

then the crystal may grow. Its growth in the surface plane is limited by the interference of other crystals.

The electron micrographs and light micrographs of the oxidation experiments are shown in Figures 4 to 14. Table III summarizes the information taken from the electron micrographs. The films consist of small oxide crystals 100 to 2500 Å. in size, largely of irregular shapes with a few films showing definite crystal shapes. The oxide crystals are of the order of  $10^{-3}$  to  $10^{-5}$  of the linear dimension of the metal crystal or grain and  $10^{-6}$  to  $10^{-10}$  of the area.

The crystal size is a function of both time and temperature. The effect of temperature can be shown in the series of oxidation experiments on cobalt and on nickel. For the nickel oxidation series the average oxide crystal size increases from 400 Å. at 400° C. to 600 Å. at 550° C., while in the cobalt oxidation series the average oxide crystal size increases from 450 Å. at 200° C. to 1000 Å. at 500° C. The time effect on the oxide crystal size can be seen from an analysis of the cobalt, copper, and iron experiments.

The oxide films are largely nonuniform, as they consist of thicker and thinner sections. This indicates a multilayer film of oxide crystals. Thus, nucleation occurs in contact not only with the initial thin oxide layer but with other oxide crystals. This multilayer nucleation process does not form oxide crystals in as regular a manner as in the first layer. Therefore, clustering of crystals in the outer layers is noticed and nonuniform films are formed. Local concentrations of impurities or a small void in the initial oxide layer may partially account for this phenomenon.

It is noticed from an analysis of the electron micrographs that frequently one crystal appears to overlap an adjacent one, causing a broad boundary zone to appear. This may be the result of (1) the physical overlap of two crystals, or (2) occurrence of the contact zone between crystals at an angle to the electron beam. Diffraction effects may give the same effect as physical overlapping of the crystals. This overlapping phenomenon is noticed in many of the films.

The irregular shape of the oxide crystals in the first layer of the oxide film is to be expected. If a second or third layer of crystals is formed on top of the initial layer in a nonuniform manner, the previous restraints are relaxed and the new crystals may assume a more normal growth (Figure 6).

The oxides formed during the oxidation of columbium, tungsten, and chromium gave the smallest average crystal size. The largest crystals are formed during the oxidation of copper, iron, molybdenum, nickel, and cobalt. The first group probably form the more protective films against oxidation under the conditions of the experiment. If the materials are compared at the same temperature, nickel and cobalt would be included in the first group and not in the last. The more protective metals appear to form more uniform films, although the correlation is not general.

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## Detection of Palladium Using Pararosaniline Hydrochloride A Spot Test Procedure

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The reaction between palladous chloride and *p*-fuchsin has been studied. *p*-Fuchsin reacts with palladous chloride at a mole ratio of 2 to 3, apparently with the formation of a double salt. A spot test is proposed which is sensitive to 0.01 microgram of palladium at a limiting concentration of 1 part in 750,000. The reaction is highly selective.

**D**URING polarographic analyses in which pararosaniline hydrochloride was used as a maximum suppressor, it was observed that the pararosaniline hydrochloride color faded gradually upon the addition of palladous chloride. The investigation then under consideration included approximately one hundred different ions, and since the fading took place only in the presence of the palladous salt, it was thought that the reaction was sufficiently specific to warrant further study. In the investigation,

emphasis was placed on the adaptation of the reaction for use as a spot test, although considerable effort was directed toward elucidating the nature of the reaction.

#### REAGENTS AND CHEMICALS

Schultz No. 511 pararosaniline hydrochloride (*p*-fuchsin) from the National Aniline and Chemical Company, Inc., was made up to a strength of 0.01%, and c.p. palladium chloride to 0.01% (in respect to palladium) in distilled water. One per cent solutions of substances to be studied for interfering effects were made from c.p. chemicals; 2 *N* sodium hydroxide and 2 *N* acetic acids were used in adjusting the hydrogen-ion concentration of the test solutions.

#### APPARATUS

Spectrophotometric studies were made using a Model D Beckman spectrophotometer and 1.00-cm. cells.

Table I. Comparison of *p*-Fuchsin, Dimethylglyoxime, and *p*-Nitrosodiphenylamine Tests for Palladium

	<i>p</i> -Fuchsin <sup>a</sup>	Dimethylglyoxime	<i>p</i> -Nitrosodiphenylamine
Positive interferences	Au <sup>+++</sup> , Hg <sup>+</sup> , Pt <sup>++++</sup>	Au <sup>+++</sup>	Au <sup>+++</sup> , Pt <sup>++++</sup>
Negative interferences	Tl <sup>+</sup> , Bi <sup>+++</sup> , CN <sup>-</sup> , C <sub>2</sub> O <sub>4</sub> <sup>-</sup> , basic NH <sub>4</sub> <sup>+</sup> , F <sup>-</sup> , CNS <sup>-</sup> , formate, aniline, pyridine	Be <sup>++</sup> , Ga <sup>+++</sup> , basic NH <sub>4</sub> <sup>+</sup> , BO <sub>2</sub> <sup>-</sup> , S <sup>-</sup> , S <sub>2</sub> O <sub>3</sub> <sup>-</sup> , CN <sup>-</sup> , Fe(CN) <sub>6</sub> <sup>-</sup> , CNS <sup>-</sup> , C <sub>2</sub> O <sub>4</sub> <sup>-</sup>	Basic NH <sub>4</sub> <sup>+</sup> , NO <sub>2</sub> <sup>-</sup> , CN <sup>-</sup> , Fe(CN) <sub>6</sub> <sup>-</sup> , Fe <sup>-</sup> , (CN) <sub>5</sub> <sup>-</sup> , CNS <sup>-</sup>
Masking interferences	Sn <sup>++</sup> , V <sup>+++</sup> , MoO <sub>4</sub> <sup>-</sup> , I <sup>-</sup> , Ir <sup>+++</sup> , hypophosphite	Ti <sup>+++</sup> , hypophosphite, V <sup>+++</sup> , CrO <sub>4</sub> <sup>-</sup> , I <sup>-</sup> , Fe <sup>++</sup> , Fe <sup>+++</sup> , Rh <sup>+++</sup> , Ir <sup>++++</sup>	Ag <sup>+</sup> , Ti <sup>+++</sup> , Sn <sup>++</sup> , hypophosphite, VO <sub>2</sub> <sup>-</sup> , S <sup>-</sup> , Cr <sup>+++</sup> , CrO <sub>4</sub> <sup>-</sup> , MoO <sub>4</sub> <sup>-</sup> , I <sup>-</sup> , Co <sup>++</sup> , Ru <sup>+++</sup> , Ir <sup>++++</sup>
Sensitivity	LI = 0.01 microgram LC = 1:750,000	LI = 0.18 microgram LC = 1:100,000	LI = 0.005 microgram LC = 1:750,000

<sup>a</sup> Positive interferences listed refer to reactions with *p*-fuchsin. Actual test based on use of this reagent, however, is free from positive interferences.

## EXPERIMENTAL

Figure 1 shows the transmittancy curves for solutions of pararosaniline hydrochloride, palladous chloride, and a mixture of these two solutions. These transmittancy curves were determined using 0.005% solutions of pararosaniline hydrochloride and 0.0005% palladous chloride. The reference cell contained distilled water. The red color of the fuchsin solution fades on addition of the palladium salt. The maximum transmittancy difference occurs at a wave length of 380 mμ. Visual observation of this reaction discloses that dilute solutions of palladium cause a fading of the red fuchsin color, while large concentrations of palladium react with the fuchsin to form a finely dispersed brown precipitate.

The nature of the reaction involved was next investigated. The equivalent ratio of the two reactants was determined by means of a spectrophotometric titration. This procedure was based on the observation that the slopes of the transmittancy vs. molar concentration curves for the fuchsin and the palladous chloride solutions were quite different when determined at a wave length of 380 mμ. By adding known amounts of standard 0.000999 *M* palladium solution to fixed amounts (5.00 ml.) of 0.000247 *M* *p*-fuchsin, diluting the mixture to a total volume of 10.00 ml., determining the transmittancies, and plotting the log per cent transmittancy of each mixture, it was found that the equivalence point, as indicated by the intersection of the two curves, was at a mole ratio of *p*-fuchsin to palladous chloride of 2 to 3 (see Figure 2). As a check on this determination, analyses for carbon, hydrogen, and chlorine were run which confirmed that the composition of the reaction product was 2C<sub>19</sub>H<sub>17</sub>N<sub>3</sub>HCl·3PdCl<sub>2</sub>. Analytical calculations for 2C<sub>19</sub>H<sub>17</sub>N<sub>3</sub>HCl·3PdCl<sub>2</sub>: C, 38.71; H, 3.07; Cl, 24.06. Found: C, 38.73; H, 3.43; Cl, 24.36.

The nature of the fading action due to palladium was different from the fading brought about by acids or reducing agents. This was indicated by the transmittancy curves of acid-faded and sulfur dioxide-faded *p*-fuchsin as shown by Figure 3 when compared to Figure 1.

On the basis of the analytical data presented, the authors believe that the product of the palladous chloride-pararosaniline hydrochloride reaction is a double salt. The probability that the fading action was due to oxidation-reduction was ruled out on the basis of the transmittancy curves. The possibility that an inner-complex salt was formed was rejected because the functional groups of the pararosaniline were so far apart as to prohibit the formation of stable chelate rings. Normal salt formation was considered unlikely because the reaction occurred in slightly acidic medium. The belief that the reaction results in double salt formation is of interest, since this type of reaction has not previously been considered of analytical importance (1, 8, 11).

Because of the close similarity between members of the platinum group metals, special emphasis was placed on determining the possibility that other elements of this group might react with fuchsin in a manner similar to palladium. Transmittancy curves for mixtures of

*p*-fuchsin and ions of ruthenium, rhodium, osmium, iridium, and platinum were run and it was found that the transmittancies of mixtures of the reagent with these ions were additive.

## APPLICATIONS AS A SPOT TEST

There are several tests for palladium (3-7, 9, 10, 12, 15), the most sensitive of which is the *p*-nitrosodiphenylamine reaction (15). This test is sensitive to 0.005 microgram of palladium and there are few

interfering substances. The method can also be used for quantitative determinations of the metal.

The authors have investigated *p*-fuchsin as a reagent for detecting palladium and have found it to be highly selective in its reaction. Most of the important interferences can be eliminated by simple means and since *p*-fuchsin is a common stable organic compound, and the test is so sensitive and easy to make, this method of testing for palladium should find considerable application in research and routine analytical laboratories.

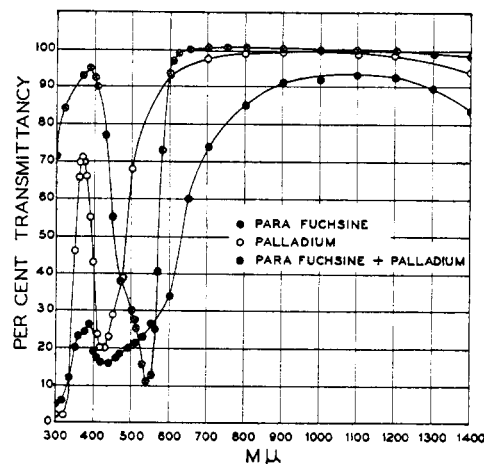


Figure 1. Transmittancy Curves

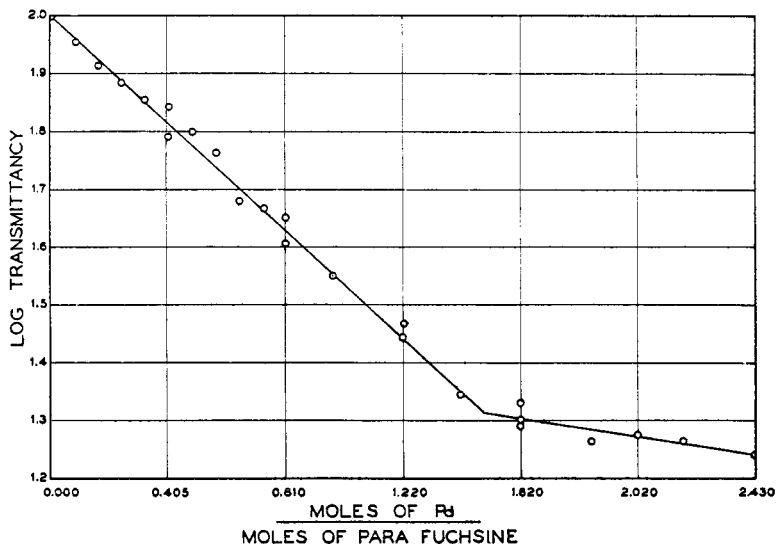


Figure 2. Equivalent Ratio of Reactants

## SCOPE OF INVESTIGATION

The interference studies were made using 1% solutions of the ions and compounds listed below (the ions are listed in their most common forms, although it is realized that in many cases they are actually present as complexes):

Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Cu<sup>++</sup>, Rb<sup>+</sup>, Ag<sup>+</sup>, Cs<sup>+</sup>, Au<sup>+++</sup>, Be<sup>++</sup>, Mg<sup>++</sup>, Ca<sup>++</sup>, Zn<sup>++</sup>, Sr<sup>++</sup>, Cd<sup>++</sup>, Ba<sup>++</sup>, Hg<sup>+</sup>, Hg<sup>++</sup>, BO<sub>2</sub><sup>-</sup>, B<sub>4</sub>O<sub>7</sub><sup>-</sup>, Al<sup>+++</sup>, Ga<sup>+++</sup>, Y<sup>+++</sup>, In<sup>+++</sup>, La<sup>+++</sup>, Ce<sup>+++</sup>, Ti<sup>+</sup>, CO<sub>3</sub><sup>-</sup>, SiO<sub>3</sub><sup>-</sup>, Ti<sup>+++</sup>, Sn<sup>+</sup>, Sn<sup>+++</sup>, Pb<sup>++</sup>, Zr<sup>+++</sup>, Th<sup>+++</sup>, NH<sub>4</sub><sup>+</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, P<sub>4</sub>O<sub>10</sub><sup>-</sup> (tetraphosphate), P<sub>6</sub>O<sub>18</sub><sup>-</sup> (hexametaphosphate), PO<sub>3</sub><sup>-</sup>, HPO<sub>4</sub><sup>-</sup>, P<sub>2</sub>O<sub>7</sub><sup>-</sup>, VO<sub>3</sub><sup>-</sup>, AsO<sub>3</sub><sup>-</sup>, HAsO<sub>4</sub><sup>-</sup>, Sb<sup>+++</sup>, Bi<sup>+++</sup>, S<sup>-</sup>, S<sub>2</sub>O<sub>3</sub><sup>-</sup>, SO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>-</sup>, Cr<sup>+++</sup>, CrO<sub>4</sub><sup>-</sup>, SeO<sub>3</sub><sup>-</sup>, SeO<sub>4</sub><sup>-</sup>, MoO<sub>4</sub><sup>-</sup>, WO<sub>4</sub><sup>-</sup>, TeO<sub>3</sub><sup>-</sup>, UO<sub>2</sub><sup>++</sup>, UO<sub>4</sub><sup>-</sup>, F<sup>-</sup>, Cl<sup>-</sup>, ClO<sub>3</sub><sup>-</sup>, Mn<sup>++</sup>, MnO<sub>4</sub><sup>-</sup>, Br<sup>+</sup>, BrO<sub>3</sub><sup>-</sup>, I<sup>-</sup>, IO<sub>3</sub><sup>-</sup>, ReO<sub>4</sub><sup>-</sup>, Fe<sup>++</sup>, Fe<sup>+++</sup>, Co<sup>++</sup>, Ni<sup>++</sup>, Ru<sup>+++</sup>, Rh<sup>+++</sup>, OsO<sub>3</sub><sup>-</sup>, Ir<sup>+++</sup>, Pt<sup>+++</sup>, CN<sup>-</sup>, Fe(CN)<sub>6</sub><sup>-</sup>, Fe(CN)<sub>6</sub><sup>4-</sup>, SCN<sup>-</sup>, acetate, oxalate, malonate, formate, adipate, succinate, phthalate, tartrate, citrate, lactate, gluconate, isoinositol, *d*-sorbitol, mannitol, sucrose, dextrose, aniline, pyridine, resorcinol.

The pH of solutions made acidic by the addition of a drop of solution of such salts as Ti<sup>+++</sup> and Sn<sup>+++</sup> was adjusted to a value of between 2 and 4, as indicated by universal indicator paper, by adding 2 to 3 drops of sodium hydroxide and then acetic acid until the desired pH was obtained. Usually 2 to 3 drops of acetic acid sufficed. The ratio of the substance being studied for interference to the palladium was 100 to 1 (14). This unfavorable ratio represented a severe study of the test and indicated what could be expected of it under ordinary working conditions.

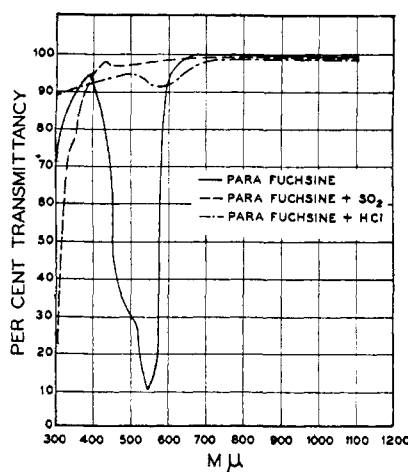


Figure 3. Transmittancy Curves

The test was carried out by placing one drop of palladium and one drop of distilled water in a depression of a spot plate. In an adjacent depression was placed one drop of a solution of the substance being studied for interference plus one drop of palladium solution, and to a third consecutive depression were added one drop of the substance and one drop of distilled water. This procedure ensured approximately equal concentrations of each reagent in any test solution. Into each of the three depressions one drop of the *p*-fuchsin was then measured. A faded brown color or a brown precipitate, depending on the concentration, constituted the test. Where the solution of the substance being studied was so acidic as to fade the *p*-fuchsin, the pH was adjusted as described above and then the volume of the solution containing only palladium salt was adjusted with distilled water before the *p*-fuchsin was added.

An investigation of the limit of identification and the limiting concentration (2) of the *p*-fuchsin test for palladium showed that the limit of identification was 0.01 microgram at a limiting con-

centration of 1 to 750,000. These limiting values were obtained using micro volumes of both the reagent and the palladium test solutions. The value for the limiting concentration does not include any volume increases due to the addition of reagents.

The interferences were classified in the manner described by West (13).

Positive interferences were given by auric gold, mercurous mercury, and large amounts of platonic platinum. These positive interferences can be obviated by making a confirmatory test with crystalline sodium hypophosphite. The hypophosphite reduces palladium in any solution with the formation, after a few seconds, of a black precipitate. Solutions containing gold or platinum alone are not visibly affected by hypophosphites, while solutions of mercurous mercury give a purple precipitate and this only upon standing. This confirmatory test should be run on solutions containing *p*-fuchsin, since otherwise mercurous mercury gives a black precipitate similar to that given by palladium. The reaction between platinum and *p*-fuchsin gives a visible effect only in solutions which contain over 5 mg. of platinum per ml.

Negative interferences were given by ammonium hydroxide, thallous thallium, nitrite, bismuth, cyanide, oxalate, and, upon standing (4 hours), fluoride, thiocyanate, formate, aniline, and pyridine. With the exception of bismuth, these negative interferences are due to competitive reactions which so reduce the effective concentration of palladium that it no longer gives its characteristic reaction with *p*-fuchsin. In the case of thallium, the reaction results in the formation of a precipitate, while in the case of the other ions, soluble complexes are formed. As a rule, these negative interferences would apply to any test for palladium.

Masking interferences were given by stannous tin, vanadous vanadium, hypophosphite, permanganate, iodide, and iridium. The tin, hypophosphite, and iodide react with palladium to give dark precipitates, while the other ions interfere, owing to the intense colors of their solutions. Of these interferences, the only one of practical significance is that of iridium; it can be eliminated by addition of thiosulfate until the color of the iridium just disappears. Excess thiosulfate should be avoided. Iridium in concentrations of less than 5 mg. per ml. does not mask the *p*-fuchsin test.

A comparison of the *p*-fuchsin test with the dimethylglyoxime and *p*-nitrosodiphenylamine tests for palladium is shown in Table I. All three tests were very satisfactory. Advantages claimed for the *p*-fuchsin test are that the positive interferences can be very easily obviated, and that no interferences of any type are given by other members of the platinum group of metals, provided that the initial concentration of the solution to be analyzed does not exceed 0.05%. Because of the nature of the test, it suffers least from masking interferences due to colored ions.

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