

B. The tower is raised a few inches, and the beads are allowed to slide out. It is then washed with a little  $\text{CO}_2$ -free water. The washing is done quickly and if the flask is then corked or the titration made immediately there is scarcely any possibility of contamination from the air. The barium hydroxide solution may be titrated by adding four drops of phenolphthalein indicator. Titrate with hydrochloric acid to the permanent disappearance of the last traces of pink color. If it is desired to determine the residual  $\text{CO}_2$  in the sample, flask B and tower A are immediately replaced by another similar flask and tower, which have been previously freed from  $\text{CO}_2$  and contain 50 cc. of barium hydroxide solution. Five cc. of concentrated hydrochloric acid are added through the separatory funnel C to the flask containing the sample. The solution is then brought to a boil and the boiling continued very gently, the total time of aspiration being 25 min.

The carbon dioxide obtained from the diastase solution is assumed to be available carbon dioxide, while that obtained from the same solution after the addition of the concentrated hydrochloric acid is assumed to be residual carbon dioxide.

#### ACCURACY OF METHOD

The accuracy of the above method and the efficiency of the apparatus and technic in preventing contamination of the reagents by the carbon dioxide of the air were tested by using measured quantities of standard barium hydroxide in the regular way in the tower and passing  $\text{CO}_2$ -free air through it for 25 min.

A number of blank determinations were made on commercial grades of flour. In no case was there found to be more than 0.008 per cent of total carbon dioxide, while in several instances the blanks were nil. The method was also tried by using ordinary flour containing no added carbon dioxide and adding known quantities of baking powder of known composition. The baking powder used was a sample which has been used in collaborative work by the Association of Official Agricultural Chemists. It had been tested by five chemists and showed an average of 16 per cent total  $\text{CO}_2$ . In one instance the sample tested contained 24 mg. of total carbon dioxide and there were recovered 23.60 mg. In another instance the sample analyzed contained 48 mg. of carbon dioxide and there were recovered 46.56 mg.

## An Electro-Volumetric Method for Lead<sup>1,2</sup>

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*In the method described in the following paper, lead peroxide, deposited electrolytically, is determined by solution in oxalic acid and titration of the excess acid with potassium permanganate. The method seems more rapid than the usual electro-gravimetric method, and is more accurate, since it involves no uncertain empirical factor. It is unaffected by hydration of the deposit and by all inclusions in the material unless they are oxidizing in nature.*

*It would also appear that this work establishes, beyond question, the fact that the substance produced by the anodic oxidation is lead peroxide, and contains no higher oxide, as has been claimed by several authors.*

IN a study of the reactions occurring in the lead accumulator,<sup>4</sup> one of the authors, with his associates, showed that the product of the oxidation of lead at an anode is  $\text{PbO}_2$ , and not a mixture of this substance with a higher oxide, as has been claimed by Féry<sup>5</sup> and others. However, in the usual electrolytic determination of lead, in which the metal is determined by weighing the dried peroxide, it has been found necessary to use an empirical factor, smaller than the stoichiometrical factor, 0.8663. A low factor may be due to contamination with a higher oxide, or to a persistent hydration of the deposit. For the practical purpose of determining lead, this would not be of importance if there were certainty as to the value of this factor. Hollard,<sup>6</sup> who believes that the discrepancy between the factor for pure  $\text{PbO}_2$  and that observed experimentally is due to a higher oxide, obtained values, with a polished anode, varying from 0.740 for small amounts of lead to 0.861 for large amounts. With a roughened electrode he obtained the average value 0.853 for all amounts of oxide, but his experimental deviations

were  $\pm 0.005$  from this factor. Treadwell,<sup>7</sup> on the other hand, recommends a *high* value of the factor, 0.886, for small amounts of oxide, and a lower one, 0.863, for larger quantities. This is far from being a summary of the work on this subject, but it is sufficient to indicate that there is considerable uncertainty as to the value of the factor.

It occurred to the writers that the oxidizing power of the deposited peroxide, on an excess of oxalic acid for instance, could be made the basis for a convenient method of determining lead. Strangely enough, this rather obvious method has received practically no attention. A search through the journals and textbooks disclosed just two references to the method as a possibility and no evidence that it has been tried. Treadwell<sup>8</sup> says, "In a large excess of oxalic acid the lead peroxide (dried at  $200^\circ$ ) goes very slowly into solution. The titrimetric determination of the peroxide is, therefore, slow and not to be recommended." Further, Scott<sup>9</sup> suggests such a method, but he states, in a personal communication, that he has not put it to actual test. It was, therefore, considered desirable to try the oxidizing property of the deposited oxide as a means of determining lead.

After some preliminary experiments with a gauze anode, it was found that the best deposits for this purpose were obtained with an anode consisting of a platinum dish, 9 cm. in diameter, roughened on the inside, and a platinum disk, rotating at about 600 r. p. m., as cathode. Small pieces of sheet lead were carefully cleaned and weighed, and dissolved in the anode dish, with 10 cc. of concentrated nitric acid and 15 cc. of water. The sheet lead was kindly furnished by the Bureau of Standards and contained impurities amounting to not more than 0.04 per cent. The resulting solution was electrolyzed with a current of about 12 amp., until the solution gave no test for lead, which was usually after about 30 min. The deposit was then washed with a little distilled water.

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<sup>4</sup> MacInnes, Adler and Joubert, *Trans. Am. Electrochem. Soc.*, **37** (1920), 641.

<sup>5</sup> *Lumière Elec.*, **34** (1916), 305; *J. Phys.*, **6** (1916), 21.

<sup>6</sup> *Bull. soc. chem.* **29** (1903), 151; **31** (1904), 239.

<sup>7</sup> "Electro-analytische Methoden," 148.

<sup>8</sup> *Loc. cit.*, 150.

<sup>9</sup> "Standard Methods of Chemical Analysis," 240.