TABLE IV.

Solution no.	Ammonia solution. cc.	Density.	Solution no.	Ammonia solution. cc.	Density.
1	0	1.0670	7	30	1.0853
2	5	1.0700	8	35	1.0883
3	10	1.0731	9	40	1.0903
4	15	1.0762	10	45	1.0874
5	20	1.0792	11	50	1.0846
6	25	1.0822	12	75	1.0702

Summary.

In this paper it has been shown that the neutral point for a weak acid and a weak base, such as citric acid and ammonia, may be accurately determined by conductivity measurements; that the presence of an excess of ammonia in the ammonium citrate solution may be ascertained by shaking out with an immiscible solvent, as chloroform, which dissolves a part of the excess of the base but neither the free acid nor the salt; and that the neutral point of the ammonium citrate solution may also be established by density determinations.

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APPLICATION OF THE "GLOW REACTION" TO THE QUALITATIVE DETECTION OF THE PLATINUM METALS.[1]

BY L. J. CURTMAN AND P. ROTHBERG.

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For a long time it has been known that the platinum metals present the rather remarkable phenomenon of condensing relatively large volumes of gases upon their surfaces at room temperatures, and also, that this property is especially pronounced if the metals are in that finely divided state obtained by the reduction of their salts. In 1823 Döbereiner[2] showed that the occlusion of gases by platinum sponge, particularly in the case of a mixture of hydrogen and air, was accompanied by the oxidation of hydrogen to water and it was noted that this reaction took place so rapidly and energetically as to cause the platinum sponge to glow intensely. From the early investigations of Döbereiner to the present day, this occlusion of gases by platinum has been the subject of much research,[3] and among other things, it has been shown that hydrogen in the occluded state acts in the same manner as nascent hydrogen[4] and that,

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[1] Presented at the March meeting of the New York Section of the American Chemical Society.

[2] Schweigger, *J. für. Chem.*, **39**, 159 (1823).

[3] J. L. Howe, "Bibliography of the Platinum Metals" in *Smithsonian Inst. Misc. Collections*, Vol. 38.

[4] T. Graham, *Proc. Roy. Soc.*, **16**, 422 (1868).

in general, the presence of metallic platinum in the finely divided state greatly accelerates the oxidation of many oxidizable gases.[1]

Although this property of platinum has been made use of in the analysis of gases and in various commercial processes, the authors are not aware of any record which shows that the occlusion of gases and their oxidation in the presence of the platinum metals, more particularly the glow accompanying the oxidation of some gases, has been utilized as a method for the detection of platinum and its allied metals. It was the object of this investigation to determin the reliability for qualitative purposes of the "glow reaction" obtained by passing a mixture of air and illuminating gas over very finely divided platinum. To that end it was necessary, first, to decide upon a simple method of carrying out the reaction; second, to determin the minimum amount of each of the platinum metals that would give the test; and third, in the case of platinum to ascertain the influence and possible interference of other substances.

Method of Making Tests.—The following method was selected and though it may not be the most delicate or refined method possible, it has decided advantages as a practical method, because of the simple apparatus necessary and the great rapidity with which it may be applied.

The substance to be tested is brought into solution by any of the common methods and about 0.2 cc. of this solution is absorbed in a piece of thin asbestos paper by alternately dipping the paper into the solution and heating until the required volume has been absorbed. Experience showed the above volume (0.2 cc.) to give the best results in these tests. The moist paper held by one end in a pair of tongs is now heated to redness in the Bunsen flame, then removed, and after the redness has ceased, but while the paper is still hot, it is brought into a stream of a mixture of illuminating gas and air from a Bunsen burner. If platinum is present, the asbestos paper will begin to glow.[2] The glow must last for some time and can be brought back after it has once died out by again heating the paper and holding it in the stream of gas.[3] The burner must be arranged

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[1] W. Henry, *Phil. Trans.*, 14, 266 (1824); Phillips, *Am. Chem. J.*, 16, 163.

[2] In the absence of substances which on ignition leave a heavy residue, failure to obtain the glow at this point would show that the metal tested for was not present in the volume absorbed in an amount as great as that indicated below as the limit for that metal. It is obvious that the given solution must be concentrated according to the refinement of the analysis to such an extent that 0.2 cc. will contain sufficient metal to give the test. For example, should it be desired to ascertain whether 0.05 mg. of platinum were present in 500 cc. of a given solution, concentration to such a point would be necessary that 0.2 cc. should contain 0.002 mg. platinum (the limit for that metal). In the above example 20 cc. of the solution must be concentrated to 0.2 cc. If smaller quantities were to be detected, it would be necessary to concentrate a larger amount of the solution.

[3] This cannot be done indefinitly if the quantity of metal is small, owing perhaps to mechanical loss or change of state of the platinum black, as shown by Berthelot, *Compt. rend.*, 94, 1377 (1882).

to supply a fairly good mixture of illuminating gas and air and the pressure must not be too great.

It is also essential for the greatest sensitiveness of the test that the asbestos paper be very thin. In these experiments pieces of asbestos paper 0.5 × 3.0 cm. and 0.3 mm. thick were employed, only approximately half being used to absorb the liquid. The intensity of the glow can be somewhat increased by having the gas warm. This can be easily accomplished by slightly warming the upright tube of the burner before passing the gas through it.. All the results given below, however, have been obtained with the gas at room temperatures.

Determination of the Limits of the Test.—To determin the smallest quantity of each of the platinum metals that would give an unmistakable glow under the conditions of the above method, the following experiments were performed.

Platinum.—For this metal crystals of Merck's chloroplatinic acid were dissolved in water and the yellow solution thus obtained standardized and found to contain 0.00214 g. platinum per cc. Portions of this solution were successively diluted and known volumes of the solutions thus obtained were absorbed in asbestos paper and the test applied. The smallest amount of platinum that gave a reliable glow was that contained in 0.1 cc. of a colorless solution whose strength was 0.02 mg. platinum per cc. The limiting amount for platinum is therefore 0.002 mg. As this quantity of platinum was contained in 0.1 cc., the dilution was one part in fifty thousand.[1]

Palladium.—0.4856 g. Merck's palladium foil were dissolved in aqua regia and repeatedly evaporated to dryness with the addition of hydrochloric acid. The residue was then taken up with 100 cc. of water,

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[1] It would seem from the figure for the dilution that the glow test is less sensitive than the potassium iodide test proposed by Field, *Chem. News*, 45, 262 (1882), and now in general use in testing for small quantities of platinum. Field obtained a test for platinum in a dilution of one part in two million by allowing the solution tested to stand for some time after the addition of the potassium iodide. But it is to be noted that the amount of platinum present was 1 mg., a quantity five hundred times as great as that necessary for the glow test. It is obvious that the *small amount* and not the *dilution* is significant in stating the sensitiveness of the glow reaction. For, whatever the initial dilution be, the solution to be tested can by proper concentration give a glow test provided the limiting amount of platinum be present. To compare the two tests several solutions containing the limiting amount of platinum one part in 50,000 were prepared, and Field's test applied to each of them. Extreme care was taken with these tests which were controlled by blanks run under the same conditions, yet no change of color could be observed in the solutions though they were frequently examined for a period of two days. Similar solutions, however, very readily gave excellent glow tests. Again the potassium iodide test requires modification, if Fe (=ic), Ni, Pb, Cu, Hg, Bi, Au and substances yielding darkly colored solutions in general be present, whereas, as shown below, the glow test can for practical purposes be applied to solutions containing all the metals.

giving a dark brown solution containing 0.004856 g. palladium per cc. Portions of this solution were successively diluted and the test applied in the same manner as for platinum. As small a volume as 0.1 cc. of a colorless solution containing 0.0049 mg. palladium per cc. was found to be the smallest amount that gave a good glow. Thus the limit for palladium under the conditions of the test is 0.0005 mg.

Iridium.—Powdered iridium[1] was converted to sodium hexachloroiridate by intimately mixing the iridium with sodium chloride and heating the mixture in an atmosphere of chlorine. The fused mass thus obtained was dissolved in water, filtered and the reddish brown filtrate obtained used for the iridium tests. This solution was found on analysis to contain 0.004 g. iridium per cc. The limiting quantity of iridium that gave the test was 0.005 mg. This amount was contained in 0.1 cc. of a pale yellow solution formed by diluting one cc. of the original solution to 75 cc. The determinations for iridium were made under rather unfavorable conditions as the salt used contained an excess of alkali, the presence of which, as shown below, is not favorable to the test.

Rhodium.—A dark brown solution of rhodium tetrachloride was standardized and found to contain 0.1156 g. of rhodium per cc. Portions of this solution were repeatedly diluted and known volumes tested. The limit for this metal was found to be 0.0009 mg., which quantity was contained in 0.1 cc. of a colorless solution.

Osmium.—Finely divided metallic osmium was converted to sodium hexachlorosmate by the same method as that employed for the preparation of the corresponding iridium compound. Fairly strong solutions of this salt failed to give a glow. Solutions of sodium osmate, obtained by absorbing in sodium hydroxide the osmium tetroxide vapors which were distilled over in heating metallic osmium with fuming nitric acid, gave similar negative results. The failure to obtain the test with this metal is very likely due to the volatility of the osmium salts under the conditions of the test.

Ruthenium.—With this metal negative results were also obtained, even from fairly strong solutions of K_2RuCl_5, $K_4Ru(CN)_6.3H_2O$, and $K_2RuNOCl_5$.[2]

The cause of these negative results is probably the same as that stated for similar results obtained with osmium.

Having established the method and the limits for the various metals, it was thought desirable to ascertain the possible interference of other substances present in a solution to be tested for platinum. To this end, solutions were made containing chloroplatinic acid and a salt of

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[1] Obtained through the kindness of Belais and Cohn, New York, to whom we wish to express our thanks.

[2] These salts were obtained through the kindness of Prof. J. L. Howe, of Washington and Lee University, to whom we wish to acknowledge our thanks.

a foreign metal whose influence it was desired to determin. The amount of platinum present in the volume absorbed in no case deviated much from the average, which was 0.01 mg. In every case a distinct glow was obtained and the following table shows the ratio of the foreign metal to the platinum in the solutions tested.

RATIO OF THE METAL TO PLATINUM, 10,000 TO 1 OR GREATER.

Metal.	Compound used.
Silver	$AgNO_3$
Mercury	$HgNO_3.H_2O$
	$Hg(NO_3)_2.{}^1/_2H_2O$
	$HgCl$
Bismuth	$Bi(NO_3)_3.5H_2O$
Copper	$CuSO_4.5H_2O$
Cadmium	$Cd(NO_3)_2.3H_2O$
Antimony	$SbCl_3$
Tin	$SnCl_2.2H_2O$
Aluminium	$AlCl_3.6H_2O$

RATIO OF METAL TO PLATINUM, 3,000 TO 1 OR GREATER.

Metal.	Compound used.
Lead	$Pb(C_2H_3O_2)_2.3H_2O$
Chromium	$Cr(NO_3)_3.9H_2O$
Iron	$FeCl_3.6H_2O$
Nickel	$NiCl_2.6H_2O$
Cobalt	$CoCl_2.6H_2O$
Manganese	$MnCl_2.4H_2O$
Zinc	$ZnSO_4.7H_2O$
Barium	$BaCl_2.2H_2O$
Strontium	$SrCl_2.6H_2O$
Calcium	$CaCl_2$
Magnesium	$Mg(NO_3)_2.6H_2O$
Ammonium	NH_4Cl
	Sulfur
	Starch
	Gelatin

RATIO OF METAL TO PLATINUM, 1,000 TO 1 OR GREATER.

Metal.	Compound used.
Beryllium	$BeSO_4.4H_2O$
Lanthanum	$La(NO_3)_3.6H_2O$
Thorium	$Th(NO_3)_4.12H_2O$
Uranium	$UO_2(NO_3)_2.6H_2O$
Cerium	$Ce(NO_3)_3$
Erbium	$Er(NO_3)_3.6H_2O$
Zirconium	$Zr(NO_3)_4.5H_2O$
Yttrium	$Yt(NO_3)_3.4H_2O$
Tungsten	$Na_2WO_4.2H_2O$
Arsenic	As_2O_3
	$Cu_3(AsO_4)_2.4H_2O$
Praseodymium	$Pr(NO_3)_3.6H_2O$
Neodymium	$Nd(NO_3)_3.6H_2O$
Cesium	$CsCl$
Rubidium	$RbCl$.

Comments on Table and Further Experiments on Interfering Substances.—It is to be understood in the interpretation of the above table that the numbers given do not represent the maximum ratios of foreign metal to platinum that might be present in a solution tested for platinum except in the case of lead and arsenic. These metals hindered the test when present in proportions greater than those stated above; but with all the other metals tried, a good test was obtained in the ratios mentioned, and as these were fairly high no attempt was made to determin the maximum quantity of each metal in the presence of which the test would still apply. Uniform ratios, however, were not used because of the different solubilities of the various salts, and because of the comparative rarity of some of them.

Relatively large quantities of the alkalies were found to interfere and experiments made with solutions of Na_2SiO_3, Na_2CO_3, NaOH, $Na_2B_4O_7$, Na_2SO_4, NaCl, $NaKC_4H_4O_6$, NaF, KCl and LiCl showed eight hundred parts of alkali metals to one of platinum to be approximately the greatest ratio of alkali to platinum that would glow under the conditions of the test.[1]

With gold, experiments performed on a solution of auric chloride gave a maximum ratio of 500 parts of gold to one of platinum. On adding a crystal of oxalic acid and precipitating the gold, a test was obtained on a solution containing 2500 parts of gold to one of platinum.

In general it may be said that all substances which, after ignition, leave a heavy residue on the asbestos paper, impair the sensitiveness of the test insofar that quantities of platinum near the limit will not glow under these conditions. Also, solutions which are acid with strong nitric acid attack the asbestos paper, swelling it up and thus also decreasing the sensitiveness of the test. It can, however, be seen from the above results that none of the common metals offers any interference to the glow tests unless present in quantities that are considerably larger than the quantity of platinum.

Furthermore, the test was applied directly without going through any separations, to a sample of "black sand," of California, to platinum residues, sweepings and various forms of platinum waste. In each case a good test was obtained.

Tests made on solutions of palladium containing respectively lead, arsenic, and sodium (the least favorable of the common metals) seem to warrant the belief that palladium will be as little affected by the presence of other metals as was found in the case of platinum.

Summary.

1. The oxidation of the constituents of illuminating gas, particularly of hydrogen, with finely divided platinum, palladium, rhodium, or iridium

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[1] Phillips finds a similar interference of alkali in experiments on the oxidation of gases by means of palladiumized asbestos, *Am. Chem. J.*, 16, 168.

as catalytic agent is accompanied by a glow which is distinctly characteristic of these metals. Hence this glow may be used as a qualitative test for these metals.

2. This test is sensitive to extremely small quantities of the metals, the limits being: platinum, 0.002 mg.; palladium, 0.0005 mg.; rhodium, 0.0009 mg.; and iridium, 0.005 mg.

3. The presence of other substances does not for practical purposes interfere with this test. In fact, the test may be applied directly to a solution without preliminary treatment for the separation of other substances.

4. In an analysis where all the platinum metals are to be considered, this test may serve to show the presence of the platinum group with the exception of osmium and ruthenium, and also to confirm the presence of platinum, palladium, rhodium and iridium, when the metals have been separated. In most practical work, the "glow reaction" becomes distinctly a test for platinum, the most common metal of the group. For this latter purpose the glow test recommends itself strongly, because of its sensitiveness and the rapidity with which it gives results.

[Contribution from the Laboratory of Analytical Chemistry of the College of the City of New York.]

A STUDY OF THE FACTORS INFLUENCING THE SYSTEMATIC QUALITATIVE DETERMINATION OF BARIUM.[1]

By Louis J. Curtman and Edward Frankel.

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Experience with qualitative unknowns has shown that by means of a systematic qualitative analysis it is almost impossible to detect as much as 25 and in many cases 50 milligrams of barium with the group reagent $(NH_4)_2CO_3$. The failure to obtain the test at this point is due to losses which are entailed throughout the analysis. These may be accounted for under the following heads:

1. Influence of the hydrogen sulfide group;
2. Influence of the ammonium sulfide group;
3. Sensitiveness of the group and confirmatory reagent;
4. Influence of the presence of impurities (sulfates) in the various reagents employed.

1. *Hydrogen Sulfide Group.*—To determin the losses involved in the precipitation and removal of the metals of the copper group by hydrogen sulfide, a typical metal such as copper was taken. This metal furthermore possesses the advantages that its sulfide offers no difficulty in filtering and

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[1] Read at the March meeting of the New York Section of the American Chemical Society.