Short Communication

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IODIMETRIC AND IODOMETRIC DETERMINATION OF HYDRAZINE MODIFIED PROCEDURES

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Two of the early methods for the determination of hydrazine are (a) oxidation of hydrazine with iodine[1–4] at pH 5–7.4 and (b) reduction of alkaline $K_3Fe(CN)_6$ by hydrazine to $K_4Fe(CN)_6$ followed by the determination of the ferrocyanide by ceriometry.[5] The pH restrictions have rendered method (a) tedious and unattractive. The main disadvantages of method (b) are the regulation of the amount of $K_3Fe(CN)_6$ to be used and the concentration of HCl. In the present communication these procedures have been modified to overcome these snags. Since there is no reaction between $NaHCO_3$ and iodine, hydrazine solution, even strongly acidic, was oxidised by iodine solution containing the bicarbonate. It was also observed that $MgCO_3$ could be substituted for $NaHCO_3$. Alternatively, following the suggestion of Cuy and Bray,[6] hydrazine was oxidised with excess alkaline $K_3Fe(CN)_6$ followed by the determination of the unreacted ferricyanide by the thiosulphate method.[7]

Experimental

Procedure 1

Iodimetry. From a burette test solution of hydrazine sulphate was run into a known volume of standard iodine solution containing 2–6 g $NaHCO_3$. The end-point was noted by using freshly prepared starch solution. The titration was also repeated using $MgCO_3$ instead of $NaHCO_3$

Procedure 2

Iodometry. Hydrazine sulphate solution was added to an excess of a standard solution of $K_3Fe(CN)_6$. The mixture was made alkaline with NaOH and shaken 3–4 min in order to oxidise hydrazine completely. It was then acidified with CH_3COOH followed by addition of 2 g KI and 50 ml 15% $ZnSO_4$ solution. The liberated iodine was titrated against standard sodium thiosulphate.

These procedures were checked against the iodate method for the determination of hydrazine. The results of these analyses are given in Tables 1 and 2.

TABLE 1. DETERMINATION OF HYDRAZINE SULPHATE: IODIMETRY, IODOMETRY AND THE IODATE METHOD.

Wt. of hydrazine sulphate (g/25 ml)	pH	Wt. of hydrazine sulphate found (g/25 ml)		
		Iodimetry	Iodometry	Iodate method
0.0814	2.3	0.0810	0.0816	0.0817
0.0814	2.3	0.0812	0.0813	0.0812
0.0814	2.3	0.0812	0.0815	—
0.0814	2.3	0.0815	0.0817	—
0.0814	2.3	0.0816	0.0815	—
0.1283	0.0*	0.1282	0.1283	0.135
0.1283	0.0	0.1282	0.1284	0.136
0.1283	0.0	0.1280	0.1284	—
0.1283	0.0	0.1285	0.1283	—
0.1283	0.0	0.1284	0.1286	—

*$H_2SO_4 > 1M$.

Results and Discussion

The accuracy of these modified procedures is comparable with that of the iodate method (Table 1). In both the procedures the error in the assayed values of hydrazine sulphate is less than ±0.5%. In the iodimetric titration when carbonates of Zn, Ca, Sr, and Ba were substituted for $NaHCO_3$ the end-point was not sharp and the error in the results was more than 1%. In the iodimetric titration the amount of the carbonates should be about 1 g in excess of the theoretical amount required to neutralize the acidity of the solution. In iodometry the amount of $K_3Fe(CN)_6$ should be at least 10% in excess of the theoretically required quantity. The results were not affected by the addition of large excess of $K_3Fe(CN)_6$. These procedures are independent of the acidity of hydrazine solution and do not require adjustment of pH during titration. Another additional advantage of these methods is that the possibility of oxidation of hydrazine by atmospheric oxygen is eliminated which is inherent in the earlier iodimetric methods. The iodate method[7] appears to lack accuracy for assaying hydrazine sulphate solutions containing high concentration of H_2SO_4 (Table 1). The modified procedures are suitable for analysing any salt of hydrazine.

TABLE 2. IODIMETRIC DETERMINATION OF HYDRAZINE USING $NaHCO_3$ AND $MgCO_3$.

Wt. of hydrazine sulphate (g/25 ml)	pH	Wt. of hydrazine sulphate determined (g/25 ml)	
		$NaHCO_3$	$MgCO_3$
0.1528	2.1	0.1526	0.1524
0.1528	2.1	0.1522	0.1530
0.1528	2.0	0.1522	0.1526
0.1528	2.0	0.1528	0.1530
0.2248	1.8	0.2246	0.2250
0.2248	1.8	0.2246	0.2244
0.2248	1.8	0.2242	0.2250
0.2248	1.8	0.2250	0.2246

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References

1. J.M. Kolthoff, J. Am. Chem. Soc., **46**, 2009 (1924).
2. R.A. Penneman and L.F. Audreith, Anal. Chem., **20**, 1058 (1948).
3. E.J. Cuy and V.C. Bray, J. Am. Chem. Soc., **46**, 858 (1924).
4. V.P. Tolstikov and P.A. Epik, Khim. Technol., **12**, 57 (1969).
5. E.J. Cuy and W.C. Bray, J. Am. Chem. Soc., **46**, 1786 (1924).
6. A.I. Vogel, *A Text Book of Quantitative Inorganic Analysis* (Longmans Green, London, 1961), third edition.
7. C.J. Dernback and J.F. Mehlig, Ind. Eng. Chem. (Anal Ed.), **14**, 58 (1942).