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ANALYTICAL APPLICATIONS FOR SEMI MICRO DETERMINATION OF SOME OXIDANTS. USING RAPID POTENTIOMETRIC METHOD

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SUMMARY

This investigation is an application of the method involving determination of H_3AsO_4, KIO_3, $KBrO_3$, $KMnO_4$, and $K_2S_2O_8$ as oxidants. The method is based on reduction of oxidants by hydrazine sulphate in different pHs, adding a measure excess of hydrazine to reduce the oxidant, then unreacted hydrazine oxidized by iodine dissolved in acceti acid. The liberated iodide was then potentiometrically titrated against Ag(I) using silver amalgam as the indicator electrode.

INTRODUCTION

Angeli(1) and others(2-8) all of whom obtained hydrogen azide by action of the salts of nitrous acid on hydrazine. Subsequently, alkyl nitrites were also found to react with hydrazine hydrate in alcoholic solution in the presence of alkali to give high yields of the alkali azide(3,9-12). Zaky(13) used peroxodisulfate as oxidant for determination of vanadium, chromium and manganese. Ismail(14) described a method for determination of some reductants. Issa and Zaky(15) determined a gold (III) using hydrazine as reductant.

EXPERIMENTAL METHODS

Deionized water was used. The chemicals were of the highest purity available.

0.0123M KIO_3, 0.0148M $KBrO_3$, 0.0157M $KMnO_4$, 0.0106M $K_2S_2O_8$, 0.0365M hydrazine sulphate, and 0.0442M $AgNO_3$ were prepared by dissolving the calculated amounts in requisite volume of water. 0.0158M H_3AsO_4 was prepared by dissolving it in least amount of

NaOH, then acidifye the solution. Iodine solution (3%) was prepared by dissolving the calculated amount of the previously sublimed solid substance in acetic acid (50%).

Apparatus:

The titration cell consists of a 150ml Pyrex beaker, a mechanical stirrer, a 5ml microburette (1 division X 0.02 ml), and a silver amalgam indicator electrode in conjunction with a reference saturated calomel electrode as the other half cell. The two electrodes were fitted to a Metrohm Herisau Potentiometer Model E 512.

Procedures:

To an aliquot portion of AsO_4^{3-}, IO_3^-, BrO_3^-, MnO_4^-, and $S_2O_8^{2-}$, add a measured excess of hydrazine, then adjust the acidity at pH = 6, 4, 5, 4, and 6 respectively for AsO_4^{3-}, IO_3^-, BrO_3^-, MnO_4^-, and $S_2O_8^{2-}$, then add excess of iodine solution, boil about 10 min. to ensure complete equilibrium and for expel iodine liberated in all cases, iodine and bromine in case of bromate. Back-titrate iodide set free with Ag(I) to obtain iodide equivalent oxidant.

RESULTS AND DISCUSSION

Tables 1 to 5 list the results of determination of AsO_4^{3-}, IO_3^-, BrO_3, MnO_4, and $S_2O_8^{2-}$ as estimated by the present method as well as the well-known conventional ones, which indicate that my adopted method is accurate and reliable. The end point potential breaks are quite sharp and large in magnitude as shown in the tables.

The quantitativnes of the redox reactions involving AsO_4^{3-}, IO_3^-, BrO_3^-, MnO_4^- and $S_2O_8^{2-}$ as oxidants and hydrazine as reductant, may be predicted by considering the standard reaction potentials of the half-reactions involved:

$$H_3AsO_4 + 2H^+ + 2e^- \longrightarrow HAsO_2 + 2H_2O \qquad E^\circ = +0.559\ V$$

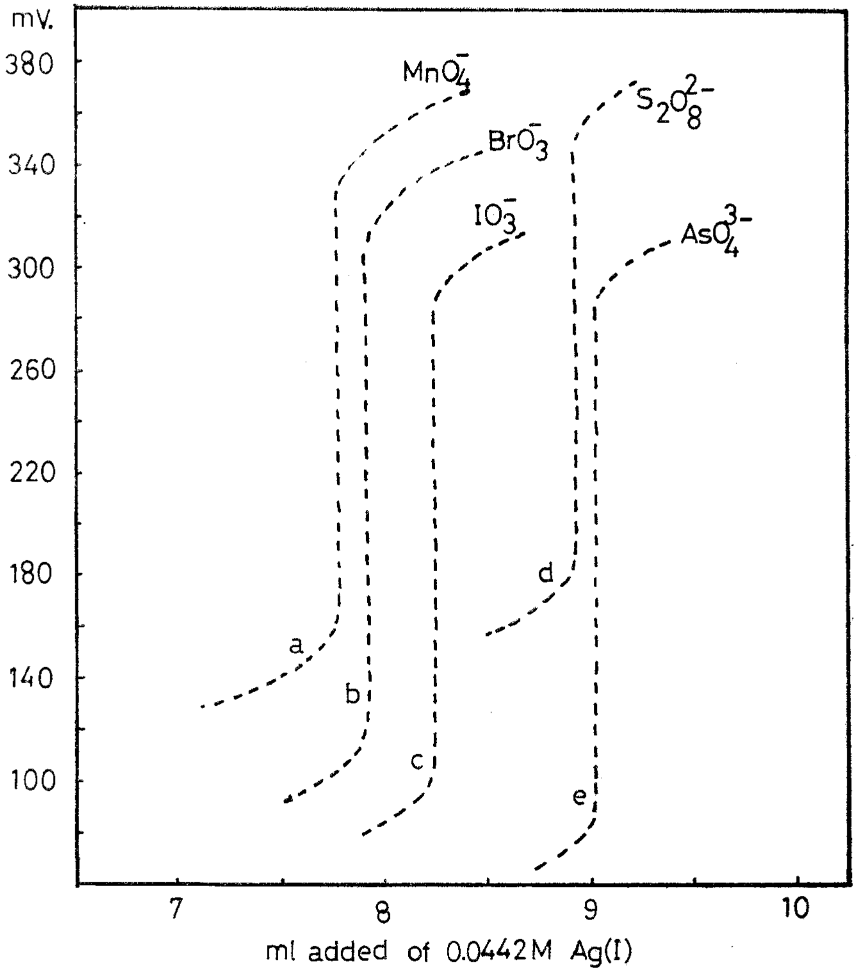
$$IO_3^- + 6H^+ + 5e^- \longrightarrow 1/2\ I_2 + 3H_2O \qquad E^\circ = +1.195\ V$$

$$BrO_3^- + 6H^+ + 5e^- \longrightarrow 1/2\ Br_2 + 3H_2O \qquad E^\circ = +1.520\ V$$

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \qquad E^\circ = +1.510\ V$$

$$S_2O_8^{2-} + 2\ e^- \longrightarrow 2SO_4^{2-} \qquad E^\circ = +2.010\ V$$

$$N_2H_4 \longrightarrow N_2 + 4H^+ + 4e^- \qquad E^\circ = +0.220\ V$$



a) 1.2 ml 0.0157M MnO_4^- + 3ml 0.0365M N_2H_4

b) 1.2 ml 0.0148M BrO_3^- + ” ” ”

c) 1.2 ml 0.0123M IO_3^- + ” ” ”

d) 2.0 ml 0.0106M $S_2O_8^{2-}$ + ” ” ”

e) 1.2 ml 0.0158M AsO_4^{3-} + ” ” ”

Table 1. Determination Of $AsO^{3}{}_{4}^{-}$

No	ml	$AsO^{3}{}_{4}^{-}$ (mg)		Error	Titrant
		Taken	Found	(±)	(mV/0.1 ml)
1	0.3	0.673	0.670	0.45	181
2	0.8	1.795	1.791	0.22	182
3	1.0	2.243	2.240	0.13	188
4	1.2	2.692	2.689	0.11	186
5	1.6	3.589	3.583	0.17	190
6	2.0	4.486	4.480	0.13	196

Table 2. Determination of IO_3^-

No	ml	IO_3^- (mg)		Error	Titrant
		Taken	Found	±	(mV/0.1ml)
1	0.3	0.790	0.786	0.51	193
2	0.8	2.106	2.101	0.24	190
3	1.2	3.159	3.153	0.19	188
4	1.6	4.212	4.204	0.19	201
5	1.8	4.738	4.731	0.15	203
6	2.0	5.264	5.257	0.13	210

Table 3. Determination of BrO_3^-

No	ml	BrO_3^- (mg)		Error	Titrant
		Taken	Found	(±)	(mV/0.1 ml)
1	0.3	0.741	0.736	0.67	199
2	0.8	1.977	1.971	0.30	198
3	1.2	2.966	2.960	0.20	196
4	1.6	3.955	3.948	0.18	203
5	1.8	4.449	4.441	0.18	207
6	2.0	4.943	4.936	0.14	212

Table 4. Determination of MnO_4^-.

No	ml	MnO_4^- (mg)		Error	Titrant
		Taken	Found	(±)	(mV/0.1 ml)
1	0.3	0.744	0.740	0.54	161
2	0.6	1.489	1.485	0.27	166
3	0.8	1.985	1.980	0.25	159
4	1.2	2.977	2.971	0.20	170
5	1.6	3.970	3.962	0.20	172
6	2.0	4.962	4.953	0.18	178

Table 5. Determination of $S_2O_8^{2-}$.

No	ml	$S_2O_8^{3-}$ (mg)		Error	Titrant
		Taken	Found	(±)	(mV/0.1 ml)
1	0.3	0.859	0.853	0.70	155
2	0.5	1.432	1.426	0.42	159
3	0.8	2.291	2.285	0.26	151
4	1.0	2.864	2.857	0.24	157
5	1.8	5.155	5.150	0.10	160
6	2.0	5.728	5.721	0.12	169

By the use of the relation $E^\circ = (0.0591/n) \log K$, where E° is the standard potential, n is the number of electrons evolved to reduce one mole of AsO_4^{3-} or IO_3^- or BrO_3^- or MnO_4^- or $S_2O_8^{2-}$ and K is the equilibrium formation constant of the reaction. The logK values were calculated to be 52.72, 215.48, 147.20, 146.36 and 75.13 for AsO_4^{3-}, IO_3^-, BrO_3^-, MnO_4^-, and $S_2O_8^{2-}$, respectively. Such values indicate that the above reaction should proceed quantitatively toward completion. The degree of completion of the reactions (α) is calculated according to $\alpha = \log K/n_1 + n_2 = 6.59$ for AsO_4^{3-}, 23.94 for IO_3^-, 16.36 for BrO_3^-, 16.26 for MnO_4^-, and 12.52 for $S_2O_8^{2-}$.

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