

I.	II.	III.
0.30727	$3.859 \times 10^{-1}$	$3.85 \times 10^{-1}$
0.30070	$4.994 \times 10^{-1}$	$5.00 \times 10^{-1}$
0.40916	$7.092 \times 10^{-2}$	$7.09 \times 10^{-2}$
0.51105	$1.303 \times 10^{-3}$	$1.31 \times 10^{-3}$
0.61377	$2.317 \times 10^{-4}$	$2.32 \times 10^{-4}$
0.71630	$4.153 \times 10^{-5}$	$4.16 \times 10^{-5}$
0.92261	$1.270 \times 10^{-11}$	$1.27 \times 10^{-11}$
1.0230	$2.474 \times 10^{-14}$	$2.48 \times 10^{-14}$

hydrogen-ion concentration. Its advantages can be readily appreciated inasmuch as conversion tables and calculations are not needed, and readings can be both quickly and accurately obtained.

The writer wishes to acknowledge his indebtedness to Eberbach and Son Company of this city who so kindly undertook the construction of this apparatus.

ANN ARBOR, MICH.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF ARMOUR & COMPANY.]

## THE PREPARATION OF HYDROCHLOROPLATINIC ACID BY MEANS OF HYDROGEN PEROXIDE.

By PAUL RUDNICK AND R. D. COOK.

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In the preparation of hydrochloroplatinic acid, for use as a reagent in the determination of potassium or for other purposes, such as determinations of atomic weights of platinum and chlorine, many writers<sup>1</sup> have emphasized the necessity for completely removing nitric acid and for completely oxidizing the hydrochloroplatinic acid formed. If the nitric acid is not completely removed by repeated evaporation with concentrated hydrochloric acid, nitrosoplatinic chloride (PtCl<sub>4</sub>(NO)<sub>2</sub>) is formed, which eventually contaminates the product and compounds made from it. The directions usually given for the removal of nitrates seem to be somewhat vague and uncertain in their results. On the other hand, the solution in nitrohydrochloric acid and evaporation with hydrochloric acid results in the formation of hydrochloroplatinous acid (H<sub>2</sub>PtCl<sub>4</sub>), which must be oxidized to hydrochloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>). This has always been accomplished, so far as the literature shows, by saturating the solution with chlorine and heating to expel the excess. The objection to the presence of either of these compounds is very well stated by J. W. Mellor,<sup>2</sup> who says:

"Dissolve the gray powder at as low a temperature as possible in hydrochloric

<sup>1</sup> T. Knösel, *Ber.*, **6**, 1159 (1873); G. Krause, *Z. Anal. Chem.*, **14**, 184 (1875); E. Dulliver, *Compt. rend.*, **84**, 444 (1877); H. Precht, *Z. Anal. Chem.*, **18**, 509 (1879); J. S. Stas, *Chem. News*, **73**, 5 (1896); H. W. Wiley, *THIS JOURNAL*, **19**, 258 (1897); *Chem. News*, **75**, 214 (1897).

<sup>2</sup> J. W. Mellor, "Quantitative Inorganic Analysis," 240 (1913).

acid, and add nitric acid in small quantities at a time. In this way some nitrosoplatinic chloride ( $\text{PtCl}_4\text{NO}_2$ ) is formed. This must be destroyed, since it leads to low results in the determination of potassium. Evaporate the solution with water, whereby the nitrosoplatinic acid is decomposed into hydrochloroplatinic acid with evolution of nitrogen oxides. Some of the latter still remain in solution. Hence, add more water and hydrochloric acid, and again evaporate. These operations are repeated until no more nitrous fumes are evolved. During these operations, some hydrochloroplatinous acid is formed ( $\text{H}_2\text{PtCl}_4$ ). This is particularly objectionable, since it leads to high results when the chloroplatinic acid is used for the determination of potassium."

H. C. P. Weber,<sup>1</sup> in preparing hydrochloroplatinic acid for the determination of the atomic weight of chlorine, dissolved the platinum by making it the anode of an electrolytic cell containing strong hydrochloric acid. The solution had to be oxidized later by passing chlorine through it as described above. W. Dittman and J. McArthur<sup>2</sup> made hydrochloroplatinic acid for determining the atomic weight of platinum by dissolving platinum black in hydrochloric acid while passing chlorine into the solution, but they state that this was very tedious.

While these methods obviate the difficulty caused by the presence of nitric acid, they require expensive equipment or are so slow as to be prohibitive. The use of hydrogen peroxide in the form of a 30% solution (perhydrol) had been suggested by one of us some years ago for completing the oxidation of the platinum chloride solution used in the determination of potassium and has been successfully employed for this purpose ever since. Recently the idea suggested itself to us that hydrogen peroxide might possibly replace nitric acid in the solution of platinum black in nitrohydrochloric acid, and on trial this proved to be correct. The addition of hydrogen peroxide readily effects the solution of platinum black in hydrochloric acid, yielding a solution of hydrochloroplatinic acid which is at once free from the nitroso compound and completely oxidized to  $\text{H}_2\text{PtCl}_6$ . This reaction was briefly reported by T. Fairley<sup>3</sup> in 1875, who is as briefly quoted by Gmelin-Kraut,<sup>4</sup> but these inconspicuous statements seem to have escaped the attention of later writers. C. Marie<sup>5</sup> even reports that "hydrogen peroxide in acid or alkaline solution appears to be without action on platinum," but this is no doubt due to the fact that he operated on platinum foil at ordinary temperature and not on platinum black. The reaction is apparently the result of a coincidence of three reactions. The catalytic influence of platinum black on the decomposition of hydrogen peroxide has long been known. With its oxidizing power thus enhanced, the hydrogen peroxide oxidizes the

<sup>1</sup> THIS JOURNAL, 30, 29 (1908); U. S. Bur. Stand., *Sci. Paper* 82 (1908).

<sup>2</sup> *Trans. Roy. Soc. Edinburgh*, 33, 561 (1887).

<sup>3</sup> *Brit. Assoc. Adv. Sci.*, 45, 42 (1875); *Ber.*, 8, 1600 (1875).

<sup>4</sup> "Handbuch der Anorganische Chemie," Vol. 5, Part 3, 170.

<sup>5</sup> *Compt. rend.*, 146, 476 (1908).

hydrochloric acid, liberating nascent chlorine, which in turn combines with the platinum.

The reagent for the precipitation of potassium may be prepared as follows: 10 g. of dried, but not ignited, platinum black are covered with 50 cc. of concentrated hydrochloric acid, warmed to about 50° or 60° and 3% hydrogen peroxide slowly added, keeping just enough present to maintain a moderate evolution of chlorine, which will be seen to originate entirely on the platinum. When the platinum has been entirely dissolved, evaporate the solution to a volume of 100 cc., when it is ready for use. The use of peroxide as dilute as 3% may cause the volume to become too great during the operation. In this case it will be necessary to evaporate to a smaller bulk before the platinum has all been dissolved.

If "perhydrol" or concentrated hydrogen peroxide is available, it will be possible to keep the volume below 100 cc., thus shortening the time necessary to prepare the solution. The concentrated peroxide had best be added from a buret to avoid a large excess at one time, which might cause loss from frothing. We have found it convenient to prepare peroxide of 20% to 30% strength by distilling commercial hydrogen peroxide under a pressure of 4-5 cm. and at a temperature of 35-45°. On concentration to one-eighth of the original volume, 80% of the hydrogen peroxide remains in the residue and the loss from decomposition is negligible.

We take this opportunity of acknowledging the assistance rendered by Mr. W. C. Beaumont in the work described in this paper.

CHICAGO, ILL.

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## THE EFFECT OF VARIOUS SUBSTANCES ON THE PHOTOCHEMICAL OXIDATION OF SOLUTIONS OF SODIUM SULFITE.

BY J. HOWARD MATHEWS AND MARY ELVIRA WEEKS.

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The phenomenon of "negative catalysis," *i. e.*, the inhibition of a reaction by the addition of a small amount of a foreign substance which appears unchanged in the end products of the reaction, is even more difficult of explanation than is the phenomenon of positive catalysis, for which science has as yet found no explanation which is generally accepted. While each of several individual explanations which have been offered for particular cases of catalytic action are satisfactory for those cases, none of the various explanations so far offered may be applied to all cases of catalysis. The intermediate compound theory, which is probably more widely accepted than any other, furnishes a satisfactory explanation for a considerable number of cases, but for many others it is entirely inadequate. By the postulation of the existence of certain ephemeral