Diphenylcarbazone as an Internal Indicator in Volumetric Analysis. Part I. Determination of Ferrocyanide by Lead Nitrate

By G. S. DESHMUKH

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The standard methods of ferrocyanide determination may be classified broadly as follows: (a) those leading to its quantitative oxidation under certain operative conditions by such oxidants like Ce^{IV}, KIO_3 and $KMnO_4$ [1-3]; (b) those involving the formation of stable complexes of known composition, especially the titration of zinc salt solutions against $K_4Fe(CN)_6$ [4] and (c) titrations with $AgNO_3$ [5] or $Pb(NO_3)_2$ [6] using fluorescein or sodium alizarin sulfonate as adsorption indicators. According to Müller and Gäbler, potentiometric titration of standard lead nitrate against $K_4Fe(CN)_6$ gives reproducible and accurate results.[7]

It is known that in the well known microtest for Hg^{++} by diphenylcarbazone, Pb^{++} interferes due to its reaction with the reagent to develop an intense red or pink color. An aqueous solution of $K_4Fe(CN)_6$ does not, however, produce any characteristic color on the addition of diphenylcarbazone other than the brown or orange color of its alcoholic solution. This, as also the fact that besides Alizarine S no other indicator has been successfully adopted for the titrimetric detemination of ferrocyanide by $Pb(NO_3)_2$; suggested the investigation of this volumetric procedure using diphenylcarbazone as an internal indicator.

Experimental

Standard solutions of lead nitrate were prepared by dissolving accurately weighed quantities of a Merck's guaranteed reagent grade sample in appropriate volume of water; the lead content was checked by the chromate method. Laboratory reagent grade $K_4Fe(CN)_6$ was used for preparing solutions of various concentrations. The quantity of ferrocyanide in an aliquot portion of the solution was determined by standard ceric sulfate with ferroin as the indicator and potentiometrically. To 10 ml. of $K_4Fe(CN)_6$ about 1 ml. of the saturated alcoholic solution of diphenylcarbazone was added and the brown or orange colored solution was titrated slowly with constant stirring against standard lead nitrate. With the formation of lead ferrocyanide, the color faded gradually to pale yellow or brown and the end point was marked with a sharp change to purple. This is easy to detect and does not involve the risk of over-titration. It is, however, possible to rectify the error due to surpassing of the end point by running in a measured quantity of ferrocyanide and continuing the titration as usual. A reverse titration indicating a color change from purple to pale yellow or almost colorless though possible, was found to be less sharp and accurate. The molecular ratio of Pb: $K_4Fe(CN)_6$, calculated from the quantity of $Pb(NO_3)_2$ reacting with ferrocyanide at the equivalent point, showed that the composition of the precipitate corresponds to $Pb_2Fe(CN)_6$ or $2Pb—1K_4Fe(CN)_6$. These results are shown in the Table.

1) H.H. Willard and P. Young, *J. Amer. Chem. Soc.*, **55**, 3260 (1933).
2) R. Lang, *Z. anorg. allgem. Chem.*, **142**, 280 (1925).
3) R.E. Oesper, "Newer Methods of Volumetric Chemical Analysis" Chapman and Hall Ltd. London. (1938) p. 185-87.
4) W.H. Cone and L.C. Cady, *J. Amer. Chem. Soc.*, **49**, 356 (1927). Cf. also I. M. Kolthoff, *Chem. Weekbl.*, **24**, 303 (1927).
5) A.J. Berry and P.J. Durrant, *Analyst*, **55**, 613 (1930).
6) R. Burstein, *Z. anorg. allgem. Chem.*, **164**, 219 (1927).
7) E. Müller and K. Gäbler, *Z. analyt. Chem.*, **62**, 29 (1923).

TABLE I

Expt. No.	Gms. of $Pb(NO_3)_2$ in 250 ml.	Vol. of $Pb(NO_3)_2$=10 ml. $K_4Fe(CN)_6$ ml.	Weight of $K_4Fe(CN)_6$ By $Ce(SO_4)_2$ (g.) a	By Diphenylcarbazone (g.)	By Potentiometry (g.)
1	2.2775	16.20	0.0820	0.0820	0.0822
2	2.8060	48.80	0.3044	0.3042	0.3040
3	1.2335	35.5	0.0974	0.0973	0.0973
4	2.8060	24.3	0.1518	0.1516	0.1518
5	3.1416	19.6	0.1358	0.1356	0.1355
6	3.1126	18.6	0.2582	0.2586	0.2584
7	1.2335	14.8	0.04052	0.04054	0.3436
8	4.2162	36.7	0.3436	0.3438	0.3436

It is seen from a comparative study of the data that the above procedure yields accurate and reproducible results. It may also be mentioned that the limitation of using N/30 or even more dilute solutions of $K_4Fe(CN)_6$, inherent in Burstein's method[6] is not necessarily imposed on the present procedure. Since as a precipitant potassium ferrocyanide destroys immediately the pink or red color developed by Pb^{++} with diphenylcarbazone, the general difficulty of the unusual stability of the lead color met with in the case of other internal indicators[8] is not encountered in these titrations.

8) B. S. Evans, *Analyst*, **64**, 2 (1939).

Summary

A simple and direct method of estimating ferrocyanide by standard lead nitrate with diphenylcarbazone as an internal indicator has been described. The results are accurate and compared favorably with those obtained by other classical procedures.

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Chemical Laboratories,
Banaras Hindu University,
Banaras, India