. E.

Observations are returned in 3 short tables.

Summary

An indirect procedure for the determination of V^{5+}, Ce^{4+} and Cr^{6+} is given. Three reductants, viz., ascorbic acid, arsenous oxide and hydrazine have been employed for reduction of each oxidant. Iodine monochloride

has been used as catalyst in the reduction of V^{5+} and Ce^{4+} by arsenous oxide. Reduction of Ce^{4+} with hydrazine presented certain difficulties and is not pursued at the present stage. The excess reductant in each case is determined amperometrically with chloramine T at the rotating platinum wire micro-electrode, and an impressed potential of +0.3 volt vs. S.C.E. The titrations are performed at a pH of 4.3~4.9, using citrate-citric acid buffer. For titration of excess arsenous oxide and $N_2H_4 \cdot H_2SO_4$, 0.25 ml. of iodine monochloride (0.005 M) has been employed as catalyst. The procedure, which is rapid and accurate, has been employed for determination of amounts up to 1.05 mg. vanadium, 5 mg. cerium and 0.86 mg. chromium.

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Division of Analytical Chemistry
Banaras Hindu University
Banaras, India