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Amperometric Determination of V(V), Cr (III), Mn (VII), Cr (VI) and Fe (III) with 3–Mercaptopropanoic acid

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Amperometric determination of V(V), Cr(III), Mn (VII), Cr (VI) and Fe (III) is reported with the help of 3-mercaptopropanoic acid (MPSH). The fundamental reaction involved in case of the first two species is complexation while that in case of Mn (VII) is oxidation of MPSH; the last two species do not interact chemically with the acid and the new methods reported are based on the phenomenon of current compensation. Metal ion: MPSH ratio is 1 : 2 for V(V) and Cr (III), 1 : 4 for Cr (VI) and 1 : 0.66 for Fe (III); this ratio for Mn (VII) is 1 : 1 if the metal ion is used as titrant and 2 : 1 if MPSH is used in that capacity. Tolerance for diverse foreign ions has also been worked out.

INTRODUCTION

3-Mercaptopropanoic acid (MPSH) has been employed as a complexing agent for some metal ions[1–4] and also used as analytical reagent for amperometric determination of few[5,6]. The present work was undertaken with a view to further probe the latter potentiality of the acid.

EXPERIMENTAL

All the titrations were performed at DME (versus SCE) employing a manual polarograph (Toshniwal, India, model CLO2A). Only analytical grade chemicals and doubly distilled water were used. NH_4VO_3, $Cr(NO_3)_3.9H_2O$, $KMnO_4$, $K_2Cr_2O_7$ and $Fe_2(SO_4)_3{\cdot}xH_2O$ were used as source compounds of V(V), Cr (III), Mn (VII), Cr (VI) and Fe (III) respectively. V(V)[7], Cr (III)[8] and Fe (III)[9] solutions were standardized gravimetrically and Cr (VI) and Mn (VII) volumetrically.[9] MPSH solution was prepared afresh daily and standardized[10]. Amperometric determination of metal ion solution of any particular concentration was carried out atleast thrice. Purified nitrogen was employed for deaeration. Titration potentials for V(V) and Cr (III) were selected in the limiting region of the anodic wave of MPSH, and that for Mn (VII), in the limiting region of the first cathodic wave of the metal ion. Titration potentials for Cr (VI) and Fe (III) were common to the limiting regions of the cathodic wave of the respective metal ion as well as the anodic wave of MPSH; 0.0V for Fe (III) was selected to avoid addition of gelatin required to suppress a maximum present in the region of *ca.* 0.05V through −0.20V.

RESULTS AND DISCUSSION

MPSH is known to undergo reversible, one electron oxidation at DME in certain supporting electrolyte[5,6]. Anodic limiting region of the acid and cathodic limiting region of metal ions in different media of interest are mentioned in Table 1. all the conditions required for the amperometric determination of various metal ions as well as complete amperometric data have also been included in Table-1. It may be pointed out that the maximum percentage errors mentioned in this Table were encountered only for the minimum concentrations given there-in. In case of certain metal ions, even more dilute solutions (0.025 mM for Mn^{VIII} and Cr^{VI} and 0.05 mM for Fe^{III}) could be determined though with slightly higher error of *ca.* 4.0%; maximum concentration of any metal ion determined was 5.00 mM. It is apparent from the Table-1 that determination with MPSH as titrant is more successful for dilute solutions of Mn (VII) and Fe (III).

In the absence of any indication for any other type of chemical interaction, complexation has been presumed to be the basis of new methods for V (V) and Cr (III). It is noteworthy that a reference to the isolation of 1 : 3 Cr (III)–MPSH complex is already available in literature[11] and the formation of a lower species, here, is understandable in view of the fact that MPSH has to face stiff competition from the other ligand, Cl^-, present in the medium.

Amperometric titrations involving permangnate solution resulted in the discharge of its pink colour; brown precipitate (tested to be MnO_2) also appreared in the cell solution after the end point was crossed, if the concentration of the metal solution was not less than 1.00 mM. 1 : 1 Titrimetric molar ratio obtained when metal ion was employed as titrant, is proposed to be due to following redox reaction:

$$2C_3H_6O_2S + 2KMnO_4 \rightarrow C_3H_5O_2S - SO_2H_5C_3 + 2MnO_2 + 2KOH + O_2$$

Formation of the dimer of the type given in the equation has often been reported during oxidation of thio-acids[12–14]. Oxygen (reducible at DME) did not disturb the titration as whatever little amount was evolved after addition of each aliquot of titrant was bound to be expelled by the stream of nitrogen, passed into the solution before recording the current.

The titrimetric molar ratio obtained when MPSH was used as titrant was 2 : 1. It is proposed that the additional $KMnO_4$ used up in the reaction, initiated this time in presence of its excess, brought about the oxidation of the organic dimer formed in the 1 : 1 reaction:

TABLE 1
TITRATION CONDITIONS AND AMPEROMETRIC DATA

Metal	Medium	Cathodic limiting region of metal wave (–E)	Anodic limiting region of MPSH wave (–E)	Titration potential (–E)	Titrant	M : MPSH	Minimum concen. determined (mM)	Maximum percentage error (St. deviation)
V (V)	(i) 0.1M KCl	1.55–1.70	0.00–0.10	0.05	Metal	1 : 2	0.10	3.000 (0.004)
	(ii) 0.5M NH_4OH + 0.5M NH_4Cl	1.00–1.20* 1.35–1.75**	0.10–0.35	0.20	Metal	1 : 2	0.10	4.000 (0.003)
Cr (III)	0.05M NH_4OH + 0.05M NH_4Cl	1.55–1.67* 1.80–1.95**	0.00–0.30	0.20	Metal	1 : 2	0.10	3.000 (0.004)
Mn (VII)	0.1M K_2SO_4	0.00–1.60*	0.00–0.10	1.00	MPSH	2 : 1	0.05	2.000 (0.002)
		1.75–1.95**		1.00	Metal	1 : 1	0.10	2.000 (0.002)
Cr (VI)	1M NH_4OH + 1M NH_4Cl	0.40–1.30* 1.50–1.65**	0.15–0.42	0.40	MPSH	1 : 4	0.050	2.000 (0.002)
Fe (III)	0.1M NH_4Cl	>0.00–1.2	>0.00–0.15	0.00	MPSH	1 : 0.66	0.10	1.800 (0.002)
				0.00	Metal	1 : 066	0.10	2.000 (0.001)

*First wave
**Second wave.

$$C_3H_5O_2S\text{-}SO_2H_5C_3 + 2KMnO_4 + O_2 \text{ (from 1 : 1 reaction)} \rightarrow 2MnSO_4 + 2CH_3COOK + CH_3COOH$$

The free CH_3COOH shall be neutralized by the KOH formed in 1 : 1 reaction, and also the oxygen evolved in that reaction used up in 2 : 1 reaction before being expelled by the stream of nitrogen. MnO_2 (ppt.) appeared in this reaction also and Mn^{2+} and CH_3COO^- ions too were detected in the cell solution.

The determinations of Cr (VI) and Fe (III) did not entail any chemical interaction and were solely the consequence of current compensation phenomenon. This is indicated by the fact that titration could not even be initiated at potentials which fell in the limiting region of the metal or MPSH alone. Also the titrimetric ratio (1 : 4 for Cr (VI) and 1 : 0.66 for Fe (III)) was always the reverse of the ratio of id/c of the metal and MPSH which was found to be 6.440 : 1.610 for Cr (VI) and 1.650 : 2.500 for Fe (III) in respective media. The nature of the amperometric curves also, almost a straight line with insignificant change of slope at the null point falling on the residual current line, further substantiated the operation of current compensation phenomenon. Determination of Fe(III) could be carried out employing any of the species as titrant though in case of Cr (VI), use of the metal species in that capacity did not yield good results, and hence, this form of the titration is not recommended in this case. It may also be mentioned that the results obtained by the authors in case of Fe (III) were contrary to those reported by Fernando and Freiser[2], *i.e.* emergence of transient blue colour and oxidation of MPSH by Fe (III). It is just possible that at the dilutions involved and in the medium selected for amperometric determinations, the redox reaction did not take place.

Determination of Fe (II) and Fe (III) in a mixture

Fe (II) interfered seriously in the estimation of Fe (III) due to its complexation with MPSH[6]. However, 0.4 M ammonium sulphate acted as efficient masking agent for it and Fe (III) could be accurately determined even in presence of twenty fold excess of Fe (II). Based on this, an indirect method for estimating Fe (II) as well as Fe (III) content of any mixture solution was developed. In one experiment, Fe (III) content was determined as above. Then in a different experiment, total iron content was determined as Fe (III) or Fe (II) by oxidising[9] its Fe (II) content with HNO_3 (and removing the excess of HNO_3) or reducing its Fe (III) content with H_2S (and expelling the excess H_2S). A comparison of the two experiments yielded the amount of Fe (II) content. Mixture solutions containing both the species in the concentation range of 5.00 mM–0.25 mM could be analysed with the maximum percentage error of less than two.

Checking of interference of foreign ions and selectivity

Study of interference of foreign ions in the new amperometric methods was carried out for three concentrations of each metal species viz. 5.00 mM, 1.00 mM and 0.50 mM. Table 2 includes safe limits of foreign ions in the cell solution. Non-interfering species did not interfere even when present simultaneously in the cell solution. However, for these selectivity tests, the maximum concentration of each species taken was 0.25 mM to avoid supersaturation.

TABLE 2

SAFE LIMIT OF THE CONCENTRATION OF FOREIGN IONS IN THE CELL SOLUTION WITH RESPECT TO THE CONCENTRATION OF THE METAL SPECIES

Foreign ion	V (V)		Cr (III)	Mn (VII)	Cr (VI)	Fe (III)
Medium	0.1M KCl	0.5M NH_4OH + 0.5M NH_4Cl	0.05 NH_4OH + 0.05M NH_4Cl	0.1M K_2SO_4	1M NH_4OH + 1M NH_4Cl	0.1M NH_4Cl
NO_3^-	b	b	b	b	b	b
SO_4^{2-}	b	b	b	b	b	b
SCN^-	b	b	b	b	b	b
CH_3COO^-	b	b	b	b	b	b
WO_4^{2-}	b	b	1/10	b	b	1/5
Ox^{2-}	10t	b	b	b	b	5t
$S_2O_3^{2-}$	1/5	1/10	1/5	a	1/10	a
Mg (II)	b	b	b	b	b	b
Al (III)	b	b	b	b	b	b
Mn (II)	b	a	a	—	a	a
Cr (III)	b	a	—	1/10	a	b
Cr (IV)	a	a	a	a	–	a
Mn (VII)	a	a	a	—	a	a
Fe (II)	a	1/15	1/20	1/20	a	a
Fe (III)	a	a	a	a	a	—
Co (II)	b	a	a	1/10	a	a
Cu (II)	a	a	a	a	a	a
Cd (II)	1/5	1/10	1/10	1/15	a	b
Mo (VI)	a	a	a	a	1/5	b
Ni (II)	b	a	a	b	a	a
V (V)	—	—	1/10	1/10	a	a

a = Serious interference even when the concn. of foreign ion is 1/20 of the metal;
b = No interference even when the foreign ion is 20 times that of ion;
t = Times.

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