3-Hydroxy-1-*p*-sulfonatophenyl-3-phenyltriazine as a Colorimetric Reagent for Palladium

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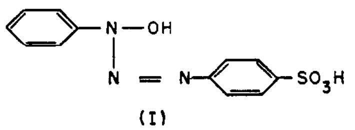
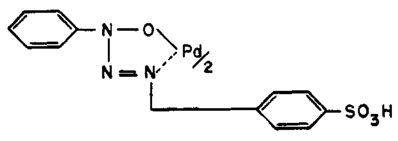
▶ 3-Hydroxy-1-p-sulfonatophenyl-3-phenyltriazine is an excellent reagent for the colorimetric estimation of palladium, either as such or in the presence of nickel(II), copper(II), iron(III), cobalt(II), silver, and especially members of the platinum group—platinum(IV), rhodium(IV), iridium(III), and ruthenium(III). Apart from its other highly desirable qualities, such as solubility of the reagent and the complex in water, almost instantaneous development of color and stability for 24 hours in a wide range of temperature, wide range of permissible pH (1.7 to 4.4), and easy adjustment using mineral acid alone, the reagent has great tolerance for the members of the platinum group and is superior to other palladium reagents used so far for this purpose.

THE USE of 3-hydroxy-1,3-diphenyltriazine as a gravimetric reagent for palladium has been described (7). Its high selectivity toward palladium and its fairly high sensitivity suggested that the sulfonic acid derivative of such a compound, either as such or in the form of its sodium salt (both soluble in water) should prove useful as a colorimetric reagent for palladium. 3 - Hydroxy - 1 - *p* - sulfonatophenyl-3-phenyltriazine (I)



(I)

has proved to be an excellent reagent for the colorimetric estimation of palladium as such or in the presence of other elements, especially the members of the platinum group. The soluble palladium complex formed by it may be best represented by the chelate structure (II).



(II)

In many respects, it is superior to other known palladium reagents for the colorimetric estimation of palladium.

3 - Hydroxy - 1 - *p* - sulfonatophenyl-3 - phenyltriazine posesses many of the properties of an ideal colorimetric reagent.

It is stable toward heat, light, and air, and can be preserved indefinitely at room temperature.

It is soluble in water, and the aqueous solution remains practically unaltered up to 48 hours.

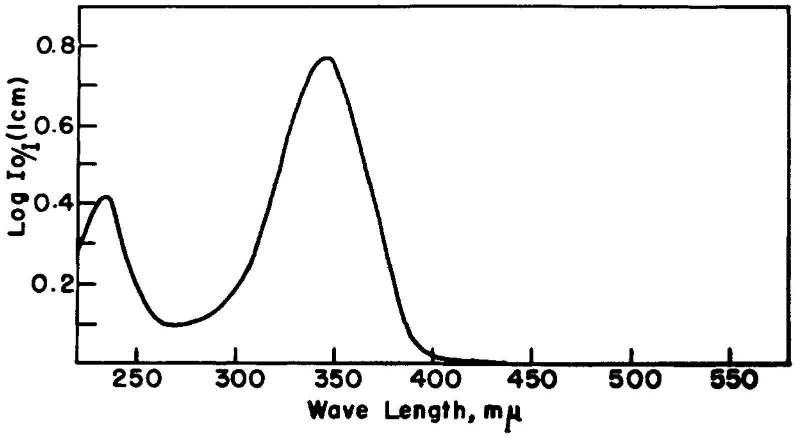


Figure 1. Spectral characteristics of reagent

9.3 p.p.m. of sulfonic reagent in water

The palladium complex is soluble in water.

Color development with palladium is almost instantaneous. Full development takes place in less than 5 minutes and the intensity remains unaltered, even after 24 hours.

Color development is not sensitive to pH variation, but remains steady between pH 1.7 and 4.4. pH can be adjusted with mineral acid alone. Color intensity is also unaffected by variation in temperature from 25° to 85° C. Full development of color takes place without any undue excess of reagent.

Color development follows Beer's law.

The reagent and its complex have reasonably well separated absorption peaks, so that excess reagent does not interfere in the photometric estimation.

Color development is very highly selective. There is no interference from most foreign ions, including other members of the platinum group.

EXPERIMENTAL

Preparation of Reagent. Because of the soluble nature of the reagent, the following procedure should be strictly followed, to avoid possible loss.

Sulfanilic acid (8.6 grams) was dissolved in 40 ml. of 5% sodium hydroxide solution and 3.5 grams of sodium nitrite was added. To this solution crushed ice was added and the reaction mixture was slowly poured into 20 ml. of concentrated hydrochloric acid, also containing crushed ice, with mechanical stirring. The diazonium salt thus obtained was then slowly added under mechanical stirring to 5.4 grams of phenylhydroxylamine dissolved in 125 ml. of 20% v./v. alcohol and containing a sufficient quantity of crushed ice. Small portions of sodium acetate (50 grams in 100 ml. of water) were added occasionally to the reaction mixture to prevent it from becoming too acidic. The temperature during the entire course of reaction was kept at about 0° C. The precipitated sulfonic acid derivative was filtered under suction, washed twice with a small amount of ice water, and crystallized from a large volume of alcohol. It was obtained as 5 grams of light green crystals, actually the sodium salt of the sulfonic acid, which had no sharp melting point. It started decomposing at 157° C.

Analysis. Found: C, 43.8; H, 4.0; N, 12.42; S, 10.48%. $(C_{12}H_{10}N_3O)SO_3Na.H_2O$ requires: C, 43.3; H, 3.9; N, 12.32; S, 9.9%.

Solubility, 2.9 grams per 100 ml. of water at 23° C.

Spectral Characteristics. In aqueous solution, $\lambda_{max} = 235, 345$ mμ; log E = 4.1782, 4.4405 (Figure 1).

Reagent solution, 0.1% w./v. solution in distilled water.

Standard Palladium Solutions. Approximately 0.5 gram of palladium chloride was dissolved in a little water containing 3 ml. of concentrated hydrochloric acid and the volume was made to 500 ml. The palladium content was determined by using dimethylglyoxime and 3-hydroxy-1,3-diphenyltriazine (developed by the authors) and was found to be 0.6216 gram of palladium per liter. When 159.9 ml. of this solution was made to 1 liter, it contained 100 γ of palladium per ml. This stock solution was further diluted 10 times, so that 1 ml. of the diluted solution contained 10 γ of palladium.

Solution of Diverse Ions. The reagent grade soluble salts, usually chloride, nitrate, or sulfate, were employed for the preparation of the solutions of inorganic ions. The solutions were diluted in such a way that they contained 1 mg. of the metallic element per ml.

Instruments. A Beckman pH meter, Model H-2, was used for pH measurements. Absorbance measurements were made with a Beckman quartz spectrophotometer, Model DU, using 1.00-cm. quartz cells for the ultraviolet region and Corex cells for the visible region. Visual color comparisons were made in 50-ml. Nessler tubes of the standard type.

Absorption Curves for Palladium Complex and Reagent. Twenty milliliters of palladium solution containing 10 p.p.m. of palladium was pipetted into a 100-ml. measuring flask, and 0.1 ml. of 1*N* hydrochloric acid was added, so that the pH after dilution was about 3.0. Then 5 ml. of 0.1% w./v. aqueous reagent solution was added and after a little shaking the volume was made to 100 ml. The resulting solution contained 2 p.p.m. of palladium.

A blank solution was prepared by pipetting 5 ml. of the reagent solution into a 100-ml. flask and making the volume up to the mark. There was no difference in the blank solution prepared as given above and that prepared by adding 0.1 ml. of hydrochloric acid to bring the pH to about 3.0. Hence addition of the acid in the blank solution was not considered imperative.

Figure 2 gives the absorbance curves of the palladium complex with a "reagent-blank solution" and reagent solution with water as blank. The absorbance of the reagent solution falls sharply after 390 mμ and is almost negligible at 430 mμ. The absorption peak of the palladium complex, in this region, is at 413 mμ, which is also true for the palladium complex of the parent reagent, 3-hydroxy-1,3-diphenyltriazine (7). However, as there is no substantial fall in absorbance up to 420 mμ, where the interference by the reagent is also decreased, 420 mμ was considered a suitable wave length for the palladium estimations; 430 mμ can also be used with advantage, as at this wave length interference by the reagent is almost negligible and so water can be used as a blank.

Effect of pH. Solutions used for studying the effect of pH on color reaction were prepared as directed above, except that different amounts of 1*N* hydrochloric acid, 1*N* sulfuric acid, or 1*N* nitric acid, and 10% w./v. sodium acetate or sodium potassium tartrate were added, so that the final pH values ranged from 1.2 to 6.5. When 1*N* hydrochloric or 1*N* sulfuric acid was used for adjusting pH, the range of constant maximum absorbance was between 2.5 and 4.4. At pH below 2.5, there was a slight turbidity, resulting in lower absorbance. However, when nitric acid was used, the pH range increased and was between 1.7 and 4.4 (Figure 3). pH can be better adjusted by using acid alone without sodium acetate or sodium potassium tartrate, as these buffering agents give turbidity when used in higher concentrations. Hence in the estimations, only 1*N* nitric acid was used for the adjustment of pH, which was kept between 2.5 and 3.0 to increase the specificity of the reagent

Table I. Tolerance of Diverse Ions

Ion	Added as	Limiting Concn., P.P.M.
Ni(II)	Chloride	10
Cu(II)	Sulfate	3
Fe(II)	Sulfate	2
Fe(III)	Sulfate	20
Co(II)	Sulfate	2
Rh(IV)	Sulfate	10
Ir(III)	Chloride	30
Pt(IV)	Chloride	40
Ru(III)	Chloride	1
Ag(I)[a]	Nitrate	75

[a] For testing tolerance of silver, a solution of palladium nitrate was used.

Reagent Concentration and Mole Ratio. A series of solutions was prepared in which the mole ratio of palladium to reagent was from 1:1 to 1:15. pH was adjusted to about 2.5 by using 0.2 ml. of 1*N* nitric acid. Absorbance was measured for each solution after about 5 minutes at 430 mμ, using water as blank. Figure 4 shows the effect of moles of reagent per mole of palladium on absorbance. The fact that there is no sharp peak indicates that the complex is appreciably dissociated in solution. Full color development is ensured at 1 to 8 ratio of palladium to reagent.

Rate of Reaction and Stability of Complex. The color formation of palladium complex with the reagent was almost instantaneous and the color was very stable. There was no difference in the absorbance taken after 5 minutes and after 24 hours.

Table II. Properties of 3-Hydroxy-1-*p*-sulfonatophenyl-3-phenyltriazine, *p*-Nitrosodiphenylamine, *p*-Nitrosodiethyl, and Dimethylaniline

Properties	*p*-Nitroso-diphenylamine	*p*-Nitroso-diethyl or Methylaniline	3-Hydroxy-1-*p*-sulfonatophenyl-3-phenyltriazine
Solubility	Insol. in water, moderately sol. in alcohol	Slightly sol. in water, sol. in alcohol	Sol. in water
Time of maximum color intensity	30 min.	5 min.	5 min.
Stability of color	1 to 2 hours	4 hours	24 hours or more
pH	2.0 to 2.1	4.0 to 5.0	1.7 to 4.4
Use of buffer	Absolutely essential	Absolutely essential	Not necessary
Temp. effect	Must keep within 5° C.	Slight difference at 20° C. variation	No difference up to 60° C. variation
Concn. of sodium chloride permissible	0.03*M*	0.05*M*	0.025*M*
Tolerance of diverse ions, p.p.m.			
Ni(II)	20	15	10
Cu(II)	50	3	3
Fe(II)		Data not given	2
Fe(III)	30	2	20
Co(II)	10	10	2
Rh(IV)	1	1	10
Ir(III)	1	1	30
Pt(IV)	20	20	40
Ru(III)	. . .	Data not given	1
Ag(I)	200	200	75
Au(III)	1	0.5	0

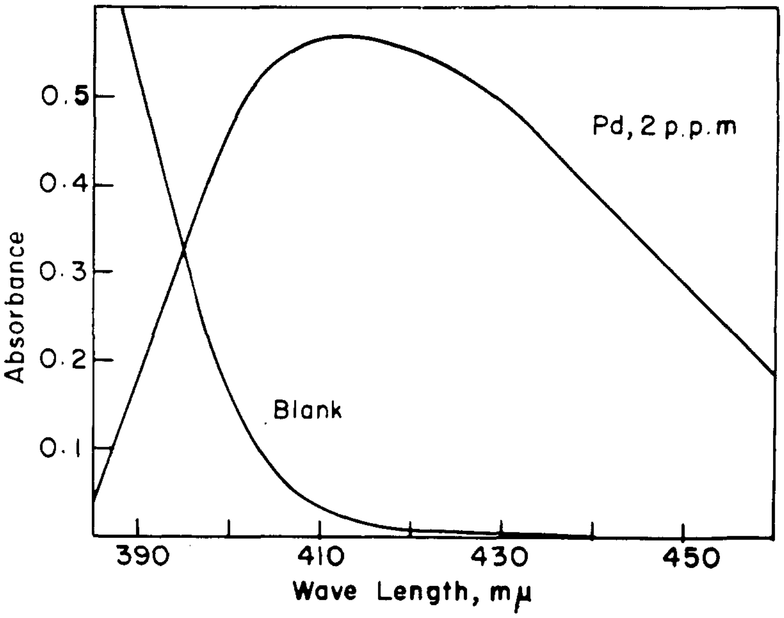


Figure 2. Absorbance curves

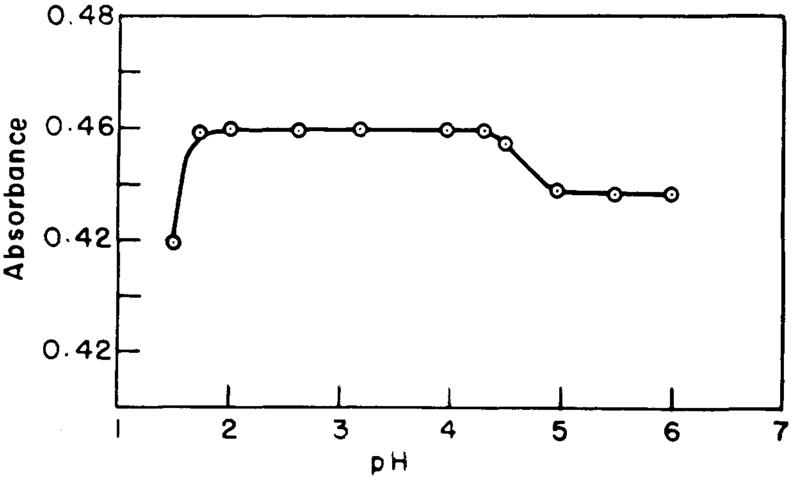


Figure 3. Effect of pH

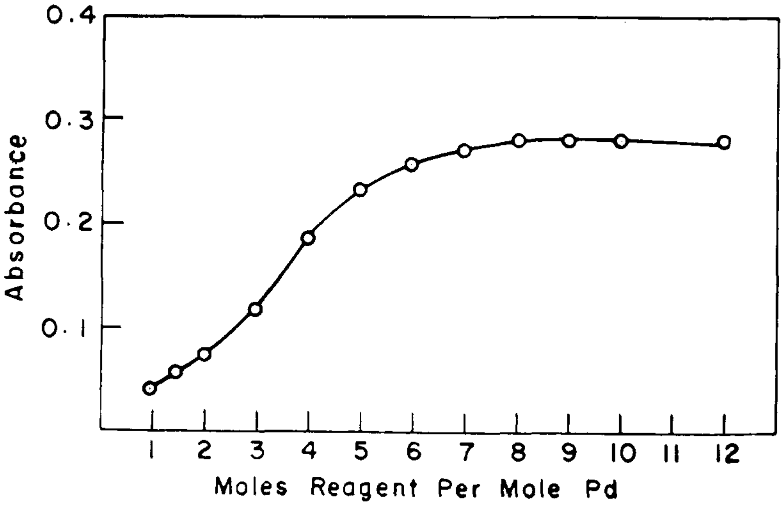


Figure 4. Effect of reagent concentration

Beer's Law. Aliquot portions of standard palladium solution were pipetted into 100-ml. flasks, so that the palladium concentration finally corresponds to 0.2 to 6 p.p.m., and 0.2 ml. of 1*N* nitric acid and 10 ml. of the reagent solution were added. The volume was made up to the mark and the absorbance was measured after about 5 minutes both at 420 mμ using reagent as blank and at 430 mμ using water as blank. Beer's law is obeyed in both cases. A 420 mμ the concentration range is from 0.2 to 5 p.p.m. and at 430 mμ it is from 0.4 to 6 p.p.m. of palladium. Larger amounts of palladium can be estimated at higher wave lengths—i.e., 435 to 450 mμ.

Effect of Temperature on Reaction. Two 10-ml. samples of standard palladium solution containing 10 p.p m. of palladium were taken in two beakers. To one, 0.2 ml. of 1*N* nitric acid and to the other 0.1 ml. of 1*N* hydrochloric acid was added, followed by 5 ml. of the reagent solution in each case. Then 50 ml. of water was added to each beaker and the contents were kept for heating on a water bath. Initial temperature was 25° C. The beakers with the contents were heated to 85° C. and maintained at the temperature for about 10 minutes. After cooling, the contents were separately transferred into 100-ml. flasks and volume was made up to the mark. The blank reagent solution was treated simultaneously in a similar way. Absorbance was measured at 420 mμ. There was no difference in the absorbance at 25° and 85° C., and the use of hydrochloric acid or nitric acid for the adjustment of pH made no difference.

It can, therefore, be concluded that there is no change in color intensity over a temperature range of 25° to 85° C.

Sensitivity of Reaction. Fifty-milliliter solutions containing 0.5 ml. of the reagent solution, 0.1*N* hydrochloric acid, and 0.02 to 0.10 p.p.m. of palladium solution were prepared in Nessler's cylinders. The 0.05-p.p.m. palladium solution was easily distinguishable from a blank. Thus the sensitivity of the color reaction could be taken to be 1 part of palladium in 20,000,000 parts of solution.

Spot plate sensitivity was determined by taking 0.05 ml. of standard palladium solution to a depression of a white porcelain spot plate, and adding 0.05 ml. of 0.1*N* hydrochloric acid and 0.05 ml. of 0.05% reagent solution; 0.05 γ of palladium in 0.15 ml. of solution could be distinctly detected.

Effect of Adding Neutral Salts (sodium chloride used). Ten milliliters of standard palladium solution containing 10 p.p.m. was pipetted into a 100-ml. flask and 1*N* hydrochloric or 1*N* nitric acid was added for pH adjustment. Different quantities of 5% sodium chloride solution, followed by 5 ml. of reagent solution, were added. The permissible concentration was found to be $0.025M$. There was no appreciable difference between hydrochloric and nitric acid.

Tolerance of Diverse Ions. Ten milliliters of standard palladium solution containing 10 p.p.m. of palladium was pipetted into a 100-ml. flask and the diverse ion solution was added. The pH was adjusted by adding 0.2 ml. of $1N$ nitric acid, 5 ml. of reagent solution was added, and the volume was made to 100 ml. The final solution contained 1 p.p.m. of palladium. The absorbance was measured after 5 to 10 minutes at 420 mμ, using reagent as blank, and also sometimes at 430 mμ using water as blank.

An ion was considered to interfere if the resulting solution differed by 0.005 in absorbance from that containing only palladium without any diverse ion. Table I summarizes the tolerance of the diverse ions as parts per million of ions.

Iron(III) reacts with the reagent at low pH; it shows a peak at about 400 mμ and interferes with the palladium estimation. This interference, however, was completely eliminated by masking it with 1 ml. of 5% sodium fluoride.

The color of iridium chloride was bleached by addition of the reagent, but this created no interference.

Gold(III) is reduced by the reagent to the metallic state and hence interferes. Lead salts also created some interference in the estimation of palladium, which is difficult to explain.

In examining the tolerance of various diverse ions, only those ions which normally occur with palladium or are usually present in the important alloys of palladium have been employed. Considering the specificity of the reagent at low pH, it is certain that palladium could be estimated in the presence of many other elements without interference, but the actual experiments were not carried out.

DISCUSSION

For a fuller understanding of the qualities of 3-hydroxy-1-*p*-sulfonatophenyl-3-phenyltriazine as a colorimetric reagent a comparison with other reagents (*1–6, 8, 9*) is desirable. The majority of these do not possess many of the desirable properties required by a colorimetric reagent. In certain cases the pH adjustment is very rigid and the range allowed is almost unworkable; in others, the colored complex has to be extracted with solvent before taking absorbance. Very often, the colored complexes are stable over only a short period and very susceptible to temperature variation. Above all, in many cases, neither the reagents nor the complexes formed by them are soluble in water. For these reasons, comparison is confined to *p*-nitrosodiphenylamine and *p*-nitrosodialkylaniline, which are currently favored for this purpose. These reagents have been developed by Yoe and Overholser (*8, 9*). The comparative data are given in Table II.

In many respects 3-hydroxy-1-*p*-sulfonatophenyl-3-phenyltriazine is very superior to other known reagents. The exceptional stability of its palladium complex is mainly due to the fact that it is an inner complex and not a coordination complex, as are most of the other reagents discussed.

Difficulties of partial salting out of the complex in the presence of an excess of neutral salts could possibly be counteracted by introducing a second sulfonic group in the reagent. Such a compound, as well as its complexes will be much more soluble in water and may prove more useful as a colorimetric reagent.

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Use of Ion Exchange Resins for Determination of Uranium in Ores and Solutions

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▶The separation of uranium from the ions interfering with its analysis is accomplished by the adsorption of the uranium(VI) sulfate complex on a quaternary ammonium anion exchange resin. Interference of such ions as iron(III) and vanadium(V) is avoided by their preferential reduction with sulfurous acid so that they, as well as other cations, are not retained by the resin. Uranium is eluted for analysis by dilute perchloric acid. The method is applicable to both solutions and ores.

The use of ion exchange resins of the quaternary ammonium type to separate uranium(VI) from the ions that interfere in its determination was first described at the International Conference on the Peaceful Uses of Atomic Energy (*4*). As a result of recent declassification of some U. S. Atomic Energy Commission reports (*2, 3*) it is now possible to disclose the complete experimental procedure for this separation.

In the interim since the Geneva Conference a method has been published for the determination of uranium in solution, similarly based on the adsorption of uranium on an ion exchange resin (*1*). The present procedure is somewhat simpler in the reagents required and has been adapted to the analysis of ores.

ORE SOLUTION

Two methods for the opening of uranium-bearing ores were investigated in