THE MICRODETERMINATION OF PALLADIUM WITH ALPHA-FURIL DIOXIME AND CYCLOHEXANEDIONEDIOXIME

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Lucien Barnes, Jr.

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By

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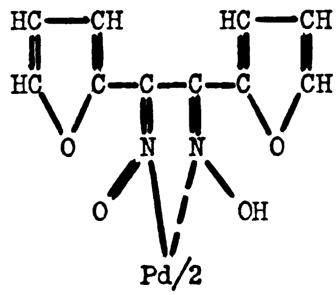
INTRODUCTION

With the increased use of organic reagents for the quantitative determination of the elements, the 1,2-dioximes have received considerable attention as specific reagents for the determination of nickel and palladium. Of these, dimethylglyoxime is undoubtedly the best known. Other reagents that have been investigated include alpha-furildioxime, cyclohexanedionedioxime, alpha-benzildioxime, and benzoylmethylglyoxime.

Dimethylglyoxime, as a reagent for the determination of palladium and nickel, has three disadvantages that have had an influence on leading investigators to study the possibility of using other reagents. These disadvantages are:

1. The limited water solubility of dimethylglyoxime makes it necessary to prepare the reagent solution in alcohol or acetone, which, in turn, increases the chance of coprecipitation of the reagent.
2. The gravimetric conversion factor with dimethylglyoxime is not as favorable as it is with the other more heavily substituted dioximes.
3. It has been reported (1, 2) that often it is necessary to allow a long period of standing to insure complete precipitation of palladium with dimethylglyoxime.

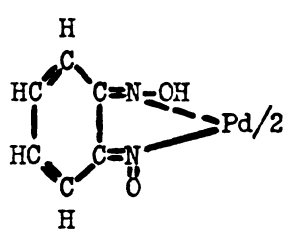
B. A. Soule (3) in 1925 investigated the use of alpha-furildioxime for the qualitative detection and quantitative determination of nickel. He found it to be much more sensitive than dimethylglyoxime as a qualitative reagent, and to be soluble in hot water to the extent of about one percent. Soule was also able to use the reagent successfully for the macro-gravimetric determination of nickel. In 1942, D. R. Beasecker (4) developed an accurate method for the microdetermination of palladium and nickel using alpha-furildioxime as the precipitating agent, and his procedure was adopted here for subsequent work with the reagent. From a strongly acid solution, palladium yields with alpha-furildioxime an amorphous yellow-orange colored precipitate having the structure:



Cyclohexanedionedioxime, commonly referred to as "nioxime", was first prepared by Wallach (5), who found it to be a more sensitive qualitative reagent for nickel than dimethylglyoxime, and stated that it had the further advantage of greater water solubility. In 1940 Diehl (6) suggested its use as an analytical agent, but stated that there was no satisfactory method for its synthesis. This difficulty was overcome in 1945 when G. F. Smith (7) and his co-workers successfully developed two methods for the preparation of nioxime. One of Smith's methods was later greatly improved by C. C. Hach (8), and the reagent may now be purchased from the Hach Chemical and Oxygen Company, Ames, Iowa. Johnson and Simmons (9), in 1946, used nioxime in the gravimetric determination of nickel, but reported high results which they attributed to occlusion of excess reagent. In 1948, Voter, Banks, and Diehl (8), successfully used nioxime for the determination of nickel, applying a correction factor for the amount of reagent coprecipitated when the nickel present exceeded fifteen milligrams. Later, these same investigators used the reagent for the macrodetermination of palladium (10). The advantages claimed for the use of nioxime were:

1. It is soluble to the extent of 0.8 g/100 ml. in cold water, thus making it convenient to use and minimizing coprecipitation of the reagent, and separation of the excess reagent on standing.
2. After a brief period of digestion at 60 degrees centigrade, filtration may be made from the hot solution, thereby shortening the time required for the determination with no loss of accuracy involved.
3. Palladium could be determined in the presence of platinum in amounts up to one tenth of a gram.
4. The presence of a one hundred and fifty percent excess of reagent does not affect the accuracy of the determination.

From solutions of pH range zero to five, palladium forms a bright yellow colored precipitate with nioxime, the structural formula of which is indicated below:



The object of this study is:

1. To determine the effect of certain foreign ions upon the microdetermination of palladium using alpha-furildioxime as the precipitating agent.

2. To find a complexing agent for ferric iron so that palladium may be determined quantitatively in its presence with alpha-furildioxime.

3. To develop a micromethod for the determination of palladium using nioxime as the precipitating agent.

EXPERIMENTAL

I. The Microdetermination of Palladium With alpha-Furildioxime

A. Preparation and Standardization of a Palladium Chloride Stock Solution: A stock solution of palladium dichloride was prepared by dissolving 1.0 g. of palladium dichloride in seventy-five milliliters of 1:9 hydrochloric acid. The resulting solution, when made up to a volume of fifteen hundred milliliters, had a concentration of approximately 0.4 mg. of palladium per milliliter, and a pH of 1.3 as measured by the glass electrode.

The stock solution was standardized by three methods: 1. A microstandardization using dimethylglyoxime. 2. A microstandardization using alpha-furildioxime. 3. A macrostandardization using dimethylglyoxime to serve as a check on the two microstandardizations.

The procedure for the macrostandardization of the stock solution with dimethylglyoxime was that of Gilchrist and Wichers (11) and is as follows: Twenty-five milliliters of the stock solution were diluted to one hundred milliliters with distilled water, two milliliters of concentrated hydrochloric acid (12 M) were added, and the palladium was precipitated by slowly adding 3.4 ml. of a one percent solution of dimethylglyoxime in alcohol. The solution was allowed to stand for three hours, and was then filtered through a previously weighed filtering crucible. The precipitate was washed with dilute hydrochloric acid (1:99), then with hot water, dried at 120°C, and weighed as palladium dimethylglyoxime. The standardization was repeated using fifty milliliter samples. Applying this procedure to the microstandardization, five milliliters of the stock solution were pipetted into previously weighed Schwarz-Bergkampf Pyrex filter beakers. Two drops of concentrated hydrochloric acid (12 M) were added, and the palladium precipitated with 0.7 ml. of a one percent solution of dimethylglyoxime. The solution was allowed to stand for three hours at room temperature. It was then filtered, washed with dilute (1:99) hydrochloric acid, then with hot water, dried for periods of one hour at 120°C, and weighed to constant weight as palladium dimethylglyoxime which contains 31.67% palladium.

For the microstandardization with alpha-furildioxime the method as developed by Beasecker (4) was employed: Five milliliters of the stock solution were pipetted into previously weighed filter beakers, 0.5 ml. of concentrated hydrochloric acid (12 M) was added, the solution was heated on the water bath, and the palladium precipitated by the addition of two milliliters of a hot one percent aqueous solution of alpha-furildioxime. The solution was agitated to hasten coagulation of the precipitate, and allowed to remain on the bath for ten minutes. The precipitate was filtered one hour later, washed three times with warm hydrochloric acid (1:99), and then six times with hot water. It was then dried to constant weight at 120°C, the initial drying period consisting of two hours, and the subsequent drying periods one hour. Palladium furildioxime contains 19.58% palladium. The results of the standardizations are indicated in tables I and II.

TABLE I

Macrostandardization of $PdCl_2$ Stock Solution

Using Dimethylglyoxime

Mg. Pd / 25 ml.	Mg. Pd / 5 ml.
10.546	2.109
10.578	2.116
10.609	2.122
10.641	2.128
Mg. Pd / 50 ml.	
21.210	2.121
21.219	2.122
21.171	2.117
	Average: 2.119

TABLE II

Microstandardization of $PdCl_2$ Stock Solution

Using Dimethylglyoxime and Alpha-Furildioxime

Dimethylglyoxime	Alpha-Furildioxime
Mg. Pd / 5 ml.	Mg. Pd / 5 ml.
2.116	2.115
2.119	2.115
2.117	2.118
2.120	2.116
2.113	2.115
2.116	2.121
Average: 2.117	Average: 2.117

The mean result of the two microstandardizations is 2.117 mg. Pd / 5 ml., and this figure was taken as being the true concentration of the stock solution.

B. The Reagent Alpha-Furildioxime: A one percent solution of alpha-furildioxime was prepared by dissolving one gram of the reagent in one hundred milliliters of warm water. The solution was then filtered four times through number 42 Whatman filter paper to remove traces of a brown sediment that were originally present. Upon cooling, the reagent crystallized into fine white needles in a colorless solution. It is, therefore, necessary to warm the reagent solution before use. After a period of four or five weeks, when exposed to daylight, the solution takes on an amber color, and small brown colored particles are observed on the bottom of the container. Upon warming, these brown colored particles do not dissolve, however if they are filtered off prior to use, the reagent solution still yields accurate results, as will be indicated later in this report.

C. Apparatus: One type of filter beaker was used throughout this experiment. This type, known as the Schwarz-Bergkampf filter beaker, is made of Pyrex and has a capacity of approximately ten milliliters. The advantage of using this type beaker over the conventional filterstick technique, is that they are decidedly easier to handle. The beakers are cleaned readily, and very few were found to pass precipitate through the sintered glass disc that serves as the filter. All weighings were made in a constant temperature balance room (78° F) on an Ainsworth optical lever microbalance. This balance weighs directly to micrograms. Counterpoise weighing was used exclusively.

The procedure used in weighing was the same as that used by Beasecker (4), and is as follows: After removing the sample beakers and counterpoise from the drying oven, they were allowed to cool for exactly thirty minutes, next to the microbalance, in a desiccator over Dehydrite. The counterpoise and sample beaker were then placed upon the balance pans, the approximate weight found, and the exact weight recorded five minutes later. By rigorous adherence to the above time schedule it was usually possible to obtain constant weights, within five micrograms, upon the third or fourth weighing. However, during very humid weather, it was exceptionally difficult to obtain constant weights. It was observed that constant weights were obtained most readily when the relative humidity was in the neighborhood of fifty to fifty-five percent.

D. The Effect of Sodium, Sulfate, and Ferric Ions: The effect of sodium and sulfate ions upon the determination of palladium with alpha-furildioxime was determined by adding an aqueous solution of sodium sulfate to samples of the stock solution, and carrying out the precipitation in the regular manner. It was noticed, that during the filtration, the normal yellow-orange colored precipitate developed cracks. Therefore it is suggested, that when carrying out the determination in the presence of these ions, not too much time be allowed to elapse between the time that the precipitate is aspirated dry and the subsequent washing. The results in table III indicate that sodium and sulfate ions do not appreciably interfere with the determination.

The effect of ferric iron, in the form of ferric chloride is also indicated in table III. The results are slightly high, and therefore, palladium cannot be accurately determined in the presence of ferric ions unless some suitable complexing agent for the iron is present. The precipitate contaminated with iron is brown in color.

TABLE III

Effect of Sodium, Sulfate, and Ferric Ions

Upon the Determination of Palladium With Alpha-Furildioxime

Other Substances Present		Mg. Pd Present	Mg. Pd Found	Error Mg.	Error %
Substance	Mg.				
Na_2SO_4	5	2.117	2.115	-0.002	-0.10
Na_2SO_4	5	2.117	2.123	+0.006	+0.28
Na_2SO	5	2.117	2.111	-0.006	-0.28
Fe^{+3}	2	2.117	2.125	+0.008	+0.38
Fe^{+3}	2	2.117	2.125	+0.008	+0.38
Fe^{+3}	2	2.117	2.127	+0.010	+0.47
Fe^{+3}	2	2.117	2.126	+0.009	+0.42

E. The Effect of Citrate, Tartrate, and Versene in Complexing Ferric Iron: In the attempt to find a suitable complexing agent for ferric iron, citric acid, tartaric acid and Versene (the sodium salt of ethylenediamine tetra acetic acid) were used. In the cases of citric and tartaric acids, one milliliter of a forty percent solution of the acid was added to the sample of the stock solution containing two milligrams of ferric iron. With Versene, six tenths of a milliliter of a thirty-five percent solution was used. The results are shown in table IV, and indicate that none of these agents effectively complex the iron.

TABLE IV

The Effect of Citrate, Tartrate, and Versene

in Complexing Ferric Iron

Mg. Fe^{+3} Present	Complexing Agent Present	Mg. Pd Present	Mg. Pd Found	Error Mg.	Error %
2	Citric Acid	2.117	2.146	+0.029	+1.37
2	Citric Acid	2.117	2.134	+0.017	+0.81
2	Citric Acid	2.117	2.144	+0.027	+1.27
2	Tartaric Acid	2.117	2.153	+0.036	+1.70
2	Tartaric Acid	2.117	2.150	+0.033	+1.56
2	Tartaric Acid	2.117	2.147	+0.030	+1.42
1.2	Versene	1.270	1.297	+0.027	+2.12
1.2	Versene	1.270	6.529	+5.259	+415
1.2	Versene	1.270	1.288	+0.018	+1.42

F. The Effect of Orthophosphate and Pyrophosphate in Complexing Ferric Iron: The next agent investigated in the search for a complexing agent for ferric iron was orthophosphate. One half milliliter of a forty percent solution of orthophosphoric acid was added to the sample of the stock solution prior to precipitation. The results listed in table V indicate that orthophosphoric acid does complex the iron. The precipitate was of the normal yellow-orange color. Similarly, three milliliters of a four percent solution of tetrasodium pyrophosphate were added to samples of the stock solution containing two milligrams of ferric iron. The results in table V show that pyrophosphate also effectively complexes ferric iron when alpha-furildioxime is used as the precipitating agent for palladium.

TABLE V

The Effect of Orthophosphate and Pyrophosphate

in Complexing Ferric Iron

Mg. Fe^{+3} Present	Complexing Agent	Mg. Pd Present	Mg. Pd Found	Error Mg.	Error %
2	H_3PO_4	2.117	2.118	+0.001	+0.05
2	H_3PO_4	2.117	2.119	+0.002	+0.10
2	H_3PO_4	2.117	2.120	+0.003	+0.14
2	H_3PO_4	2.117	2.114	-0.003	-0.14
2	H_3PO_4	2.117	2.118	+0.001	+0.05
2	H_3PO_4	2.117	2.117	0.000	0.00
2	$Na_4P_2O_7$	2.117	2.119	+0.002	+0.10
2	$Na_4P_2O_7$	2.117	2.118	+0.001	+0.05
2	$Na_4P_2O_7$	2.117	2.116	-0.001	-0.05

G. <u>The Effect of Long Standing and Exposure to Daylight on a Solution of Alpha-Furildioxime:</u> As was previously mentioned, the reagent solution of alpha-furildioxime changes, over a period of weeks, from a colorless solution to amber when exposed to daylight. Brown colored particles may be observed on the bottom of the container which do not dissolve upon warming. A solution that had been exposed to daylight for six weeks was warmed, the insoluble residue filtered off, and the filtered solution used for determining palladium in the usual manner. As can be seen from table VI, such a solution is capable of yielding accurate results.

TABLE VI

The Effect of Long Standing and Exposure to Daylight on a Solution of Alpha-Furildioxime

Mg. Pd Present	Mg. Pd Found	Error Mg.	Error %
2.117	2.118	+0.001	+0.05
2.117	2.116	-0.001	-0.05
2.117	2.117	0.000	0.00
2.117	2.119	+0.002	+0.10

II. The Microdetermination of Palladium With Cyclohexanediondioxime

A. The Reagent Cyclohexanedionedioxime: G. F. Smith (7) and his co-workers suggested the name "nioxime" for the reagent cyclohexanedionedioxime, and after their successful synthesis of the compound, its use in the macrodetermination of palladium was investigated by Voter, Banks, and Diehl (10). They found that quantitative precipitation of the palladium was obtained at pH values from 0.7 to 5, but could not be assured at lower pH values. It was found that the determination could be carried out in the presence of the following ions: chloride, sulfate, nitrate, acetate, tartrate, sulfosalicylate, uranyl, ruthenium, beryllium, sodium, potassium, lithium, barium, strontium, calcium, aluminum, lanthanum, zinc, cadmium, and platinum in amounts up to one tenth of a gram. Aurous ions formed a precipitate with nioxime, so the determination of palladium could not be conducted in the presence of gold.

The procedure suggested by these investigators for the macrodetermination of palladium with nioxime is as follows: Adjust the volume of the solution, containing from five to twenty milligrams of palladium, to approximately two hundred milliliters. The pH may vary from one to five depending upon the other ions present. Heat the solution to 60°C. and add 0.43 ml. of an 0.8% aqueous solution of nioxime for each milligram of palladium present. Digest for thirty minutes at 60°C., with occasional stirring. Filter while hot through a previously weighed filtering crucible of medium porosity, wash five times with hot water, and dry for one hour at 110°C. The factor for palladium is 0.2743.

An 0.8% aqueous solution of nioxime was prepared by dissolving 0.8 gram of the reagent in cold water. The solution was filtered three times through number 42 Whatman filter paper in an attempt to remove traces of a milky like suspension that appeared upon agitation of the solution. However, a slight suspension remained even after repeated filtration.

Several series of microdeterminations of palladium using nioxime as the precipitating agent were conducted, following essentially the procedure outlined above. The description and results of these determinations follow:

B. Application of the Method of Voter, Banks, and Diehl (10) to the Microdetermination of Palladium: Initially, two sets of conditions were studied in adapting the macromethod of these investigators to the microdetermination of palladium. These were: 1. The effect of drying the precipitate at 120°C. 2. The effect of drying the precipitate at 110°C. It was found that when the precipitate was dried at 120°C., it had a tendency to gradually lose weight after each period in the oven, thus making it difficult to obtain constant weights. On the other hand, when the precipitate was dried at 110°C., no loss of weight was observed with subsequent dryings, and constant weights were readily obtained.

The procedure used in the microdeterminations was as follows: Five milliliters of the stock solution were pipetted into previously weighed filter beakers, and these were placed upon a water bath at 60°C. The palladium was precipitated with 1.2 ml. of an 0.8 % solution of nioxime, and the solution allowed to digest at 60°C. for one half hour. The bright yellow precipitate that formed did not settle readily, had a tendency to cling to the sides of the beaker, and was considerably lumped together. It was necessary to agitate the solution vigorously to break up these lumps of precipitate. The precipitate was filtered while hot, washed five times with hot water, dried at 120°C. or 110°C., and weighed to constant weight as palladium cyclohexanedionedioxime. The results of this series of determinations are shown in tables VII and VIII.

During the first nine determinations, in which the precipitate was dried at 120°C., the precipitate was not agitated as thoroughly as it was during all subsequent determinations. This fact might serve to explain some of the high results shown in table VII, but it fails to account for the three abnormally high results shown in table VIII, because in this latter series of determinations the precipitates were thoroughly broken up during the period of digestion.

It should be noted, that while the average of all the determinations listed in tables VII and VIII, is near the correct value, the precision of the determinations is poor, some values being abnormally high and others abnormally low.

The procedure outlined above is, therefore, in need of modification before the successful microdetermination of palladium may be carried out using nioxime as the precipitating agent.

TABLE VII

The Microdetermination of Palladium With Nioxime, Precipitate Dried at 120°C.

Mg. Pd Present	Mg. Pd Found	Error Mg.	Error %
2.117	2.123	+0.006	+0.28
2.117	2.106	-0.011	-0.52
2.117	2.110	-0.007	-0.33
2.117	2.118	+0.001	+0.05
2.117	2.100	-0.017	-0.80
2.117	2.118	+0.001	+0.05
2.117	2.124	+0.007	+0.33
2.117	2.125	+0.008	+0.38
2.117	2.126	+0.009	+0.42
2.117	2.129	+0.012	+0.57
2.117	2.106	-0.011	-0.52
2.117	2.109	-0.008	-0.38
2.117	2.110	-0.007	-0.33
2.117	2.110	-0.007	-0.33
2.117	2.102	-0.015	-0.71
Average:	2.114		
Average deviation: 0.008			

TABLE VIII

The Microdetermination of Palladium With Nioxime, Precipitate Dried at 110°C.

Mg. Pd Present	Mg. Pd Found	Error Mg.	Error %
2.117	2.135	+0.018	+0.85
2.117	2.110	-0.007	-0.33
2.117	2.115	-0.002	-0.10
2.117	2.119	+0.002	+0.10
2.117	2.138	+0.021	+0.99
2.117	2.116	-0.001	-0.05
2.117	2.138	+0.021	+0.99
2.117	2.116	-0.001	-0.05
2.117	2.114	-0.003	-0.14
2.117	2.114	-0.003	-0.14
2.117	2.108	-0.009	-0.43
2.117	2.108	-0.009	-0.43
2.117	2.117	0.000	0.00
2.117	2.101	-0.016	-0.76
2.117	2.106	-0.011	-0.52
Average:	2.117		
Average deviation: 0.008			

C. The Effect of Increased Standing Time Upon Completeness of Precipitation: Reference to tables VII and VIII show that many of the results obtained using nioxime are low. It was thought that a possible remedy to this situation might be to allow the precipitates to stand for one hour at room temperature prior to filtration. The results in table IX show that the errors are still largely negative, and that evidently the longer period of standing prior to filtration is not important.

TABLE IX

Effect of Allowing Solution to Stand at Room Temperature

For One Hour Prior to Filtration

Mg. Pd Present	Mg. Pd Found	Error Mg.	Error %
2.117	2.114	-0.003	-0.14
2.117	2.112	-0.005	-0.24
2.117	2.120	+0.003	+0.14
2.117	2.124	+0.007	+0.33
2.117	2.102	-0.015	-0.70
2.117	2.113	-0.004	-0.19
2.117	2.094	-0.023	-1.09
2.117	2.093	-0.024	-1.13
2.117	2.118	+0.001	+0.05
Average:	2.110		
Average deviation: 0.009			

D. The Effect of pH: The effect upon quantitative precipitation, of increasing and of decreasing the pH of the stock solution was studied next. A series of determinations was conducted in which the pH of samples of the stock solution was raised to approximately three by the addition of 0.9 ml. of a one molar solution of sodium acetate. Another series was run at a pH of approximately 0.3, by the addition of 0.2 ml. of concentrated hydrochloric acid (12 M) to the samples of the stock solution. The results of these experiments are shown in tables X and XI, and indicate, that within the ranges studied, pH is apparently not a critical factor in the microdetermination of palladium with nioxime. In view of these results, the remaining determinations were made on the unaltered stock solution, the pH of which was 1.3.

TABLE X

The Effect of Precipitation at pH 3.

Mg. Pd Present	Mg. Pd Found	Error Mg.	Error %
2.117	2.125	+0.008	+0.38
2.117	2.122	+0.005	+0.24
2.117	2.119	+0.002	+0.10
Average: 2.122			
Average deviation: 0.005			

TABLE XI

The Effect of Precipitation at pH 0.3

Mg. Pd Present	Mg. Pd Found	Error Mg.	Error %
2.117	2.126	+0.009	+0.43
2.117	2.115	-0.002	-0.10
2.117	2.128	+0.011	+0.52
Average: 2.123			
Average deviation: 0.007			

E. <u>The Effect of Washing the Precipitate With an Electrolyte</u>: It was thought, that perhaps the reason for the low results so far encountered, might be due to colloid formation, thus causing some of the precipitate to pass through the filter. Therefore, a series of determinations was made in which the precipitate was washed, first five times with hot hydrochloric acid (1:200), and then five times with hot water. In this series of washings the total volume of wash liquid used was approximately twelve to fifteen milliliters. In all determinations previous to these the total volume of wash liquid used was approximately twenty milliliters. The precipitate of palladium cyclohexanedionedioxime did not settle as readily as the precipitate of palladium furildioxime, and it had a great tendency to cling to the sides of the beaker; consequently it was necessary to use a larger volume of wash liquid, to insure thorough washing, than is ordinarily used in microdeterminations. It was also observed, that in all of the nioxime filtrates, there was present an appreciable amount of a white precipitate. This precipitate was noticeable in the filtrate after the third or fourth washing, and did not appear to dissolve upon warming. The nature of this precipitate is unknown.

The results of this series of determinations are listed in table XII, and while still slightly low, they show better precision than the results obtained under other conditions studied. The improvement in results may be due to the effect of washing with a smaller volume of hot water.

TABLE XII

Effect of Washing the Precipitate

With an Electrolyte

Mg. Pd Present	Mg. Pd Found	Error Mg.	Error %
2.117	2.114	-0.003	-0.14
2.117	2.117	0.000	0.00
2.117	2.114	-0.003	-0.14
2.117	2.109	-0.008	-0.38
2.117	2.111	-0.006	-0.28
2.117	2.110	-0.007	-0.33
2.117	2.114	-0.003	-0.14
2.117	2.123	+0.006	+0.28
2.117	2.113	-0.004	-0.19
Average:	2.114		
Average deviation:	0.004		

The recommended procedure for the microdetermination of palladium with nioxime is, therefore, as follows: Pipette a five milliliter sample of the solution containing the palladium into a previously weighed filter-beaker, adjust the pH to between one and five, according to the other ions present, and place on a water bath at 60°C. Add 0.5 - 0.6 ml. of an 0.8% aqueous solution of nioxime for each milligram of palladium present, and digest for one half hour at 60°C., with frequent agitation of the solution to break up any lumpy precipitate present. Filter while hot, wash five times with hot 1:200 hydrochloric acid, and then five times with hot water. Dry at 110°C., and weigh as palladium cyclohexanedionedioxime. It is suggested that the first drying period be for two hours, and that each subsequent period be one hour.

F. The Effect of Platinum and Iron: Voter, Banks, and Diehl (10), were able to determine palladium with nioxime in the presence of up to four times as much platinum. Experiments conducted in this laboratory with equal amounts of palladium and platinum, (2 mg. Pd to 2 mg. Pt) indicate that the results for palladium in the presence of platinum are high. The platinum was added to samples of the stock solution in the form of chloroplatinic acid. Two sets of determinations were run:
1. A series in which the precipitate was allowed to digest thirty minutes at 60°C. prior to filtration. 2. Another series in which the precipitate was allowed to digest forty-five minutes at 60°C. prior to filtration. In both cases the precipitate was green in color, rather than yellow. Apparently, as can be seen from the results in table XIII, the amount of platinum precipitated is a function of time. The precipitate that first forms, in the presence of platinum, is of the normal yellow color, but

after a period of about ten to fifteen minutes have elapsed, the precipitate grows darker in color. One sample, in an unweighed beaker, was filtered after digesting for ten minutes at 60°C. This precipitate was of normal color, but palladium precipitated in the filtrate, therefore it was not deemed advisable to shorten the period of digestion.

The effect of ferric iron, added in the form of ferric chloride, is shown in table XIV. The results are high, and obviously palladium cannot be determined with nioxime in the presence of iron unless some suitable complexing agent for the iron is present. The palladium precipitate contaminated with iron was brownish yellow in color.

TABLE XIII

The Effect of Platinum

Mg. Pt Present	Digestion Period	Mg. Pd Present	Mg. Pd Found	Error Mg.	Error %
2	30 min.	2.117	2.162	+0.045	+2.12
2	30 min.	2.117	2.165	+0.048	+2.26
2	30 min.	2.117	2.160	+0.043	+2.03
2	45 min.	2.117	2.230	+0.113	+5.34
2	45 min.	2.117	2.219	+0.102	+4.82
2	45 min.	2.117	2.226	+0.109	+5.15

TABLE XIV

The Effect of Ferric Iron

Mg. Fe Present	Mg. Pd Present	Mg. Pd Found	Error Mg.	Error %
2	2.117	2.137	+0.020	+0.95
2	2.117	2.138	+0.021	+0.96
2	2.117	2.131	+0.014	+0.66

G. The Effect of Orthophosphate in Complexing Ferric Iron: One half milliliter of a forty percent solution of orthophosphoric acid was added to samples of the stock solution containing two milligrams of ferric iron. The results are high, as shown in table XV. Therefore, orthophosphate does not effectively complex ferric iron when nioxime is used as the precipitating agent for palladium.

TABLE XV

The Effect of Orthophosphate in Complexing Ferric Iron

Mg. Fe Present	Mg. Pd Present	Mg. Pd Found	Error Mg.	Error %
2	2.117	2.134	+0.017	+0.80
2	2.117	2.140	+0.023	+1.09
2	2.117	2.138	+0.021	+0.99
2	2.117	2.135	+0.018	+0.85
2	2.117	2.138	+0.021	+1.09
2	2.117	2.133	+0.016	+0.76

SUMMARY

The effect of sodium and sulfate ions upon the microdetermination of palladium with alpha-furildioxime is negligible. Ferric iron interferes, but may be effectively complexed with ortho or pyrophosphate.

An accurate gravimetric method for the microdetermination of palladium with nioxime has not as yet been worked out. The method as developed here, yields results that can only be described as fair. Platinum and ferric iron cause high results, and as yet no complexing agent for the iron has been found.

Nioxime as a precipitating agent for the microdetermination of palladium, offers no advantages over alpha-furildioxime other than solubility in cold water, and the fact that filtration may be made from a hot solution after a brief period of digestion at 60°C. Alpha-furildioxime, on the other hand, possesses the following advantages over nioxime:
1. It is capable of consistently yielding highly accurate results.
2. The conversion factor for palladium is more favorable with alpha-furildioxime (0.1958), than with nioxime (0.2743). 3. Palladium may be determined in the presence of iron, using ortho or pyrophosphate as a complexing agent, with alpha-furildioxime. This cannot be done with nioxime using orthophosphate as the complexing agent. 4. The work of Beasecker (4) indicates that in the presence of platinum, the results with alpha-furildioxime are not as high as they are with nioxime.
5. The precipitate of palladium furildioxime settles readily and has very little tendency to cling to the sides of the beaker, thus it is easier to handle than the precipitate formed with nioxime.

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