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## The Determination of Palladium and Nickel With Alpha-Furildioxime\*

SHERMAN A. REED WITH CHARLES V. BANKS

Although alpha-furildioxime has been known for over forty years, a recent survey of the literature disclosed its use as an analytical reagent has been very limited. Its preparation and use as a reagent for nickel was described by Soule (1), however, no data was found concerning its application to the detection or determination of palladium. Since it is well known that the 1,2-dioximes in general react with palladium as well as nickel to form characteristic, insoluble and highly colored complexes, it was evident that further investigation of the compound should be made. The interest in this laboratory has been concerned principally therefore with the alpha-furildioxime complex of palladium; however, the reports of earlier investigations with nickel were so conflicting it seemed necessary to review this work also.

Alpha-furildioxime was first reported by Tschugaeff (2) in 1905 as one of twelve 1,2-dioximes found to form colored complexes with nickel. It was not until 1925 however that Soule (1) described it as a water soluble compound, suitable for analytical work and recommended it as a specific reagent for the detection and determination of nickel. Ogburn (3) in 1926 used the reagent in alcohol solution to successfully separate platinum from osmium, ruthenium, rhodium and iridium. Feigl (4) in the same year reported that it was not as satisfactory for qualitative work as dimethylglyoxime or cyclohexanedionedioxime (Nioxime). Harwood and Theobald (5) on the other hand found alpha-furildioxime to be more sensitive as a qualitative reagent for nickel than dimethylglyoxime but obtained high results when using it for quantitative work.

Studies in this laboratory have shown alpha-furildioxime to be a more sensitive reagent for the detection of nickel and palladium than dimethylglyoxime. In acid solution it is highly selective for palladous ion, thus effecting a rapid quantitative separation from other heavy metals.

### PREPARATION AND PHYSICAL PROPERTIES

Many attempts to prepare alpha-furildioxime in this laboratory according to the method outlined by Soule (1) were unsuccessful. Revision of the procedure however gave satisfactory quantities of pure compound suitable for analytical use (6). The reagent when purified by recrystallization from water separates as white crystals of the monohydrate, which melt at 84-85°C expelling the molecule of water to form the anhydrous compound; melting point 166-168°C.

To determine the solubility of alpha-furildioxime, twenty grams

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of the monohydrate was dissolved in 500 ml. of boiling water. After the solution was cooled and allowed to stand for two weeks at room temperature the excess reagent was filtered out and three 100 ml. portions of the clear filtrate were pipetted into 400 ml. beakers containing excess nickel. The solutions were adjusted to pH 7.0 by adding ammonia dropwise and digested for one hour on a steam bath at 80°C. The precipitates were collected in weighed filter crucibles of medium porosity, washed five times with hot water and dried in an oven at 130° for one hour. Using  $(C_{10}H_7O_2N_2)_2Ni$  as the composition of the precipitate, the solubility of the monohydrate was found to be 0.079 g. per 100 ml. of water.

REAGENTS

A 2 per cent solution of alpha-furildioxime in 30 per cent ethanol was used.

The standard nickel solution was prepared by dissolving 8.0062 g. of Mond nickel\* in aqua regia. The solution was evaporated to near dryness five times with hydrochloric acid to remove nitrate ions and diluted with water. The total solution was weighed and the concentration of nickel calculated. The nickel was then determined electrolytically in three weighed aliquants of the solution. The average value was found to be 0.002087 g. nickel per gram of solution. (See Table I).

TABLE I  
Standardization of Nickel Solution

Sample No.	Weight of Nickel Solution Taken <i>Grams</i>	Weight of Nickel Found <i>Gram</i>	Gram of Nickel per Gram of Solution
1	51.58	0.1077	0.002088
2	50.35	0.1050	0.002086
3	47.91	0.1000	0.002087
As calculated from total weight of solution.....			0.002087
Average.....			0.002087

\*Obtained from the International Nickel Company.

A standard palladium solution was prepared from commercial palladium chloride. The salt was purified by first removing any platinum as ammonium chloroplatinate (7) and then precipitating the palladium with dimethylglyoxime. This complex was destroyed with aqua regia and the resulting solution evaporated to near dryness five times with concentrated hydrochloric acid to eliminate nitrate ions. The palladium content of the diluted solution was determined by precipitating the palladium in weighed aliquants with dimethylglyoxime. The solutions were allowed to stand over night to insure complete precipitation.

1948] DETERMINATION OF PALLADIUM AND NICKEL 269

TABLE II

Standardization of Palladium Solution with Dimethylglyoxime

Sample No.	Wt. of Palladium Solution Taken <i>Grams</i>	Weight of Precipitate <i>Gram</i>	Weight of Palladium Found <i>Gram</i>	Gram of Palladium per Gram of Solution
1	20.30	0.1277	0.04044	0.001992
2	19.03	0.1197	0.03791	0.001992
3	21.70	0.1367	0.04329	0.001995
			Average	0.001993

Portions of this solution were evaporated to dryness and analyzed spectrorgraphically. Calcium, magnesium, aluminum, silicon, copper, boron, chromium, barium and platinum were present in quantities of less than 100 ppm while only traces of manganese, silver, zinc, and nickel were found. Gold, iridium, osmium, rhodium and ruthenium were not detected.

The salts of ruthenium, osmium, rhodium, iridium and platinum used in the following samples were also analyzed spectrorgraphically. Only trace quantities of calcium, silicon, magnesium, lead, chromium and aluminum were found as impurities.

#### SENSITIVITY AND QUALITATIVE TESTS

Sensitivity tests made with nickel were in excellent agreement with those reported by Harwood and Theobald (5). One part of nickel in 6,000,000 parts of an aqueous solution is readily detected after filtering the solution on paper or allowing it to stand over night. The optimum sensitivity was obtained at pH 10.8-11.0.

Palladium was found to give a deep yellow precipitate or coloration, depending on the amount of palladium present. A series of palladium solutions was made up in 100 ml. volumetric flasks with concentrations ranging from one to twenty parts of palladium in twenty million parts of solution. The solutions were made acid by adding one drop of concentrated hydrochloric acid to each flask. To each sample was added 1 ml. of 2 per cent alpha-furildioxime solution followed by vigorous shaking. Observations made ten minutes later showed that a definite yellow coloration was exhibited in each flask. Each flask was compared with a blank of equal volume containing palladium of equal concentration with no reagent and also with a reagent blank containing only acid and alpha-furildioxime. Observations made at various intervals are recorded in Table III.

TABLE III  
Sensitivity of Alpha-furildioxime for Palladium

Parts of Palladium in Twenty Million Parts of Solution	Observation
20	Yellow-orange precipitate in 20 minutes
10	" " " " "
5	" " " " 8 hours
2	" " " " 24 hours
1	No precipitate after standing 10 days

Qualitative tests showed that alpha-furildioxime reacts, under various conditions, with several other common metal ions to give colored solutions or precipitates.

Other metallic ions found to react with the reagent are given below.

TABLE IV  
Other Ions Found to React with Alpha-furildioxime

Ion	HCl Solution	NH <sub>4</sub> OH Solution
Ir <sup>++++</sup> (red)	Colorless solution	No reaction
Cu <sup>+</sup>	Yellow precipitate	Blue-Black precipitate
Cu <sup>++</sup>	Greenish-brown solution; precipitates on standing	Deep green solution
Fe <sup>++</sup>	Pink or green solution	Purple precipitate
Fe <sup>+++</sup>	Deep brown solution; precipitates on standing	Brown precipitate
Bi <sup>+++</sup>	No reaction	Yellow-green precipitate
Rh <sup>++++</sup>	No reaction	Yellow precipitate
PtCl <sub>6</sub> <sup>---</sup>	Red-brown precipitate when heated	No reaction
OsO <sub>6</sub> <sup>---</sup>	Yellow precipitate	Yellow precipitate
Co <sup>++</sup>	Greenish-brown solution	Brown-black precipitate; dissolves in excess NH <sub>4</sub> OH to give brown solution
Au <sup>+++</sup>	Yellow-brown precipitate when heated	No reaction

Nickel does not interfere with the detection of palladium in 5N hydrochloric acid solutions in which the nickel:palladium ratio is as high as 10:1.

The following ions gave no detectable reactions: Zn<sup>++</sup>, Cd<sup>++</sup>, Cr<sup>+++</sup>, La<sup>+++</sup>, SbO<sub>2</sub><sup>-</sup>, In<sup>+++</sup>, Pb<sup>++</sup>, Mn<sup>++</sup>, Ba<sup>++</sup>, ZrO<sup>++</sup>, MoO<sub>4</sub><sup>---</sup>, AsO<sub>3</sub><sup>=</sup>, CrO<sub>4</sub><sup>=</sup>, Ag<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, ReO<sub>4</sub><sup>-</sup>, RuCl<sub>5</sub>OH<sup>---</sup>, Th<sup>++</sup>, UO<sub>2</sub><sup>++</sup>, WO<sub>4</sub><sup>---</sup>, MnO<sub>4</sub><sup>-</sup>, and Fe(CN)<sub>6</sub><sup>=</sup>.

## GRAVIMETRIC DETERMINATION OF PALLADIUM

Palladium is precipitated with alpha-furildioxime, through the union of one palladium ion with two molecules of alpha-furildioxime, as  $\text{Pd}(\text{C}_{10}\text{H}_7\text{O}_2\text{N}_2)_2$ . Even though two hydrogen ions are liberated, precipitation is readily obtained in mineral acid solution. Quantitative precipitation is obtained from pH values ranging from 0.2 to 8, however at values above pH 6 the precipitate is quite voluminous and does not coagulate readily. The effect of various anions upon the quantitative determination of palladium was studied. Those samples precipitated from sulfate, nitrate and perchlorate medium were freed of chloride by first evaporating with the respective acid. Chloride was present in samples to which complexing agents such as tartrate, citrate and sulfosalicylate were added. Results obtained indicate that these ions do not affect the determination. Each result included in Table V is representative of five such determinations made simultaneously.

TABLE V  
Effect of Various Anions on the Determination of Palladium

Anion Present	Anion Grams	Palladium Taken Gram	Weight of Precipitate Gram	Palladium Found Gram	Error Mg.
Chloride .....	3.5	0.0214	0.1091	0.0214	0.0
Nitrate .....	3.5	0.0173	0.0892	0.0174	+0.1
Sulfate .....	3.5	0.0225	0.1155	0.0226	+0.1
Perchlorate .....	2.0	0.0182	0.0929	0.0182	0.0
Acetate .....	2.0	0.0239	0.1223	0.0239	0.0
Tartrate .....	5.0	0.0198	0.1032	0.0202	+0.4
Citrate .....	5.0	0.0165	0.0842	0.0164	-0.1
Sulfosalicylate .....	5.0	0.0202	0.0104	0.0204	+0.2

A series of determinations conducted to observe the effect of varying excesses of alpha-furildioxime indicated that 150 per cent excess reagent could be present without affecting the accuracy of the results obtained. These data are shown in Table VI. A minimum excess of thirty per cent is recommended.

TABLE VI  
Effect of Excess Reagent upon the Determination of Palladium

Trial	Excess of reagent added Per Cent	Palladium taken Gram	Weight of precipitate Gram	Palladium found Gram	Error Mg.
1	30	0.0240	0.1281	0.0241	+0.1
2	75	0.0211	0.1089	0.0212	+0.1
3	125	0.0202	0.1033	0.0201	-0.1
4	150	0.0221	0.1128	0.0221	0.0

Determinations made on a series of samples in which the amount of palladium was varied from 2 to 60 mg. indicated that quantitative

recovery of palladium was readily obtained in this range. Samples containing more than 60 mg. of palladium yield precipitates which are voluminous and difficult to filter.

TABLE VII  
Determination of Various Amounts of Palladium

Trial	Palladium taken <i>Gram</i>	Weight of precipitate <i>Gram</i>	Palladium found <i>Gram</i>	Error <i>Mg.</i>
1	0.0019	0.0105	0.0021	+0.2
2	0.0104	0.0529	0.0104	0.0
3	0.0239	0.1223	0.0239	0.0
4	0.0654	0.3366	0.0656	+0.2

Palladium was determined by a single precipitation in the presence of many common metal ions including iridium, nickel, ruthenium, platinum, copper, rhodium, bismuth and cobalt. Separations from gold and osmium were unsuccessful. The former is complexed and partially reduced to the metal when heated in the presence of alpha-furildioxime, while the latter forms a greenish-grey slime which precipitates with palladium. In the presence of Cr<sub>2</sub>O<sub>7</sub>= the palladium complex becomes deep brown on warming the solution and cannot be filtered readily.

TABLE VIII  
Determination of Palladium in the Presence of Various Cations\*

Cation present	Cation <i>Grams</i>	Palladium taken <i>Gram</i>	Weight of precipitate <i>Gram</i>	Palladium found <i>Gram</i>	Error <i>Mg.</i>
Rh++++	0.125	0.0200	0.1021	0.0199	-0.1
PtCl <sub>6</sub> =	0.250	0.0176	0.0889	0.0174	-0.2
Ru++++	0.125	0.0193	0.0984	0.0193	0.0
Ir++++	0.125	0.0197	0.0994	0.0195	-0.2
Cu++	0.200	0.0204	0.1053	0.0206	+0.2
Co+++	1.000	0.0198	0.1034	0.0200	+0.2
Fe+++	0.500	0.0183	0.0934	0.0183	0.0
Ni++++	0.200	0.0196	0.1002	0.0196	0.0
Bi+++	0.500	0.0313	0.1599	0.0313	0.0
UO <sub>2</sub> ++	{0.400	0.0186	0.0971	0.0186	0.0
Th++++	{0.300				
Be++	0.150	0.0208	0.1056	0.0207	-0.1

\*Each result included in this table is representative of five such determinations made simultaneously.  
\*\*Complexed with 10 g. tartaric acid.  
\*\*\*In 5N HCl.

## 1948] DETERMINATION OF PALLADIUM AND NICKEL 273

Separations from the alkali and alkaline earth metals, magnesium, zinc, cadmium, aluminum, lanthanum and manganous manganese were also made without difficulty.

Five samples containing 25-30 mg. of palladium, precipitated by the recommended procedure, were filtered on No. 42 Whatman paper and ignited first in air and then in hydrogen atmosphere. Quantitative recovery of palladium was obtained in each case, the error being less than  $\pm 0.2$  mg.

As a comparative test, several samples containing both platinum and palladium were precipitated with alpha-furildioxime and dimethylglyoxime. All samples contained 20 mg. of platinum and were acidified with hydrochloric acid. A single precipitation was made in each case. The results obtained are listed below.

TABLE IX  
Separation of Palladium from Platinum with  
Alpha-furildioxime and Dimethylglyoxime

Palladium taken <i>Gram</i>	Platinum taken <i>Gram</i>	Weight of precipitate <i>Gram</i>	Palladium found <i>Gram</i>	Error <i>Mg.</i>
(Alpha-furildioxime)				
0.0211	0.020	0.1076	0.0211	0.0
0.0204	0.020	0.1042	0.0204	0.0
0.0212	0.020	0.1094	0.0213	+0.1
(Dimethylglyoxime)				
0.0210	0.020	0.0666	0.0211	+0.1
0.0208	0.020	0.0664	0.0210	+0.2
0.0209	0.020	0.0665	0.0209	0.0

#### Recommended Procedure

Adjust the volume of a solution containing 5 to 50 mg. of palladium to approximately 300 ml. The pH of the solution may vary from 0.5 to 5, the lower pH giving a sharper separation from other metals present. Heat the solution to about 75°C and add sufficient reagent to give thirty per cent excess over the theoretical amount required for the palladium present. Digest on a steam bath at 80°C for twenty minutes to a half hour or until the precipitate coagulates and settles. Filter through a weighed filter crucible of medium porosity and wash with five 10 ml. portions of hot water. Dry at 130°C for one hour, cool and weigh. The factor for palladium is 0.1957.

#### Determination of Nickel

A series of samples containing known amounts of nickel was run varying such factors as pH, length of digestion period, ammonia concentration and excess reagent. Quantitative precipitation of nickel was obtained only after 200 per cent excess alpha-furildioxime had



been added and the pH of the solution was held between 5.8 and 7.5. Below pH 5.8 the nickel was not completely precipitated. In strong ammonical solutions or solutions of pH greater than 7.5 low results were consistently obtained. It was also noted that these precipitates were not the usual brick red color but changed to a light yellow-orange color during the digestion period.

Several of the precipitates were decomposed by fuming with concentrated sulfuric acid and the nickel was determined electrolytically after making the solutions ammonical. The nickel recovered was equal to the amount contained in the original sample. Calculations from these data showed that one atom of nickel had united with one molecule of alpha-furildioxime to form a different compound, i.e.,  $\text{Ni}(\text{C}_{10}\text{H}_7\text{O}_2\text{N}_2)$ . This also accounted for the change in color during digestion. Typical data are shown in the table below.

TABLE X  
Data Showing Evidence of 1:1 Complex

Weight of nickel taken <i>Gram</i>	Calculated as 1:2 complex; weight of nickel found <i>Gram</i>	Calculated as 1:1 complex; weight of nickel found <i>Gram</i>	Weight of Nickel found in precipitate by electrolysis <i>Gram</i>
0.0266	0.0165	0.0266	0.0264
0.0254	0.0153	0.0255	0.0255

It was possible to precipitate the nickel quantitatively from a hot, ammonical solution when a 200 per cent excess of reagent was added slowly with stirring and when the digestion period was not less than one hour. The precipitates were extremely difficult to filter. When nickel was precipitated as  $\text{Ni}(\text{C}_{10}\text{H}_7\text{O}_2\text{N}_2)_2$ , separation from common metallic ions, due to the character of the precipitate, was quite difficult and often incomplete. Therefore, as a reagent for nickel, alpha-furildioxime was found to have no advantages over the other organic precipitants usually used.

#### SUMMARY

Alpha-furildioxime was found to be more sensitive as a qualitative reagent for nickel and palladium than dimethylglyoxime. Under the optimum conditions 1 part of nickel was easily detected in 6,000,000 parts of an aqueous solution while 1 part of palladium in 20,000,000 parts of an aqueous solution was readily detected.

Alpha-furildioxime was found to be a satisfactory reagent for the quantitative precipitation of palladium: serving to separate palladium from nickel, platinum, cobalt, iron, and many other metals with a single precipitation from strong mineral acid solutions. The palladium alpha-furildioxime precipitate may be dried and weighed or it may be ignited to the metal.

1948] DETERMINATION OF PALLADIUM AND NICKEL 275

Alpha-furildioxime was found to quantitatively precipitate nickel but its use as a reagent for this metal is precluded by the fact that the composition of the nickel alpha-furildioxime complex varies with the pH of the solution from which it is precipitated.

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LITERATURE CITED

1. Soule, B. A., *J. Am. Chem. Soc.*, 74, 981-9 (1925).
2. Tschugaeff, *Z. anorg. Chem.*, 46, 144 (1905).
3. Ogburn, S. C., Jr., *J. Am. Chem. Soc.*, 48, 2507-12 (1926).
4. Feigl, F., *Z. Angew. Chem.* 39, 393-8 (1926).
5. Harwood, H. F. and Theobald, *Analyst*, 58, 673 (1933).
6. Reed, S. A., Banks, C. V., and Diehl, H., *J. Org. Chem.*, 12, 792-3 (1947).
7. Treadwell, F. P. and Hall, W. T., "Analytical Chemistry" Vol. II, 9th ed., p. 141, New York, John Wiley and Sons, 1942.