DETERMINATION OF LEAD PERMANGANOMETRICALLY (LOW'S METHOD)

By K. Neelakantam

(From the Department of Chemistry, Andhra University, Waltair)

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Low's method[1] for the determination of lead permanganometrically has been in use for a long time in technical analysis. This method which consists in precipitating lead as oxalate from acetic acid solution, decomposing the precipitate with dilute sulphuric acid and titrating the liberated oxalic acid with permanganate has also been adopted by the British Pharmacopœia for the assay of lead acetate. Though this method is serviceable in routine analysis, it frequently gives low results.

Morris[2] stated that low results were obtained by the B.P. method unless the precipitation was carried out in the presence of about 60% of acetic acid. On the other hand, Wetherell[3, 4] pointed out that although precipitation was complete, low results (1·6%) were obtained because of occlusion of the lead oxalate or oxalic acid in the sparingly soluble lead sulphate. It was also noted by this investigator that solution of the oxalate precipitate in dilute nitric acid before the addition of sulphuric acid was not satisfactory, the end-point being indefinite, an observation which the present author is able to confirm on the basis of experience of several years. Wetherell (*loc. cit.*), therefore, preferred the U.S.P. X method which involves the titration of the excess of oxalic acid in the filtrate. This is in agreement with the observations of Tananaev and Kobzarenko[5]. Coppock and Coppock[6] suggested nitric acid to dissolve the lead oxalate, and in order to explain the low results obtained even then, it was stated by them that results as accurate as those obtained with calcium by a similar method could not be expected for lead, since lead oxalate, according to these authors, was more soluble than calcium oxalate.

Low's method, and the similar B.P. method carried out according to the directions of Garratt[7], suffer from the defect that the presence of filter paper in a permanganate titration is not permissible in accurate work since it causes positive errors[8, 9]. To avoid this difficulty a variation in procedure such as filtering the lead oxalate on asbestos has been adopted.

The view that the greater solubility of lead oxalate than calcium oxalate is responsible for the low results obtained by Low's method is incorrect according to available data. The solubilities of anhydrous calcium and lead oxalates in 100 g. of water at about 18° C. are 0·56 and 0·15 mg. respectively and the corresponding solubility-products, $1 \cdot 78 \times 10^{-9}$ and $2 \cdot 74 \times 10^{-11}$. At 25° C. the solubility-products are $2 \cdot 57 \times 10^{-9}$ and $3 \cdot 50 \times 10^{-11}$ respectively. (*Cf.* Landolt-Börnstein Tables, 1923). Calcium oxalate is somewhat less soluble in the dilute ammonia solutions which are used for washing than in pure water but it must be remembered that washing of calcium oxalate precipitates is done with hot wash liquid whereas according to the usual procedure lead oxalate precipitates are always washed with cold water.

The instability of oxalic acid in dilute aqueous solutions and the danger of its decomposition by hot, dilute mineral acids have been pointed out by several investigators[10,11]. Quantitative procedures involving the use of oxalic and dilute nitric acids together as in the Lux method for the evaluation of lead peroxide and sesquioxide are in use but the probability of the oxidation of oxalic acid by nitric acid, rendering the latter unsuitable in oxalic acid-permanganate titrations, does not appear to have been investigated. Oxalic acid is stated to be stable towards nitric acid by Bernthesen[12] and Caven[13]. However, Garratt (*loc. cit.*) and Miller and Mc Lenan[14] have indicated that oxalic acid can actually be eliminated by evaporation with concentrated nitric acid. Experiments carried out by the present author showed that on evaporating to dryness as well as on boiling for one hour, a mixture of equal volumes of oxalic acid (0·1 N) and concentrated nitric aid, the former was oxidised to 40–60%. It was also found that appreciable oxidation took place even with ordinary dilute (1 N) nitric acid solutions in an oxalate-permanganate titration at 60–90°C. It appears probable, therefore, that the indefinite and unsatisfactory end-points obtained by Wetherell (*loc. cit.*) and the author were due to this oxidation and perhaps also to the presence of nitrous acid in the solution. To dissolve lead oxalate prior to the addition of sulphuric acid, Clowes and Coleman,[15] recommended dilute nitric acid which had previously been boiled to render it free from nitrous acid. The use of nitric acid rendered free from nitrous acid by boiling has been tried by the author and it has been found that oxalic acid is oxidised to an appreciable extent. It is, therefore, to be concluded that the use of nitric acid in the determination of lead by this method is attended with complications.

The main cause of the low results in the determination of lead appears to be, therefore, occlusion of oxalic acid by lead sulphate. For reasons given above nitric acid cannot be employed to prevent this occlusion. Since lead chloride is more soluble than the sulphate, the possibility of using hydrochloric acid in the place of sulphuric acid in the dissolution of lead oxalate and subsequent titration was investigated.

It is well known that dilute hydrochloric acid is oxidised by dilute permanganate only when present together with iron or certain other catalysts. However, the use of this acid in permanganate titrations has been frequently and unnecessirily avoided and sulphuric acid preferred. According to Gooch and Peters[16] the oxidation of dilute hydrochloric acid by dilute permanganate is induced by the oxalic acid-permanganate reaction but the error is eliminated by the addition of manganous sulphate. Baxter and Zanetti, and later Kolthoff (*ibid.*) found that no irregularities occurred in the titration even in the absence of manganous sulphate, if the initial temperature was above 70° C. Hahn and Weiler (*ibid.*), however, did not get good results in the titration of calcium oxalate dissolved in 50% hydrochloric acid at 30–40° C. even with the addition of manganous sulphate.

In the course of the present investigation on oxalate-permanganate titrations in hydrochloric acid at 60–90° C., it was found that perceptible formation of chlorine or hypochlorous acid, as indicated by smell, occurred when the concentration of the acid was greater than 1 N and the titration was rapid. If the strength was about 0·5 N and the titration performed slowly, no oxidation occurred and reproducible results could be obtained. The induction period of the oxalate-permanganate reaction, so prominent in presence of sulphuric acid, was considerably shortened when hydrochloric acid was used and practically disappered when the initial temperature and the acid concentration were high.

In the determination of lead occlusion of, oxalic acid was completely eliminated, and reproducible and accurate results were easily obtained, when hydrochloric acid was used in the place of sulphuric acid for solution and titration of the precipitates. It was also found that accurate results could be obtained using only 5–6% of acetic acid in the precipitation of the lead oxalate and hence the claim of Morris (*loc. cit.*) that 60% of acetic acid is necessary seems to be unfounded. The use of the higher concentration of acetic acid, however, yielded in the cold precipitates which were much more granular and compact and hence could be filtered after an hour, without boiling.

Experimental

Preparation and Standardisation of the Lead Acetate Solution.—Crystalline lead acetate (35·090 g. A.R. Quality) was taken, dissolved in water, acidified with 10 ml. of glacial acetic acid and made up to two litres with water.

The strength of the solution was then checked by precipitating the lead as chromate and weighing after drying at 120° C. according to standard procedure. The mean value for the acetate in 25 ml. of the solution was 0·4385 g. while the calculated value was 0·4386 g.

Titration of Oxalic Acid with Permanganate in the presence of Hydrochloric acid.—A solution of oxalic acid was prepared from 24·540 g. of the pure acid (A.R.) by dissolving in water and diluting to four litres. This solution was transferred to an amber coloured bottle and kept as much as possible in the dark. Aliquots of this solution were then titrated with standard permanganate.

The permanganate solution used in this investigation was prepared according to the procedure recommended by Kato[17] by boiling the whole of the solution, cooling and filtering through asbestos into an amber coloured bottle. The solution was standardised in the usual manner at intervals with freshly prepared standard sodium oxalate solutions using dilute sulphuric acid for acidification. The strength of the solution did not show any appreciable change during the course of this investigation.

To investigate the suitability of hydrochloric acid for these titrations an aliquot of the oxalic acid solution was treated with the calculated volume of concentrated hydrochloric acid (10 N), diluted to 100 ml. with water heated to 90° C. and slowly titrated to a definite pink, stable for at least 30 seconds, the temperature being kept at 60–90° C. during the titration. It was observed that the initial lag in the reduction of permanganate (in presence of sulphuric acid) was considerably shortened. It was also observed that if the initial temperature was above 90° C. and the acid concentration high, the induction period was practically absent. No perceptible formation of chlorine or hypochlorous acid, indicated by smell, occurred up to an acid concentration of 1 N. At 2 N and higher concentrations, however, no end-points could be obtained and evolution of chlorine occurred during the titration. The results obtained showed that with a hydrochloric acid concentration of 0·5 to 1·0 N accurate results could be obtained. However, to allow a margin of safety 0·5 N acid concentration is recommended.

Determination of Lead

(*A*) *Precipitation in the presence of 5–6% of Acetic Acid.*—The lead solution, free from mineral acid, was placed in a beaker (400 ml.) acidified with 6·5 ml. of glacial acetic acid and diluted to 100 ml. with water. An excess of a dilute solution of oxalic acid (Ca. 0·1 N) was slowly added with stirring. The contents of the beaker were then slowly heated to boiling, boiled for one minute and set aside to cool down to the laboratory temperature. The precipitate was then filtered through a filter paper (No. 42, Whatman) and washed with 100 to 150 ml. of cold water. The bulk of the precipitate was then washed down into the beaker in which the precipitation has been carried out, 50 ml. of hot, dilute hydrochloric acid (2 N) passed through the paper and finally washed thoroughly with hot water. The filtrate and washings were collected in the same beaker, the solution diluted to 200 ml., heated to 90° C. and slowly titrated with standard permanganate until a pink colour which was stable for not less than 30 seconds was obtained, the temperature being maintained throughout the titration at 60–90° C. A large number of determinations have been carried out and some of the typical results obtained are given in Table I.

TABLE I

Strength of Permanganate—0·1014 N

No.	Volume of Lead solution (ml.)	Titre values		Crystalline lead acetate		Error (mg.)
		Found (ml.)	Calculated (ml.)	Found (g.)	Calculated (g.)	
1	20·0	18·25	18·25	0·3510	0·3510	0·0
2	,,	,,	,,	,,	,	,
3	,,	18·20	,,	0·3499	,	−1·1
4	,,	,,	,,	,,	,	,
5	10·0	9·15	9·13	0·1759	0·1756	+0·3
6	,,	,,	,,	,,	,,	,,
7	,,	9·10	,,	0·1750	,,	−0·6
8	,,	,,	,,	,,	,,	,,
9	5·0	4·55	4·56	0·0875	0·0877	−0·2
10	,,	,,	,,	,,	,,	,,
11	,,	4·60	,,	0·0885	,,	+0·8
12	,,	,,	,,	,,	,,	,,

As the titrations were performed to the nearest drop (0·05 ml.) and no correction made for fractions of a drop, the concordance should be regarded as satisfactory.

(*B*) *Precipitation in the presence of* 60% *of acetic acid.*—The above experiments were repeated using 65 ml. of glacial acetic acid. The precipitates obtained were found to be more granular and compact and could be filtered after about an hour, without boiling. The analytical results, however, were of the same accuracy. It is thus evident that this high concentration of acetic acid (60%) is not necessary for quantitative precipitation of the lead oxalate. 5–6% of acetic acid is quite sufficient except that in this case the precipitate is not so granular and hence requires boiling and cooling before filtration.

Oxidation of Oxalic Acid by Nitric Acid.—To determine whether any oxidation takes place on heating oxalic acid and nitric acid together, the following experiments were performed:—

(*a*) An aliquot of the standard oxalic acid (Ca. 0·1 N) was treated with an equal volume of pure concentrated nitric acid (Ca. 16 N) and evaporated to dryness on the water-bath. The residue was dissolved in hot water, acidified with dilute sulphuric acid, heated to 90° C. and titrated with permanganate. It was found that about 40% of the oxalic acid was oxidised under the conditions of the experiment.

(*b*) A mixture of equal volumes of the oxalic acid and the concentrated nitric acid was gently boiled for about an hour, the solution diluted with water, acidified with dilute sulphuric acid and titrated in the usual manner with permanganate. It was observed that about 60% oxidation occurred.

(*c*) To determine approximately the magnitude of the oxidation with nitric acid under the conditions of an oxalate permanganate titration, experiments were carried out using (1) dilute nitric acid as ordinarily available and (2) dilute nitric acid which had been boiled and cooled. The procedure adopted was as follows : 20 ml. of the oxalic acid solution was treated with the calculated volume of the dilute nitric acid (8 N) followed by 20 ml. of dilute sulphuric acid and diluted to 100 ml. The solution was then slowly heated to 90° C. and titrated at 60–90° C. with permanganate. No appreciable difference could be observed with the two kinds of dilute nitric acid referred to and there was no special difficulty in reaching the end-points in either case. The results obtained with different concentrations of nitric acid are shown in Table II.

TABLE II

Strength of Permanganate = 0·1014 N

No.	Conc. of Nitric Acid	Titre values		Oxidation in terms of the permanganate (ml.)
		Found (ml.)	Correct (ml.)	
1	1 N	19·0	19·2	0·2
2	,,	18·9	,,	0·3
3	,,	19·0	,,	0·2
4	2 N	18·9	,,	0·3
5	,,	18·8	,,	0·4
6	,,	18·6	,,	0·6
7	4 N	18·7	,,	0·5
8	,,	18·5	,,	0·7

Appreciable oxidation occurred even under the conditions of an oxalate-permanganate titration. Nitric acid should not therefore be used in such titrations.

Summary

It has been shown that hydrochloric acid can be used for dissolving lead oxalate precipitates in the estimation of lead and also for the titration of the liberated oxalic acid with permanganate provided the concentration of the hydrochloric acid is not greater than 0·5 N. Employment of hydrochloric acid obviates the difficulties due to occlusion of oxalic acid in Low's method and the complications in the permanganate titration arising out of the use of nitric acid. Quantitative precipitation of lead as oxalate does not require 60% concentration of acetic acid. Precipitation is complete even when 5-6% of this acid is present. The use of nitric acid in oxalic acid-permanganate titrations has been shown to be not permissible.

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