JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

VOLUME 55 APRIL, 1933 NUMBER 4

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BUCKNELL UNIVERSITY]

The Quantitative Determination of Palladium by Means of Ethylene[1]

BY S. C. OGBURN, JR., AND W. C. BRASTOW

Of the six platinum metals, palladium is the most readily reactive with organic reagents with the formation of stable coördinated salts.[2] The use of these compounds, however, for the quantitative estimation of palladium, or its removal from the other metals of the group, necessitates the use of a gravimetric factor to convert the weighed precipitate to percentage of the metal present. If the metal itself is desired, the precipitate must be reduced by ignition in a stream of hydrogen. Certain reducing agents as powdered zinc or magnesium, formic acid, hydroxylamine, phenylhydrazine and others can be used to yield the metal directly from acid solutions of the metallic chloride, but in these cases platinum, if present, and usually others of the group are also precipitated.

It appears desirable, therefore, to be able to select some reducing agent which is selective in its action and which offers no particular disadvantages in the analytical procedure for the removal of palladium in the metallic condition from a mixture of the platinum metals group. Carbon monoxide acts in this capacity when introduced into strongly acid solution of the chloride of the metals[3] but offers the disadvantages of slowly reducing platinum and of tending to convert the other metals present into ionic complexes from which they are, subsequently, not easily precipitated. Of the simple unsaturated hydrocarbon gases, acetylene forms a reddish-brown precipitate which yields the metal on heating.[4] It also has a tendency to reduce slowly other metals of the group, yielding an undesirable colloidal condition.[2] Ethylene, however, seems to be admirably adapted to meet the needs of this problem. It is specific in its reduction of palladium with respect to the others of the group; it is cheap and easily obtainable in compressed form; and it offers a means of separating, quantitatively, large

---

(1) This paper is taken, in part, from a thesis submitted by W. C. Brastow to the Faculty of Bucknell University in partial fulfilment of the requirements for the degree of Bachelor of Science.

(2) Ogburn, THIS JOURNAL, **48**, 2493 (1926).

(3) Manchot, *Ber.*, **58B**, 2518 (1925).

(4) Erdmann and Makowaka, *ibid.*, **37**, 2694 (1904).

amounts of the metal which would be of value industrially as well as analytically.

Experimental Part

Preparation of Solutions.—In order to increase the range of accuracy of the analytical methods used to standardize the palladium chloride solutions, two were prepared. The one was obtained by dissolving the pure salt, $PdCl_2 \cdot 2H_2O$, in hot water containing about 7 cc. of concentrated hydrochloric acid per 100 cc. of solution, and filtering. The other was made by dissolving a weighed quantity of pure palladium wire in aqua regia. After carefully evaporating this solution to dryness on a water-bath, the residue was taken up with concentrated hydrochloric acid and the whole reëvaporated until nitrogen oxides ceased to be evolved. The evaporation to dryness was repeated and a second addition of the acid was made after which it was diluted to the same acid concentration as in the preceding case.

The solutions of ruthenium trichloride, sodium chlororhodite, potassium chloroosmate, sodium chloroiridate and chloroplatinic acid were prepared according to directions given by one of us.[2] The metallic contents of these were determined by reduction with zinc, followed by ignition in a stream of hydrogen, with the exception of the osmium solution, which was immediately filtered into a weighed Gooch crucible, washed and dried at 105°.

The metallic content of the palladium chloride solution obtained from the solution of the salt was determined by means of precipitation with dimethylglyoxime and the use of the proper gravimetric factor.

The ethylene gas used was from a cylinder as purchased in a purified form from one of the commercial producers.[5] The manufacturers' analysis as given in a private communication was: ethylene 99%; air 1%.

Standardization Results.—Ten-cc. samples of the solutions were used for each determination. At least four analyses were made with each. The maximum, minimum and mean values obtained are as follows (expressed in grams of the metal per cc. of solution):

	Maximum	Minimum	Mean
Palladium	0.02160	0.02148	0.021501
(From the salt, $PdCl_2 \cdot 2H_2O$)(Dimethylglyoxime as the reagent)			
Palladium			.019994
(From metallic wire) (Solution made from weighed sample)			
Rhodium	.0027	.0025	.002625
Ruthenium	.0032	.0030	.003125
Osmium	.0030	.0026	.002755
Iridium	.0028	.0027	.002770
Platinum	.0024	.0021	.002230

The Removal of Palladium from a Solution of Palladium Chloride.—Before attempting the separation of the palladium from all of the platinum metals in a mixture, by means of ethylene, the procedure developed was carried out with a solution of the palladium chloride alone, and was done as follows. A ten-cc. portion of the solution was heated on a water-bath to 80°. Ethylene gas was rapidly passed in until reduction was complete and the precipitate had coagulated to leave the supernatant liquid clear and colorless. After settling, the mixture was filtered through a properly prepared Gooch crucible. The precipitate was washed with warm water until the washings were free from chlorides, and then dried in an electric oven at 105° to a constant weight. A test of the filtrate with dimethylglyoxime solution showed the absence of any palladium.

---

(5) The Matheson Co., North Bergen, N. J.

During the precipitation, the color of the solution is more quickly removed, and the colloidal condition of the finely divided metal easily overcome, if agitation is effected by means of a small motor-driven stirrer. Two hours is usually required to effect the complete reduction.

Varying temperatures, up to the boiling temperature of the solution, and varying acid concentrations equivalent to from 5 to 20 cc. of concentrated hydrochloric acid per 100 cc. of solution were tried in an effort to ascertain any differences either in the rate of the reduction or its completeness. No differences were noted, except that at the lower temperatures the process of removal of the metal was appreciably retarded. With more concentrated solutions of the metal, the reduction appears to be more rapid.

In order to verify the fact that the black spongy precipitate was metallic palladium and not an organic derivative, separate determinations were made and weights taken before and after reduction in hydrogen for twenty minutes at red heat. No change in weight resulted, and in each case the percentage of the palladium checked with the quantity in the original sample, within the range of experimental error. Five analyses, each made in duplicate, gave maximum, minimum and mean values of grams of metal per cc. as follows.

Solution 1. (Palladium chloride prepared from the pure salt, $PdCl_2 \cdot 2H_2O$.)
Maximum, 0.02180 Minimum, 0.02140 Mean, 0.021683.
Theoretical value (as determined from dimethylglyoxime determination) 0.021501.
Error, +0.846%.

Solution 2. (Palladium chloride prepared from pure palladium wire.)
Maximum, 0.01998 Minimum, 0.01990 Mean, 0.019955.
Theoretical value (as determined from weighed sample), 0.019994.
Error, −0.195%.

From these results, it may be readily seen that ethylene may be used to quantitatively remove palladium from its chloride solution.

The Removal of Palladium in the Presence of All the Platinum Metals.—In order to verify the accuracy of the separation of palladium from all of the other metals of the platinum group, a mixture of solutions of each of the six metals of the concentration previously mentioned was prepared. Each 100 cc. of this solution contained the following.

	Grams	Metal %
Platinum	0.0669	18.38
Palladium	.19994	54.94
Iridium	.0277	7.61
Osmium	.0275	7.56
Rhodium	.02625	7.21
Ruthenium	.015625	4.29
Total metal content	0.363915	99.99

The reason for using an excessive amount of platinum was that it is the principal metal found associated with palladium, both in nature and in industrial materials.

The removal of the palladium by means of ethylene was made as before. The maximum, minimum and mean values for the recovered metal from three determinations, in which 100-cc. samples of the solution mixture were used, ran as follows (expressed in terms of grams of palladium recovered from each sample):

Maximum, 0.2015 Minimum, 0.1961 Mean, 0.19845
Theoretical value, 0.19994 Error, −0.746%.

In order to determine whether the palladium was contaminated with other metals of the group, the combined precipitates were dissolved in hot dilute aqua regia (in which they were completely soluble). After evaporation nearly to dryness concentrated hydrochloric acid was added to facilitate the removal of nitrogen oxides. The evaporation to dryness was repeated and the residue taken up with water containing a small amount of hydrochloric acid. Upon analyzing this solution according to the method described in a previous paper[6] it was found that no weighable amount of metals other than palladium was present. A small amount of platinum was indicated by a slight color reaction with potassium iodide and also with α-furil dioxime, but the latter did not yield a precipitate sufficient to weigh within any degree of accuracy.

It may be thus seen that the presence of the other metals of the group has but slight effect in the removal of the palladium. The percentage error shown is low in comparison with standard procedures used to effect this task. At best the analytical separations of the platinum metals are not usually as conclusive as those available for use with others so widely known. A means, therefore, which can be attained quickly to yield the metal directly is desirable. The selective action of ethylene also adds to this advantage.

Summary

A new and practical method for the determination of palladium, either alone or in mixtures of all of the other metals of the platinum group, is given. By means of the specific action of ethylene gas toward palladium in reducing it to the metallic condition, gravimetric factors need not be used, and the process of reduction of organic derivatives of the metal in hydrogen is not necessary, when the metal is desired as an end-product. In mixtures of the six platinum metals, the error in the recovery of the palladium is only about 0.75%.

[6] Ogburn, THIS JOURNAL, **48**, 2507 (1926).

LEWISBURG, PENNSYLVANIA

RECEIVED JULY 1, 1932
PUBLISHED APRIL 6, 1933

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

A Study of the Use of the Tungsten–Nickel Electrode System in Neutralizations[1]

BY N. HOWELL FURMAN AND GEORGE W. LOW, JR.

This investigation of the bimetallic electrode system, tungsten–nickel, was made in order to determine the possibilities of the system in neutralizations. Kahlenberg and Krueger[2] were the first to make a comprehensive study of the use of bimetallic systems in neutralizations. They used normal solutions of strong acid and base, and recommended especially tungsten in conjunction with one of the following: copper, nickel, silicon or cobalt. They gave no data for weak acids or bases. In a subsequent paper Holt and Kahlenberg[3] studied various systems in greater detail, using 0.1 N solution of hydrochloric acid, sodium hydroxide, ammonium

---

[1] Presented at the Eighty-third meeting of the American Chemical Society, New Orleans, La., 1932.

[2] Kahlenberg and Krueger, *Trans. Electrochem. Soc.*, **56**, 201 (1929).

[3] Holt and Kahlenberg, *ibid.*, **57**, 361 (1930).