

A MODIFIED METHOD FOR THE DETERMINATION OF LEAD PEROXIDE IN RED LEAD.

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Two general methods are used for determining how near commercial red lead corresponds to the formula Pb_3O_4 . One method depends upon dissolving the free litharge from the sample and assuming the residue to be pure Pb_3O_4 . Other methods depend upon the determination of the per cent. of PbO_2 in the material, and calculating from this value the per cent. of Pb_3O_4 in the sample.

Mr. E. E. Dunlap (J. Am. Chem. Soc. 30, p. 611) has proposed a method of determining the free litharge in red lead. He states that by digesting a sample of commercial red lead in a boiling dilute solution of lead acetate, all of the free litharge is dissolved and that the material remaining corresponds to formula Pb_3O_4 . This method is employed in many commercial laboratories. However, the writers have not obtained accordant results when it is used, because the amount of litharge dissolved by the lead acetate solution depends upon the length of time the sample is digested. The analysis of a single sample by this method gave results of 4.71% to 8.8% litharge when Mr. Dunlap's directions were carefully followed, and the time of digestion was varied from ten to thirty minutes.

For accurate results the writers believe that it is necessary to use some of the methods for the determination of PbO_2 . A number of methods have been described in the literature and most of them have been tested in this laboratory.

The method of Lux (Treadwell and Hall's Quantitative Analysis, p. 491) is based upon the fact that oxalic acid is oxidized by PbO_2 in dilute nitric acid solution. Our experience with this method is that it usually gives high results and that they are not concordant. A series of determinations on the same sample gave results varying between 35.1% and 31.54%.

The method of Diehl as modified by Topf (Treadwell and Hall, p. 531) was also tried. This method depends upon the fact that potassium iodide

reduces lead peroxide in an acetic acid solution in the presence of an excess of alkali acetate. The iodine liberated is titrated with N/10 sodium thiosulphate. This method gives concordant results when proper precautions are taken. The best results were obtained when the potassium iodide and sodium acetate were ground in a mortar, dissolved in 50% acetic acid, the sample then added and the solution diluted. It is essential that all of the lead iodide be dissolved. This is the chief objection to this method, since it usually requires considerable time and trouble to bring about the complete solution of the lead iodide.

A method which has given good results is based upon the fact that dilute nitric acid will dissolve the PbO in red lead and leave behind the PbO₂. Careful tests have shown that the concentration of the acid should be at least 1 to 20 and not stronger than 1 to 10. We proceeded as follows:

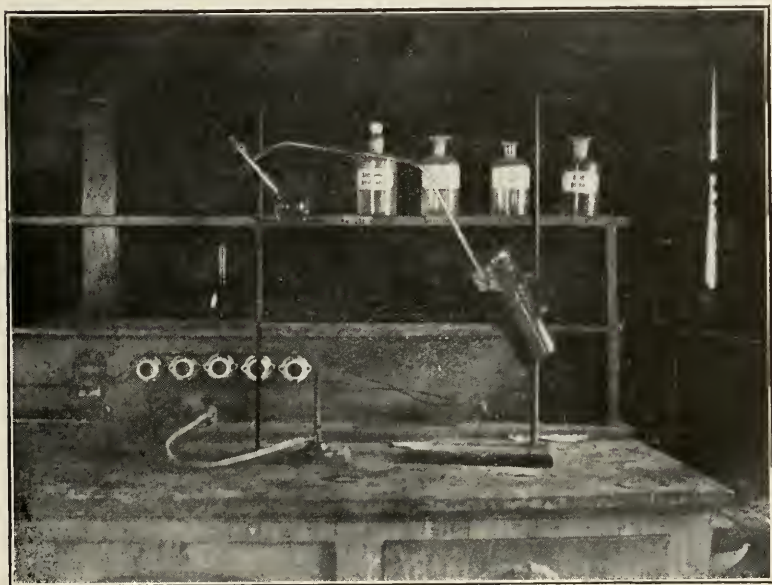
Digest a weighed quantity of about one gram in about 100 c.c. of warm dilute nitric acid (1 part acid, 10 parts water by volume) for thirty minutes. The sample is then filtered and the residue of lead peroxide washed with dilute (1 to 10) nitric acid, and then dissolved in equal parts of dilute nitric acid and hydrogen peroxide. This solution is evaporated to dryness to remove oxides of nitrogen. The evaporation carried out in a Kjeldahl flask to prevent spattering. This residue of lead nitrate is dissolved dilute nitric acid and electrolyzed in the usual way. This method gives good results but requires considerable time and very careful manipulation. A series of determinations on one sample gave the following percentage of lead peroxide: 32.04, 31.84, 31.86, 31.79, 31.89.

The most rapid method for the determination of PbO₂ is distillation with hydrochloric acid. The PbO₂ reacts with the HCl to liberate free Cl according to the following reaction:



The chief objection to this method, as described in the various books, is the cumbersome apparatus used. Cork or rubber stoppers on rubber connections of any kind can not be used because of the corrosive action of the strong HCl. After many trials we finally devised a very simple and workable apparatus. It consists essentially of a 100 c.c. distilling flask having a long bent delivery tube and provided with a perfectly fitting ground glass stopper. The complete apparatus is shown in the figure.

The determination is carried out as follows: One gram of the sample is introduced into the distilling flask, together with a few lumps of pure magnesite. The neck of the flask is washed down with 5 to 10 c. c. of distilled water, then 40 to 45 c. c. of concentrated HCl is added and the flask quickly stoppered. The delivery tube of the flask, which is drawn out to point, dips into a 100 c. c. Nessler tube containing a 3 to 4 per cent. solution of potassium iodide. The chlorine given off liberates free iodine which is soluble in the excess of potassium iodide present. The amount



of iodine liberated is determined by titration with $\text{N}/10$ normal sodium thiosulphate solution. One c. c. of $\text{N}/10$ sodium thiosulphate .01195 gm. of PbO_2 .

The flask should be gently heated at the beginning of the reaction and strongly again at the end. During the intervening time, heating is unnecessary and undesirable, since it causes a too rapid evolution of gas. The action of hydrochloric acid on the magnesite causes the evolution of enough carbon dioxide to carry over all the chlorine except the last traces. Twenty to twenty-five minutes should be allowed for the com-

plete reaction to take place. Care must be taken during the last stages of the reaction, since the magnesite is used up and the HCl gas given off being extremely soluble allows the potassium iodide solution to suck back into the flask. This is prevented by heating. Heating at this point not only prevents the sucking back of the KI solution, but is necessary in order to expel the last traces of chlorine from the flask. A second Nessler tube should be inserted and the heating continued a few minutes, in order to make sure that the reaction is complete. During the distillation the Nessler tube is surrounded by a beaker of cold water, in order to keep the temperature of the potassium iodide solution as low as possible so as to prevent the volatilization of the iodine.

This method is both quick and accurate. A series of analyses on one sample gave the following results: 31.84, 31.92, 31.92 per cent. lead peroxide. In all about fifty different samples were run by this method and in every case it was easy to check the results to within 0.10 per cent.

If a distilling flask with a ground glass stopper is not at hand, one can be made in a few minutes. Select a glass stopper of the proper size to fit the neck of the flask and fasten it in an horizontal position to the end of a slowly rotating shaft or axle fit the flask over the rotating stopper and grind with fine emery dust moistened with a mixture of equal parts of ether, turpentine, and alcohol.

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