

Short Communications

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DETERMINATION OF PEROXYDISULPHATE BY HYDRAZINE SULPHATE : MODIFIED PROCEDURES

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The volumetric procedures for the determination of alkali peroxydisulphates, involving redox reaction, are (a) Zn-EDTA method.¹ (b) reduction of acidified peroxydisulphate ($S_2O_8^{--}$) with an excess of ferrous sulphate^{2,3} followed by the determination of unreacted Fe^{++} by $KMnO_4$ ² or feric sulphate² (c) reduction of $S_2O_8^{--}$ as in (b) followed by the determination of Fe^{+++} by mercurous nitrate² (d) reduction of $S_2O_8^{--}$ with an excess of oxalic acid² followed by the determination of oxalic acid by $KMnO_4$ and (e) iodometric method.^{2,4,5} Hydrazine (redox potential 1.16 V⁵) appears to be a promising reagent for the determination of $S_2O_8^{--}$

(redox potential of $S_2O_8^{--} + 2.01^{1,6,7,8}$, because hydrazine is a stronger reductant than the reductants used in methods (a) to (e) (redox potentials are greater than 0.8^{1,6,7,8,9,10}). Due to the large difference between the redox potentials of hydrazine and $S_2O_8^{--}$ the reaction between the two is expected to be rapid and complete. However, in neutral or alkaline medium slow oxidation of hydrazine by atmospheric oxygen^{6,11} makes it unsuitable as an analytical reagent. On the other hand, hydrazine sulphate is very stable and can be stored for long without appreciable oxidation^{12,13}. Due to the protective effect of protonation hydrazine, in an acid medium, is incompletely oxidised by most oxidants except KIO_3 ³. Nevertheless, hydrazine sulphate can be readily oxidised even by weak oxidants in an alkaline medium.^{6,11} In this communication two procedures are described for the determination of $K_2S_2O_8$ by reacting it with hydrazine sulphate.

Experimental

Reagents. (1) Hydrazine sulphate A.R., (2) Potassium peroxydisulphate A.R., (3) Tartrazine indicator (0.2% aqueous solution), (4) Purified nitrogen., (5) Potassium iodide solution 10%, (6) Starch solution 1%.

TABLE I. COMPARISON OF PROCEDURES 1 AND 2 WITH FERROUS SULPHATE METHOD.

Weight of $K_2S_2O_8$ taken g/25 ml	Weight of $K_2S_2O_8$ found g/25 ml		
	Procedure 1	Procedure 2	Fe^{++} method ²
1.356	1.3547	1.3566	1.3574
1.356	1.3574	1.3574	1.3564
1.356	1.3493	1.3547	1.3564
1.356	1.3566	1.3593	1.3537
0.677	0.6760	0.6746	0.6746
0.677	0.6745	0.6746	0.6732
0.677	0.6774	0.6760	0.6774
0.677	0.6774	0.6760	0.6774
0.340	0.3380	0.3380	0.3373
0.340	0.3394	0.3387	0.3389
0.340	0.3394	0.3387	0.3366
0.340	0.3366	0.3360	0.3394
0.169	0.1693	0.1683	0.1687
0.169	0.1687	0.1696	0.1687
0.169	0.1693	0.1693	0.1681
0.169	0.1687	0.1684	0.1684

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Procedure 1. A 25 ml aliquot of saturated hydrazine sulphate solution was taken in a conical flask. The flask was flushed with nitrogen and a slow current of nitrogen was maintained in the flask through the titration. About 10 ml of 1 N NaOH was added to the flask followed by the addition of 5–10 drops of tartrazine solution. The solution in the flask was then titrated with the test solution of $K_2S_2O_8$ until the solution turned colourless³.

Procedure 2. A 25 ml aliquot of $K_2S_2O_8$ solution was taken in a conical flask. About 10 ml of 10% KI solution was added to the $K_2S_2O_8$ solution followed by 2 ml of conc. HCl and 2 ml of a saturated solution of $MnCl_2$. The solution was heated to about 60°. After cooling, about 3–4 g of $NaHCO_3$ was added to the solution and the liberated iodine was then titrated with a standard solution of hydrazine sulphate¹³ until the starch-iodine end point was reached.

Potassium peroxydisulphate is calculated as follows:
1.0 ml of 0.025 M $N_2H_4H_2SO_4$ = 13.52 mg of $K_2S_2O_8$

These procedures were checked against ferrous sulphate permanganate method.³ The results of the analyses are given in Table 1.

Results and Discussions

The accuracy of the two procedures, for the determination of $K_2S_2O_8$, is comparable with the ferrous sulphate method.² The experimental error in the assayed values of $K_2S_2O_8$ is within the permissible limit of $\pm 0.5\%$. The results were independent of the concentration of either $K_2S_2O_8$ or $N_2H_4H_2SO_4$ or both, and were not affected by the addition of excess of $NaHCO_3$. Determination of $S_2O_8^{2-}$ by methods (a) to (e) involves intermediate steps and these methods are time consuming because the reagents used in these methods cannot be stored for long. Moreover, the reagents need to be standardised frequently while in

the procedure under discussion, the titrant, hydrazine sulphate can be stored for longer periods without appreciable deterioration.

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