THE PREPARATION OF PURE PLATINUM.[1]

BY EDWARD WICHERS.

The Bureau of Standards has been working for some time on the preparation of the several platinum metals in a high degree of purity. In the course of the work on platinum in particular, some observations have been made which are of interest inasmuch as socalled pure platinum is in constant use in the collection of scientific data and in the control of industrial operations. Familiar applications are the use of the platinum resistance thermometer and the rare-metals thermocouple.

Since the chemical methods of detecting small quantities of impurities in platinum are not, in most cases, of proved reliability, it was decided to continue purification until the spark spectrum of the platinum should be as nearly as possible free from the lines of any foreign metal. It was found that repeated precipitation of ammonium chloroplatinate would yield metal of the desired purity. The platinum hereinafter described was obtained by four such precipitations, starting with material which contained significant amounts of palladium, rhodium and iridium, as well as considerable iron, tin, and other base metals. These results are given because the impression has been more or less prevalent, that pure or "thermo-element" platinum could not be prepared by this simple and economical method. The experience of Archibald,[2] as well as others, in thus preparing platinum of any desired purity has not been sufficient to dispel the idea that some more complicated and tedious process is required.

Each precipitate of ammonium chloroplatinate was drained from the mother liquor in a Büchner funnel, then washed by stirring up the salt with a considerable volume of a 15 to 20% solution of ammonium chloride, and again drained as before. This washing was always done twice and sometimes three times. The washed precipitate was dried, ignited to platinum sponge in an electrically heated muffle furnace and redissolved by aqua regia. The solution was evaporated several times with hydrochloric acid in order to remove nitric acid, before the next precipitation. The amount of platinum left in the mother liquor from the precipitation was usually not in excess of 1% of the platinum in the precipitate.

The final precipitate of ammonium chloroplatinate was ignited to sponge in a porcelain dish over a gas flame. The dish was covered with a silica plate and a stream of hydrogen run in to facilitate the decomposition and incidentally to prevent the slight loss of platinum which accompanies the ignition of ammonium chloroplatinate in the air.

[1] Published by permission of the Director of the Bureau of Standards.

[2] Archibald, *Proc. Roy. Soc. Edinburgh*, **29**, 721 (1909).

In addition to the spectroscopic tests, the thermo-electric[1] method of comparison was used. The least positive sample of Heraeus wire in the possession of the Bureau was used as a standard and will be designated in the subsequent paragraphs as "A."

The samples to be tested were prepared by melting the sponge on a piece of lime in the oxy-hydrogen flame. The buttons were cleaned with hydrochloric acid and rolled into a thin strip with a small pair of flat rolls. There was apparently no perceptible contamination with iron in this process although, as a precautionary measure, the strips were usually digested with hydrochloric acid.

The first samples prepared in this manner, although spectroscopically free from any trace of other platinum metals, invariably gave a considerable positive e. m. f. against "A." It was noted, however, that the spectrograms of these metals always showed the presence of calcium and sometimes of magnesium.

Subsequent samples were prepared in the same way, except that the precaution was taken to use an oxy-hydrogen flame in which oxygen was in considerable excess, as suggested by Mr. Fairchild of this Bureau. Strips of platinum were then obtained which showed a *negative* e. m. f. against "A," varying from 2 to 38 microvolts at about 1200°. Upon direct comparison of several of our samples, together with "A," in the spark spectrum, the samples were found to be identical in all respects except for the presence of calcium and a trace of magnesium. The variation in the intensity of the calcium lines was found to be roughly parallel to the variation in the e. m. f., the most negative sample showing only a very slight trace of calcium. This sample will be known as "K." A thermo-electric comparison was then made between "A" and 3 additional samples of Heraeus wire as well as a sample of thermo-element wire made by an American manufacturer. The last named gave 10 microvolts, two of the Heraeus wires 40 microvolts, and the third 170 microvolts at 1200°, all positive to "A." The Heraeus samples were compared spectroscopically and again showed various amounts of calcium while the most positive one also showed the presence of rhodium. None of the specimens of platinum here mentioned had been used previously and

[1] The e. m. f. developed at a hot junction between 2 dissimilar metals has long been made use of in the study of the platinum group. White (*Phys. Rev.*, **23**, 449 (1906)) employed the thermo-electric method to examine thermo-element wires for inhomogeneity and contamination during use. Burgess and Sale, and Burgess and Waltenberg (*Bur. Standards Sci. Papers* 254 and 280) applied the method to the study of the composition of platinum ware. Most alloys of platinum with other platinum metals or the base metals which are present as impurities give a positive e. m. f. against platinum itself. Thus an alloy of platinum with 1% of rhodium gives about 2450 microvolts at 1200°, positive to platinum.

all were carefully cleaned to remove any superficial impurity before the spectroscopic examination.

Similar variations are shown by the several samples of Heraeus wire employed in the thermocouples used in the researches of Day and Sosman[1] on the gas thermometer. The greatest difference is about 185 microvolts at 1500°. These wires were personally obtained by Dr. Day from W. C. Heraeus, and were believed to represent the purest platinum obtainable.

Through the courtesy of Dr. Day, a comparison was made by Dr. W. P. White, of the Geophysical Laboratory, between the least positive of these samples (hereinafter designated as "B") and sample "A." "B" registered 18 microvolts negative at 1200°. Later a direct comparison was made by us between "B" and our Sample "K," the latter giving 21 microvolts negative at 1200°. On spectroscopic examination, the H and K calcium lines were found to be visible in "K" and present with two or three times as great intensity in "B." The magnesium line of wave length 2852.13 A° was faintly visible in both spectrograms.

From the fact that no differences were found in the spectrograms other than those mentioned with respect to calcium and magnesium, it is believed that a negative e. m. f. as obtained indicates higher purity and is not caused by the presence of some contaminating substance whose combination with platinum is negative to platinum itself.

It was also observed that the samples which contained the least calcium were remarkably soft, did not wet the lime as they were fused, and showed no perceptible recalescence on cooling. Those samples which contained somewhat greater amounts of calcium were observed to wet the lime during fusion and showed a marked recalescence. A button which was properly melted but subjected to a momentary flash of a reducing flame immediately wetted the lime, showed recalescence on cooling, and gave an e. m. f. of 90 microvolts at 1200° positive to a duplicate sample which was fused only in the oxidizing flame. Strips of platinum containing appreciable amounts of calcium were found to show the characteristic calcium flame when brought to the melting point in an oxy-gas flame. Calcium was readily detected in "A" by this means.

The physical properties of the lime, and possibly its purity, seem to affect the purity of the platinum melted on it to a slight extent, but the principal factor is clearly the nature of the flame used. The data obtained seem to justify the conclusion that the calcium oxide undergoes some reduction if insufficient oxygen is used in the flame, and that the platinum takes up calcium and not calcium oxide. This was substantiated by melting nearly 200 g. of platinum in an Ajax-Northrup induction furnace, using a tall porcelain crucible lined with powdered calcium oxide tamped

[1] Day and Sosman, *Carnegie Inst. Pub.*, **157**, 1911.

around a mandrel. Under these conditions there is no possible source of reduction of the lime unless it should be by the platinum itself. The ingot which was obtained gave 5 microvolts negative to a satisfactory sample prepared from the same sponge by melting in the oxy-hydrogen flame.

A few experiments were conducted to determine the suitability of crucibles made from magnesium oxide with a small amount of magnesium fluoride as a binder. A sample of platinum was melted in such a crucible surrounded by a graphite shell to act as a conducting crucible in an Ajax-Northrup induction furnace. The platinum was held at a temperature considerably above the melting point for about 15 minutes. The resulting button was extremely hard and brittle, and analysis showed a magnesium content of 3.0%. A piece of foil similarly melted but held at about 1800° for 3 or 4 minutes showed a gain in weight equivalent to 0.33% magnesium, assuming loss of platinum by volatilization in this period to be negligible. This button was hard but could be rolled cold, and the resulting strip gave about 3000 microvolts positive to standard platinum at 1200°. Heating for several hours in the air caused the platinum to be coated with a grayish film which was removed by borax applied to the strips during the heating. The e. m. f. was now considerably lower, indicating that a portion of the magnesium had been lost. As it was thought that the contamination of the platinum with magnesium might be due to the reduction of the oxide by the graphite, another sample of platinum was melted in such a crucible, but with substitution of a tungsten shell for the graphite. The resulting platinum button was again very hard and could not be rolled, and evidently contained considerable magnesium. A sample melted in a magnesia crucible in which no magnesium fluoride was used was also very hard. Although the tungsten could have caused a reduction of the magnesia, it is probable that the real explanation lies in the dissociation of magnesium oxide, which Tiede and Birnbraüer[1] observed as taking place rapidly at 1900°. A button of platinum melted on a cupel molded from powdered magnesium oxide without a binder, by means of the oxy-hydrogen flame, was very soft and registered 14 microvolts negative at 1200° to the Bureau's standard Heraeus wire. Under these conditions the magnesia evidently does not reach the temperature required for dissociation.

A passing reference to the alloying of platinum and calcium is made by Moissan,[2] who observed that platinum, heated to boiling in the presence of lime by means of the electric arc, contained 2.54 to 3.01% calcium. Tarugi[3] states that he obtained a platinum alloy with calcium by means of

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[1] Tiede and Birnbraüer, *Z. anorg. Chem.*, **87**, 129 (1914).

[2] Moissan, *Bull. soc. chim.*, [3] **27**, 665 (1902).

[3] Tarugi, *Gazz. chim. ital.*, **29**, 1, 512 (1899).

the reaction between a platinum salt and calcium carbide. Hodgkinson, Waring and Desborough[1] obtained an alloy of the approximate composition $PtMg_2$ by passing magnesium vapors over platinum foil. In this connection the observation made some years ago by H. C. P. Weber,[2] of this Bureau is recalled. He found that certain pieces of platinum ware were alkaline to litmus after strong ignition. In one case at least Hillebrand obtained a definite qualitative test for calcium from the surface of an ignited crucible, and the inference was made that the calcium originated in the lime crucibles used for melting platinum, or in the lime salts used for polishing the finished ware. It is to be noted that while the present work indicates the presence of calcium as metal in the platinum, it would also be quite possible for ingots of platinum to inclose mechanically particles of calcium oxide, which might finally appear in the finished ware. It is clear from this that under unfavorable conditions the amount of calcium taken up by platinum may be very significant, the more so when it is considered that the calcium will be gradually brought to the surface and removed and the properties of the platinum will therefore not remain constant.

It has been mentioned that the purest samples of platinum thus far prepared still show the presence of calcium spectroscopically. The calcium content of this platinum is undoubtedly very small, the intensity of the H and K lines in Sample "K" indicating an amount which is probably not in excess of 0.0001%. An attempt will be made not only to determine the amount of calcium as definitely as possible, but also to approach still more closely the goal of absolute purity. It is proposed to make a study of the suitability of other refractories, such as thoria and zirconia, for melting pure platinum, and also to determine the optimum conditions for melting platinum on lime, inasmuch as this substance commends itself so highly because of its cheapness and availability.

It is further planned to make use of the temperature coefficient of resistance as an index of the purity of the various samples. This would furnish an experimentally determined quantity peculiar to the material examined and independent of any arbitrary standard of comparison such as must be used in the thermo-electric method. Such determinations would be of great value in the subsequent standardization of new material. This method has the added advantage that the values obtained are capable of variation in one direction only, so far as known, while the e. m. f. of a given sample may be positive or negative to absolutely pure platinum, depending upon the nature of the impurity.

    [1] Hodgkinson, Waring and Desborough, *Chem. News*, **80**, 185 (1899).

    [2] Report of Committee on Quality of Platinum Laboratory Utensils , *J. Ind. Eng. Chem.*, **3**, 688 (1911).

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THE ADSORPTION OF GASES BY METALLIC CATALYSTS.

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I. Introduction.

Theories of catalytic activity have been based frequently upon assumptions of adsorptive power on the part of the catalytic agent. Experimental investigation of such theories is in many cases possible, but hitherto a systematic attempt to apply such a test has not been undertaken. The selective action of catalytic agents suggests a starting point in such investigative work, and it is believed that a solution of the general problem of contact catalysis may be more readily attained when such a study has been accomplished. The data given in the literature for the "occlusion" of gases by the metallic elements are of little assistance because of the fact that these may cover cases of true solubility, of compound formation, and even of gaseous inclusions, whereas, in all probability, contact catalysis is concerned only with surface phenomena. Furthermore, these data generally refer to metals, the activity of which, as catalysts, has not been specifically determined for the material in the form used in the occlusion investigations.

The selective action of solid catalysts is clearly manifested in the action of catalytic poisons. Several instances of loss of catalytic activity have been found to result from the presence of certain impurities in the reactant gases. Harbeck and Lunge[1] have shown that carbon monoxide inhibits almost completely the catalytic action of platinum on a mixture of hydrogen and ethylene. Maxted[2] has found that palladium decomposes hydrogen sulfide, retains sulfur, and loses, thereby, the ability to adsorb hydrogen. Von Hemptinne[3] was surprised to find that the presence of carbon monoxide decreased materially the adsorption of hydrogen by palladium at low temperatures.

It is, perhaps, natural that most observations of adsorption have been made with the platinum metals since these were among the earliest recog-

[1] Harbeck and Lunge, Z. anorg. Chem., 16, 50 (1898).

[2] Maxted, J. Chem. Soc., 115, 1050 (1919).

[3] Von Hemptinne, Z. physik. Chem., 27, 429 (1898).