Diphenylcarbazone as an Internal Indicator in Volumetric Analysis. VII. Determination of Mercury

By G. S. DESHMUKH and A. L. J. RAO

(Received December 26, 1960)

While many gravimetric procedures are available for the determination of mercury only a few indirect titrimetric procedures have been reported in the literature. Mercury is determined by the titrimetric precipitation analysis as the thiocyanate using ferric ion as the indicator[1]. An indirect alkalimetric procedure[2] involving the addition of sodium hydroxide and potassium iodide and titrating the liberated alkali with standard acid is also known. Mercury is precipitated as iodate[3] and also as periodate[4] and in both the cases the precipitate is treated with potassium iodide and hydrochloric acid and titrated iodimetrically with standard thiosulfate. It is also precipitated as 2-(*o*-hydroxyphenyl)-benzimidazole[5] and the amount of mercury in the precipitate is determined by the bromate method.

Diphenylcarbazone as an indicator in volumetric analysis was first used by Roberts[6] and mercurimetric determination of thiocyanate using this indicator is already well known. Recent studies[7] in these laboratories have reported the applicability of this indicator to various types of titrimetric procedures. The present work deals with the direct determination of mercury by titrating with potassium iodide in presence of the above indicator.

Experimental

Reagents.—Mercuric nitrate solution was prepared by dissolving Merck's reagent grade sample in appropriate volume of water adding two drops of concentrated nitric acid and was standardized with thiocyanate. Potassium iodide solution contained an accurately weighed pure AR reagent in water and was standardized against potassium iodate. A saturated solution of diphenylcarbazone in alcohol was used as the indicator.

Procedure.—To 10 ml. of iodide solution 4~5 drops of the indicator and 2 ml. of alcohol were added. This was slowly titrated with mercuric nitrate from a burette. The original faint red brown color of the solution (due to the presence of the indicator) faded and the precipitate formed due to the addition of mercuric nitrate redissolved during the initial stage of titration. Towards the end a bright red precipitate of mercuric iodide was obtained. Mercuric nitrate was now added dropwise until the bright red precipitate turned dark. At the end point the precipitate turned reddish violet imparting a bright pink tinge to the supernatant solution. The end point is very easy to detect and there is no risk of over titration. It is, however, possible to rectify the error due to over titration by adding a measured amount of iodide and continuing the titraction in the usual way. Alternatively the reverse titration may also be carried out successfully. The molecular ratio of mercury to iodide calculated from the amount of mercury reacting with iodide at the equivalence

TABLE I

Strength of mercuric nitrate, 0.04359N
Strength of potassium iodide, 0.05107N

Sample number	Volume of iodide solution ml.	Volume of mercuric nitrate solution ml.	Amount of mercury: By KI method g.	Amount of mercury: By KNCS method g.	Difference %
1	20.0	23.25	0.2026	0.2034	0.4
2	10.0	11.60	0.1014	0.1017	0.3
3	9.0	10.50	0.09181	0.09219	0.4
4	6.0	7.00	0.06120	0.06148	0.4
5	4.0	4.70	0.04110	0.04099	0.3
6	3.0	3.50	0.03061	0.03073	0.4

1) A. I. Vogel, "A Text Book of Quantitative Analysis", Longmans Green & Co., p. 265.
2) M. N. Das, *Anal. Chem.*, **25**, 1406 (1953).
3) C. H. R. Gentry and L. G. Sherrington, *Analyst*, **70**, 419 (1945).
4) H. H. Willard and J. J. Thompson, *Ind. End. Chem., Anal. Ed.*, **3**, 398 (1931).
5) J. L. Walter and H. Freiser, *Anal. Chem.*, **25**, 127 (1953).
6) I. Roberts, *Ind. Eng. Chem., Anal. Ed.*, **8**, 365 (1936).
7) G. S. Deshmukh, This Bulletin, **27**, 623 (1954); **29**, 27 449 (1956); *Z. anal. Chem.*, **145**, 251 (1955).

point is 1 : 2 and the composition of the precipitate, therefore, corresponds to mercuric iodide.

The results of a set of typical titrations are given in Table I.

The chief advantage of this procedure is its simplicity, accuracy and the sharpness of the end point. Moreover this is a direct method for the determination which may be readily adopted in the routine analysis of mercury.

Summary

A simple and direct method of estimating mercury by standard potassium iodide with diphenylcarbazone as an indicator has been described. The results are accurate and comparable favorably with the classical procedures.

The authors wish to express their sincere thanks to Professor G. B. Singh for providing the facilities during the above work.

Chemical Laboratory
Banaras Hindu University
Varanasi-5