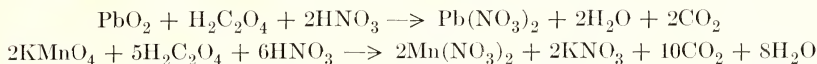


THE ANALYSIS OF ELECTROLYTICALLY DEPOSITED LEAD PEROXIDE BY THE METHOD OF LUX.

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The lead in lead peroxide may be determined, according to Lux,¹ by dissolving the sample in nitric and oxalic acids and titrating the excess of the latter with potassium permanganate, the reactions involved being represented by the following equations:



Following the conditions recommended by Scott² for applying the method, an unsuccessful attempt was made to use it³ for a peroxide deposited electrolytically on platinum. The end point in the titration with permanganate was so indefinite that the method was abandoned as unsuitable for work requiring a precision of 0.1 per cent.

MacInnes and Townsend⁴ later published results directing attention to what they believed to be the merits of the method for determining the amount of lead in electrolytic deposits of the peroxide. In view of their conclusions regarding this electro-volumetric method, consideration was given to the procedure in two investigations⁵ in the hope that a careful reproduction of the conditions recommended by these investigators would eliminate the difficulties encountered earlier. The results obtained are summarized in the present paper.

It should be noted that the method of Lux has previously been subjected to adverse criticism and modified at various times.⁶ In addition, correspondence with chemists involved revealed the fact that the method is not used by a number of industrial concerns producing or using lead and its compounds nor considered satisfactory by the U. S. Bureau of Standards.

Present Work. Since an indefiniteness in the end point was the original point of difficulty in attempting to use the method of Lux, in making a study of the procedure consideration was given first to the

¹Z. anal. Chem. 19, 153 (1880).

²Standard Methods of Chemical Analysis, 1917, p 240.

³Mellon and Reinhard—Proc. Indiana Acad. Sci. 31, 181 (1921).

⁴Ind. Eng. Chem. 14, 420 (1922).

⁵W. F. Reed—Master's Thesis, Purdue University, 1923. H. L. Wilkins—Master's Thesis, Purdue University, 1926.

⁶Tocher—Farben-Ztg. p. 214 (1899); Joshua—Dissertation, Zurich (1906); Sacher—Chem. Ztg. 35, 731 (1911); Chwala and Colle—Z. anal. Chem. 50, 209 (1911); Ipiens—*Ibid.*, 53, 261 (1914); Milbauer and Pivnicka—*Ibid.*, 53, 575 (1914); Classen-Harriman—Quantitative Analysis, p. 245 (1902); Fresenius-Cohn—Quantitative Chemical Analysis, II, 623 (1919); Schaeffer, White and Calbeck—Chemical Analysis of Lead and Its Compounds, p. 72 (1922).

“Proc. Ind. Acad. Sci., vol. 37, 1927 (1928).”

question of the effect of various factors upon the character of the color change involved in the titration of oxalic acid with potassium permanganate.

In carrying out this work the usual standards of careful analytical practice were maintained, such as the recrystallization of materials and the preparation of solutions with specially purified distilled water, the application (where necessary) of temperature corrections for volumes of standard solutions, and the standardization of potassium permanganate against sodium oxalate according to the recommendations of the U. S. Bureau of Standards.

Oxalic acid was first checked against the potassium permanganate according to the accepted scheme of adding about 15ml of sulfuric acid (1:4), diluting to about 100ml, heating to 80°C, and adding the permanganate until the appearance of a definite pink color which would persist for at least a minute. This titration was then repeated, using 40ml of 0.1 N oxalic acid, except for the addition of certain materials to the solution before titration. Four titrations were made in each case, the results in Table I representing an average of the values obtained.

TABLE I. The effect of various substances upon the titration of oxalic acid with potassium permanganate.

Exp. No.	Substance Added	KMnO ₄ Required	Percentage Error	End Point
1	15ml H ₂ SO ₄	40.15 ml	good
2	30ml HNO ₃ *	39.0	2.8	fairly good
3	15ml H ₂ SO ₄ 0.5g PbSO ₄	39.7	1.0	fairly good
4	15ml H ₂ SO ₄ 0.5g Pb(C ₂ H ₃ O ₂) ₂	39.0	2.8	fairly good
5	15ml H ₂ SO ₄ 0.5g Pb(NO ₃) ₂	38.5	4.0	fairly good
6	30ml HNO ₃ 0.5g Pb(NO ₃) ₂	39.0	2.8	poor
7	15ml H ₂ SO ₄ 30ml HNO ₃ 0.5g Pb(NO ₃) ₂	38.5	4.0	poor
8	15ml H ₂ SO ₄ 30ml HNO ₃ 0.5g Pb(NO ₃) ₂ KOH†	37.7	6.0	fairly good

* 1 : 2 acid

†Sufficient base to neutralize the nitric acid before adding the sulfuric.

The above data are in accord with the work of Ipiens⁶ to the extent that it seems to be the lead and the nitrate ions which together cause a slow fading of the permanganate, rendering the titration tedious as the end point approaches. Moreover, there was a marked decrease in the amount of permanganate required when either undissolved lead sulfate was present, or when nitric acid was substituted for sulfuric.

Several additional sets of titrations were then made in order to determine the effect of making certain changes in the general procedure. For these only a general statement is included, indicating the significant conditions and the results obtained.

In one set Experiment No. 2 was repeated, varying the quantity of nitric acid, the time of standing before titration, and the temperature

while standing. At first, increasing amounts of nitric acid required the use of decreasing amounts of permanganate, but as the concentration of acid was further increased slightly more permanganate was again required, indicating a possible connection with the fact that concentrated nitric acid will itself slowly decolorize potassium permanganate. For the latter action, the rate at room temperature is much slower than that at 80°C. As dilution of the acid decreases the rate of the reaction, the total effect for the concentrations maintained in using the method of Lux is probably small. Nitric acid through which air had been bubbled for some hours greatly reduced the effect observed with the more concentrated solutions containing untreated acid. With 30ml of nitric acid (1:2) present, no appreciable change in the volume of permanganate required was noted on allowing the solution to stand at room temperature up to two hours before titration. With the latter quantity of nitric acid again present, a small decrease, directly proportional to the time of standing, was noted when the solution was maintained at the temperature of boiling water for a time before titration.

On repeating Experiment No. 3 it was found that increasing amounts of lead sulfate necessitate the use of slightly decreasing amounts of permanganate.

The first two experiments recorded in Table I show a discrepancy indicating an error inherent in a method where calculations are based upon a permanganate solution whose value is determined in the presence of sulfuric acid but whose actual use is in connection with nitric acid. The conditions of standardization do not duplicate those of actual use. Milbauer and Pivnicka⁶ must have recognized this for they suggested using urea to avoid the deleterious effect of nitric acid. For the use of urea the following conclusions were reached in the present work: (1) The addition of 0.3g of urea when titrating in the presence of sulfuric acid alone produced no effect; (2) when titrating in the presence of nitric acid alone, the same amount of urea had some beneficial effect, but the amount of permanganate required was still much too low, compared with the amount required when sulfuric acid alone was used.

The possibility of some action of nitric acid on oxalic acid⁷ under the conditions of titration was not investigated.

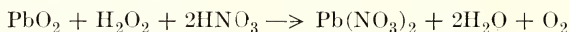
In order to try the procedure of MacInnes and Townsend on ordinary lead peroxide, a commercial sample was ground to 200 mesh size and analyzed by the authors and by several students for the content of lead. The results varied between 82 and 86 per cent. Different amounts of nitric and oxalic acid were used. As the amount of permanganate necessary to oxidize the excess oxalic acid was decreased (and hence the lead calculated was increased) by increased amounts of oxalic and nitric acids, it would seem necessary, as already intimated, to standardize the solution under conditions approximating those prevailing in actual use.

The general effect of making titrations under the above conditions is to bring a positive error into the determination. Another set of observations revealed the possibility of an effect partially compensating

⁷ *Atti Acad. Lincei* (5) 16, 399 (1907); *Compt. rend.* 124, 1349 (1897).

that just mentioned, at least in the determinations of MacInnes and Townsend. In order to check the precision of the method they dissolved a known weight of lead in nitric acid and then deposited the element electrolytically as the peroxide. Their calculations were then based upon the assumption that all the lead was deposited. Time after time in the present work it seemed impossible to make the electrolytic separation sufficiently complete to prevent obtaining a test for lead by precipitation as the chromate, according to the method of Falk.⁸ This would mean a deposit containing an amount of lead slightly less than that dissolved.

The Method of Schlossberg. As already indicated, the authors' experience with the method of Lux was unsatisfactory for work requiring a precision of 0.1 per cent. However, owing to the evident value of the suggestion of MacInnes and Townsend for avoiding, by means of a titrametric estimation, the difficulty of determining with satisfactory precision the amount of lead in an electrolytic deposit of the peroxide, attention was directed to the possibility of substituting some other solution for the oxalic acid to react with the lead peroxide. The most promising substance seemed to be hydrogen peroxide. This compound reacts with lead peroxide, in the presence of nitric acid, according to the equation



Schlossberg⁹ originally proposed it as a substitute for oxalic acid in the method of Lux. Unfortunately, hydrogen peroxide, in contact with platinum electrodes, decomposes more or less rapidly, thus introducing a complication not yet overcome. During the course of experiments with it, however, certain information was obtained which may be mentioned as being of interest when one compares it with similar information for oxalic acid. On repeating part of the experiments reported in Table I, with the substitution of commercial hydrogen peroxide for oxalic acid, it was found that the quantities of lead nitrate, lead sulfate, and nitric acid indicated therein produced no effect on the titration, allowing for an experimental error of 0.1 per cent. This indicates some connection between the use of oxalic acid and the unsatisfactory results obtained with the method of Lux.

⁸ J. Am. Chem. Soc. 32, 1564 (1910).

⁹ Z, anal. Chem. 41, 735 (1902).