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Macro—and Microdetermination of Ascorbic Acid Using Potassium Permanganate as an Oxidant in Fluoride Medium

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An accurate and precise method is given for the determination of ascorbic acid by direct visual, potentiometric and amperometric titrations with permanganate as an oxidant in fluoride medium. Amounts of ascorbic acid down to 7.08 μg could be determined accurately under the optimum conditions.

AMONG the titrimetric methods that have been reported for the determination of ascorbic acid[1-10], potassium permanganate is the favourite reagent. However, the reaction between ascorbic acid and permanganate in acid medium is sluggish and the error obtained in the determination exceeded 2%[11]. Scanity of literature reveals no study on the reaction with permanganate in acid medium containing fluoride ions using visual and potentiometric titrations. Also, an amperometric end point has not been utilized for the microdetermination of ascorbic acid using the rotating Pt-electrode vs S.C.E. as reference at zero e.m.f. The present paper is aimed at finding the optimum conditions for such methods.

Experimental

Preparation of solutions : Potassium permanganate solutions were prepared[12] and standardized[13] as recommended. Ascorbic acid solutions were prepared by dissolving the AnalaR product in doubly distilled water and standardized as recommended[2]. Other solutions including 0.48*M* sodium fluoride, 5 *M* sulphuric acid and 0.25*M* cupric sulphate were prepared from the AnalaR chemicals in doubly distilled water.

Electrical equipments and titration procedures : The potentiometric[14] and the amperometric[15] titration assemblies and the titration procedures were the same as previously described.

Results and Discussion

Titration of ascorbic acid solutions was carried out under a variety of conditions including different acidity, fluoride ion concentration, cupric ion concentration, temperature and concentration of ascorbic acid, in order to find out the optimum conditions for a successful determination and for the following reaction to take place quantitatively according to the equation

$$MnO_4^- + 2C_6H_8O_6 + 2HF_2^- + 2H^+ \rightleftharpoons 2C_6H_6O_6 + MnF_4^- + 4H_2O$$

(a) *Determination of ascorbic acid at the milligram level (visual and potentiometric titrations) :*

It is clear from the results in Table 1, that good end points corresponding to oxidation of ascorbic acid to the dehydroascorbic acid whereby permanganate is reduced to manganic are obtained at acidities varying from 0.1 to 0.22*M* sulphuric acid and sodium fluoride content of 0.24 to 0.38*M*, both in the visual and potentiometric procedures. Under these conditions, the reaction takes place quantitatively between 25 and 40°. However in the visual titrations, cupric ions should be added in ratio of 1 : 1 to 1 : 5 (cupric ions : ascorbic acid), in order to conceal the pink colour of manganic fluoride which vitiates the end point and hence renders the latter distinct. However, a blank experiment was done and the volume of $KMnO_4$ consumed by Cu^{+2} ions was subtracted from the titrant.

In the potentiometric titration, the end point is not affected by the addition of Cu^{+2} ions and the end point is the same as in the absence of Cu^{+2} ions.

The role played by F^- ions is to stabilize the trivalent manganese through the formation of the stable MnF_4^- complex ; the reduction of permanganate will then be at the manganic step and not at the manganous as the MnF_4^- complex is more stable compared to the fluorocomplex of Mn^{+2}.[16]

At lower acidities (<0.06*M*, sulphuric), the solution gets turbid due to formation of insoluble oxides of manganese. On the other hand, at acidities higher than 0.25*M* sulphuric acid, primature end points are obtained due to partial formation of bivalent manganese.

TABLE 1—POTENTIOMETRIC AND VISUAL TITRATION OF ASCORBIC ACID WITH $KMnO_4$ IN PRESENCE OF 0.1*M* H_2SO_4 AND 0.24*M* NaF (total volume 100 ml)

Ascorbic Acid			$KMnO_4$ consumed		Theoretical end point (ml)	Error %	Inflection at end point (mV/0.1 ml of titrant)
Volume (ml)	Molarity (M)	Amounts (mg)	Volume (ml)	Molarity (M)			
			Potentiometric titration				
2	0.0005	0.1761	2.51	0.0002	2.50	0.40	160
5	0.0005	0.4403	6.24	0 0002	6.25	0.16	172
5	0.0042	3.6988	5.26	0.0020	5.25	0.19	198
5	0.0480	42.2714	6.01	0.0200	6.00	0.17	218
5*	0.0480	42.2714	5.96	0.0200	6.00	0.67	202
5**	0.0480	42.2714	6.03	0.0200	6.00	0.50	226
			Visual titration in presence of 5 ml 0.25M $CuSO_4$				
8	0.0042	5.9180	8.42	0.0020	8.40	0.24	
5	0.0480	42.2714	6.02	0.0200	6.00	0.33	
5***	0.0480	42.2714	6.05	0.0200	6.00	0.83	

* 0.2*M* H_2SO_4 ; ** 0.38*M* NaF ; *** No $CuSO_4$ added.

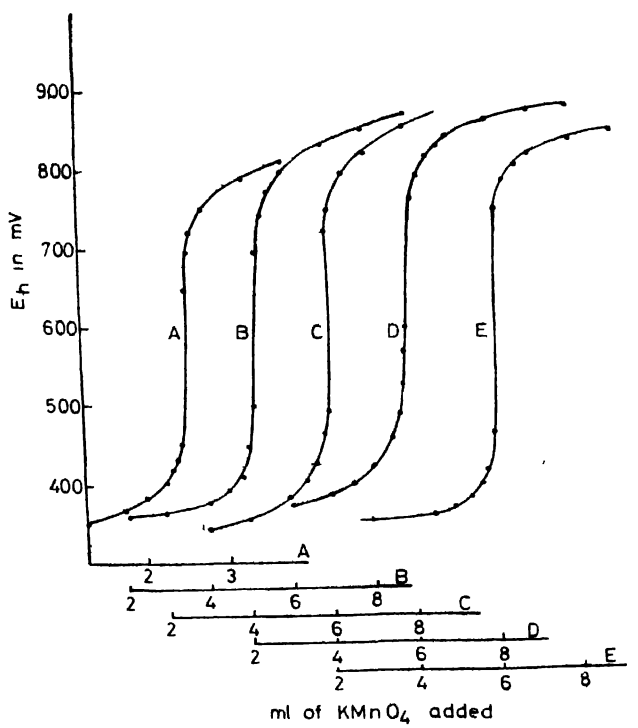

Fig. 1. Potentiometric titration of ascorbic acid with $KMnO_4$ (total volume 100 ml).
A—2 ml $5\times10^{-4}M$ ascorbic acid $2\times10^{-4}M$ $KMnO_4$; 0.1*M* H_2SO_4 ; 0.24*M* NaF.
B—5 ml $4.2\times10^{-3}M$ ascorbic ; $2\times10^{-3}M$ $KMnO_4$; 0.1*M* H_2SO_4 ; 0.24*M* NaF.
C—5 ml 0.0480*M* ascorbic ; 0.0200*M* $KMnO_4$; 0.1*M* H_2SO_4 ; 0.24*M* NaF.
D—5 ml 0.0480*M* ascorbic acid ; 0.0200*M* $KMnO_4$; 0.2*M* H_2SO_4 ; 0.24*M* NaF.
E—5 ml 0.0480*M* ascorbic acid ; 0.0200*M* $KMnO_4$; 0 1*M* H_2SO_4 ; 0.38*M* NaF.

Under the optimum conditions, amounts of ascorbic acid in the range 0.18-42.27 mg can be determined accurately with error less than 1%. The titration curves (Fig. 1), are smooth possessing one reasonable inflection at the equivalence point.

(b) *Determination of ascorbic acid at the microgram level (amperometric titration) :*

The results obtained on applying the amperometric method to determine ascorbic acid below the mg level under the optimum conditions of acidity and fluoride ion concentration, are listed in Table 2 and are represented graphically in Fig. 2. It is shown that amounts of ascorbic acid as low as 7.08 μg can be determined accurately and under the same optimum conditions for the potentiometric procedure.

TABLE 2—AMPEROMETRIC DETERMINATION OF ASCORBIC ACID

No.*	Ascorbic Acid (mg) Taken	Found	Error (%)	Standard** deviation (mg)	Total Vol. of solution (ml)
1.	0.0070	0.0071	0.28	0.0010	10
2.	0.0176	0.0175	0.28	0.0023	10
3.	0.0705	0.0710	0.67	0.0012	25
4.	0.4403	0.4387	0.36	0.0034	10
5.	0.8806	0.8810	0.04	0.0013	10
6.	0.8806	0.8792	0.16	0.0016	25
7.	1.7612	1.7619	0.04	0.0064	25
8.	4.4033	4.4226	0.43	0.0044	25
9.	17.613	17.6193	0.03	0.0134	25
10.	35.226	35.1315	0.26	0.0221	25

* Nos. (1-3), $2.01\times10^{-4}M$ ascorbic acid, $1.01\times10^{-4}M$ $KMnO_4$; (4-7) $5\times10^{-3}M$, $1.01\times10^{-4}M$ $KMnO_4$; (8-10) 0.0500*M* ascorbic acid, 0.0101*M* $KMnO_4$ determined in presence of 0.1*M* H_2SO_4 and 0.24*M* NaF.
**10 single titrations for each concentration.

The amperometric method is simple, rapid and advantageous than the potentiometric one especially

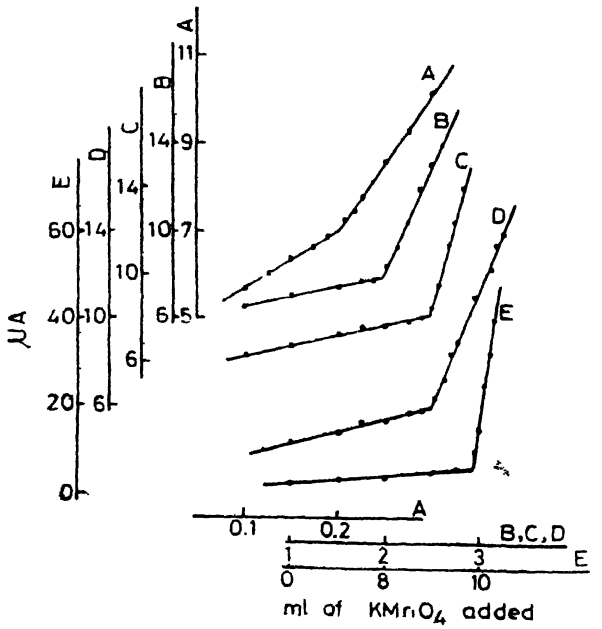

Fig. 2. Amperometric titration of ascorbic acid with $KMnO_4$ (total volume 25 ml)
A—0.2 ml $2.01\times10^{-4}M$ ascorbic acid ; $1.01\times10^{-4}M$ $KMnO_4$; $0.1M$ H_2SO_4 ; $0.24M$ NaF.
B—2 ml $2.01\times10^{-4}M$ ascorbic acid ; $1.01\times10^{-4}M$ $KMnO_4$; $0.1M$ H_2SO_4 „ $0.24M$ NaF.
C—1 ml $5\times10^{-3}M$ ascorbic acid ; $1.01\times10^{-3}M$ $KMnO_4$; $0.2M$ H_2SO_4 ; $0.24M$ NaF.
D—1 ml $5\times10^{-3}M$ ascorbic acid ; $1.01\times10^{-3}M$ $KMnO_4$; $0.1M$ H_2SO_4 ; $0.38M$ NaF.
E—4 ml $0.0500M$ ascorbic acid ; $0.0101M$ $KMnO_4$; $0.1M$ H_2SO_4 ; $0.24M$ NaF.

on dealing with lower concentrations of reductant since the minimum amount of ascorbic acid, determined by the potentiometric procedure is only 0.18 mg.

The equivalence point was reproducible. For quantitative determination of ascorbic acid, 10 samples between $5\times10^{-2}M$ and $2\times10^{-4}M$ concentrations of reductant were selected, and for every sample, the titration was repeated six times. The average error in the determination was well below ± 1%. The amperometric method can therefore be considered as a good analytical tool for determining microamounts of ascorbic acid.

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