# *Diphenylcarbazone as an Internal Indicator in Volumetric Analysis. Determination of Molybdenum by Lead Nitrate*

By G. S. DESHMUKH

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In quantitative analysis molybdenum is usually determined by its prior reduction to the lower valence stage and subsequent oxidation to the stable hexavalent form by a suitable powerful oxidant[1,2]. In view of the special precautions necessary in these titrimetric procedures, the precipitation of molybdenum oxinate and its weighing is considered more convenient and accurate[3]. This classical method still lacks the advantage of simplicity and rapidity so essential in routine analysis. It is known that Pb and Mo interfere in the colorimetric detection of $Hg^{++}$ by diphenylcarbazone due to the development of an intense pink colour by these ions with the reagent[4]. Evans reported the

1) N.H. Furman and W.M. Murray, *J. Am. Chem. Soc.*, 58, 1689 (1936).

2) R. E. Oesper, "Newer Methods of Volumetric Chemical Analysis", Chapman & Hall (London), (1938) pp. 94, 148, 176.

3) A.I. Vogel, "A Text Book of Quantitative Inorganic Analysis," Longmans Green & Co., (1945), p. 523-24.

4) F. Feigl, "Qualitative Analysis by Spot Tests", Elsevier Publishing Co. Inc., New York, (1947), p. 48.

use of diphenylcarbazide in the titration of lead nitrate against molybdate[5]. The end point is arrived at by running lead nitrate into the molybdate solution. According to him, the pink colour produced by the reaction of carbazone with lead is not easily destroyed by most precipitants. It was however, interesting to note that the colour developed by the addition of diphenylcarbazone to the neutral or faintly acidic solution of lead salt is destroyed on treatment with ammonium molybdate. The precipitate thus obtained does not show any other shade excepting a light orange yellow due to the indicator itself but turns pink sharply during the slow addition of molybdate at a stage when lead is completely precipitated. Although diphenylcarbazone has been employed as an internal indicator in mercurimetric[6,7] and other[8] titrations, its use in the determination of molybdenum by lead nitrate has not been reported in the literature of this subject. This possibility was therefore investigated in some detail and the results obtained thereof are presented in this communication.

## Experimental

Ammonium molybdate solutions of various concentrations were prepared by dissolving appropriate quantities of Merck's sample in water. The molybdenum content of an aliquot portion of the solution was determined by the oxinate method[5]. The standard lead nitrate solution contained an accurately weighed Merck's guaranteed reagent in 500 ml. of water to which 2–3 drops of nitric acid were added to prevent hydrolysis. The concentration of the solution was checked by the lead chromate method. A saturated alcoholic solution of diphenylcarbazone was used as the indicator.

To 10 ml. of $Pb(NO_3)_2$ about 1–2 ml. of the indicator was added followed by an equivalent volume of alcohol and the pink coloured solution was titrated slowly with constant vigorous stirring against ammonium molybdate. The pink colour was discharged during the initial stage of the titration with the formation of lead molybdate. The colour appeared momentarily with a further dropwise addition of molybdate but vanished immediately on swirling the contents. The end point was characterised by a rapid coagulation of the precipitate and the appearance of a sharp permanent pink flush. From a knowledge of the amount of Pb in the standard lead nitrate solution and that of molybdenum in the requisite volume of the titrant, the molar ratio Pb: Mo was calculated. The 1:1 ratio obtained indicated that the end point in the above titrimetric procedure corresponds to the quantitative formation of Pb ($MoO_4$). Under the specified experimental conditions it is therefore possible to determine molybdenum volumetrically by using lead nitrate as a primary standard. Data obtained over a fairly wide range of molybdenum concentration is returned in Table I.

Besides the sharp change of the indicator colour, its complete reversibility offered an additional advantage of rectifying errors due to overtitration. Compared with other classical methods of molybdenum determination, the outstanding feature of the present procedure is its simplicity, reproducibility and accuracy

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## Summary

The use of diphenylcarbazone as an internal indicator in the volumetric determination of molybdenum by standard lead nitrate solution is suggested. The end point is characterised by the sharp appearance of a permanent pink colour when molybdate is run into the lead solution and corresponds to the formation of Pb ($MoO_4$). The colour change is completely reversible and errors due to overtitration are therefore eliminated.

*Chemical Laboratories, Banaras Hindu University, Banaras, India*

TABLE I

| Expt. No. | Wt. of $Pb(NO_3)_2$ in 500 ml. g. | Vol. of Pb soln. taken ml. | Vol. of molybdate reqd. ml. | Wt. of Mo (g.) calcd. by oxinate | Wt. of Mo (g.) found by $Pb(NO_3)_2$ | Diff. |
|---|---|---|---|---|---|---|
| 1. | 6.3330 | 5.0 | 4.1 | 0.01830 | 0.01834 | +0.00004 |
| 2. | 〃 | 10.0 | 8.2 | 0.03661 | 0.03669 | +0.00008 |
| 3. | 〃 | 20.0 | 16.4 | 0.07323 | 0.07338 | +0.00015 |
| 4. | 5.6900 | 10.0 | 3.7 | 0.03271 | 0.03212 | −0.00059 |
| 5. | 〃 | 20.0 | 7.4 | 0.0654 | 0.06585 | +0.00045 |
| 6. | 〃 | 40.0 | 14.9 | 0.1317 | 0.13168 | −0.00002 |
| 7. | 6.3330 | 20.0 | 17.4 | 0.07331 | 0.07338 | +0.00007 |
| 8. | 12.660 | 20.0 | 17.8 | 0.1477 | 0.1468 | −0.0009 |

5) B.S. Evans, *Analyst*, **64**, 2 (1939).
6) J.V. Dubsky and J. Trtilek, *Mikrochem.*, **12**, 315 (1933).
7) J. Trtilek, *Coll. Czech. Chem. Comm.*, **10**, 242 (1938).
8) G.S. Deshmukh, *Bull. Chem. Soc.* **27**, 623 (1954).