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PREPARATION, PROPERTIES, AND ANALYTICAL APPLICATIONS OF SOME SUBSTITUTED ALICYCLIC VIC-DIOXIMES

139

by

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I. INTRODUCTION

The applications of organic reagents in analytical chemistry have increased substantially in the last few decades (24). These reagents are usually more selective for certain metallic ions than inorganic reagents and the metallo-organic compounds often possess desirable properties which make for convenient analytical applications. These properties include a quantitative separation or differentiation from other materials present, formation of a definite species, and possession of a measurable property. In gravimetric procedures this would mean the formation of a pure precipitate of definite composition obtainable in a form suitable for weighing.

When organic reagents first became popular, the practical applications far surpassed the theoretical understanding of the chemistry involved. However, in recent years investigations of the structures and strengths of the complexes have been carried out and with the aid of such knowledge, new and better organic reagents have been prepared.

One of the most widely used organic reagents is 2,3-butanedionedioxime, commonly called dimethylglyoxime. This compound is a selective precipitant for nickel(II) and palladium(II) and these metal-dioxime complexes possess nearly all of the properties desired for analytical applications. The one drawback of this reagent is that it is only slightly soluble in water and must be employed in an alcoholic solution for macro-determinations. This permits possible contamination of the metal-dioxime complex by excess reagent when the dioxime is added to an aqueous solution of the ion to be determined.

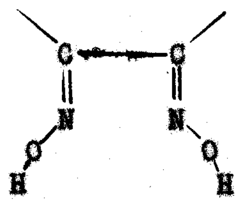
Several other compounds have been prepared in an attempt to overcome the solubility problem. All of these reagents retained the vicinal-dioxime functional group of 2,3-butanedionedioxime, but were modified elsewhere in the molecule to afford a higher solubility in water.

One of the most successful water-soluble dioximes as far as analytical applications are concerned is 1,2-cycloheptanedionedioxime (135), but the cost of the reagent is high. 1,2-Cyclohexanedioxime can be prepared at a much lower cost and has several of the advantageous properties of 1,2-cycloheptanedionedioxime, but unfortunately, the reagent contaminates the prepipitate of the metal-dioxime complex and an empirical factor is necessary.

The nomenclature employed for the organic compounds will be that prescribed by the "Definitive Report of the Commission of the Reform of the Nomenclature of Organic Chemistry" as adopted by the Commission and Council of the International Union of Chemistry in 1930 (91). Further, with compounds not covered by the I. U. C. Committee, the suggestions of Fernelius, Larsen, Marchi, and Rollinson will be followed (31). For example, by these rules the name for the complex of 1,2-cyclohexanedionedioxime with nickel (II) is bis(1,2-cyclohexanedionedioximato-N,N') nickel (II). The presence of two identical organic groups is designated by "bis" preceding the group. The "ato" ending in place of the "e" for the systematic name of the dioxime indicates that a hydrogen ion has been removed and the organic group is an anion. The letters N and N' designate the point of attachment between the metal ion and the bidentate groups as being through the nitrogens of the oximes. The Roman numeral indicates the oxidation state of the cation.

The general name used by the author for the family of organic compounds containing adjacent oxime groups is vic-dioxime. This prefix vic, an abbreviation of vicinal, emphasizes the relative position of the oxime groups and not the overall structural configuration of the molecule.

The isomeric forms of the vic-dioximes are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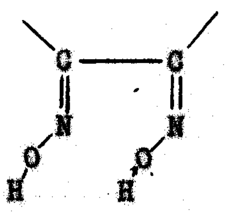
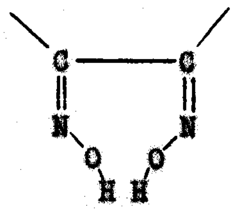

amphi-


syn- .

These three forms have also been designated alpha-, gamma-, and beta-dioximes, respectively. The vic-dioximes of interest in this work were all of the anti-form and the other isomers will not be considered.

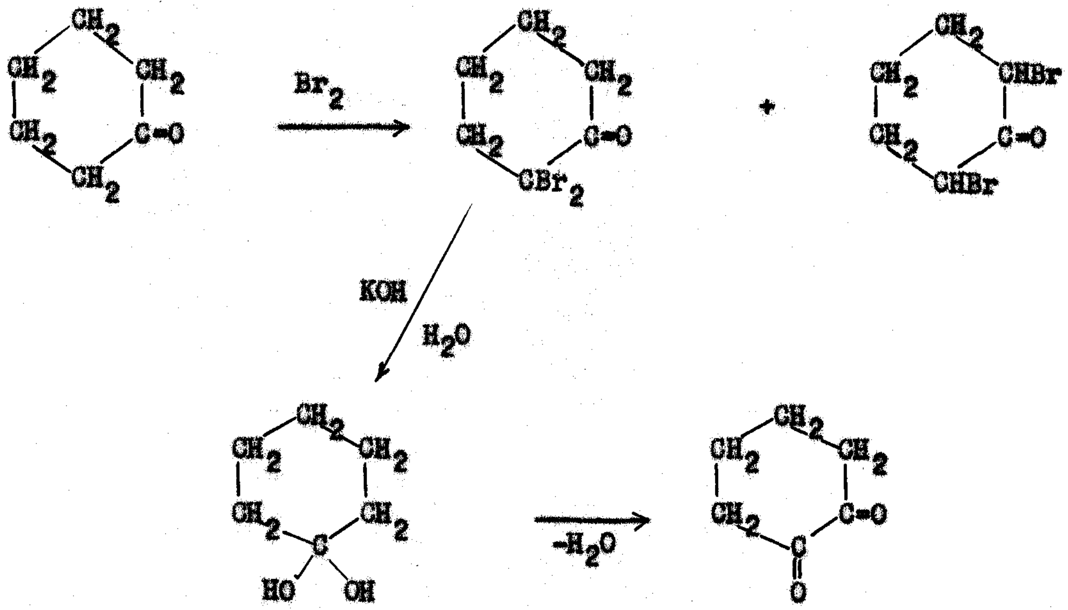
Nomenclature of an analytical or spectrophotometric nature will follow the suggestions given in "Suggested Nomenclature in Applied Spectroscopy" as adopted by the Joint Committee on Nomenclature in Applied Spectroscopy in 1952 (56).

Considering that the dioximes are prime examples of a nearly ideal organic reagent, there were two reasons for the undertaking of this research. First, it was thought that derivitives of 1,2-cyclohexanedionedioxime might possess the favorable attributes of the unsubstituted, cyclic dioxime but not exhibit the unfavorable properties. Second, the preparation and study of a series of substituted dioximes would add to the knowledge of the relationships between structure, steric factor, and properties of the vic-dioximes in particular and organic reagents in general.

II. PREPARATION OF SEVERAL ALICYLIC VIC-DIOXIMES

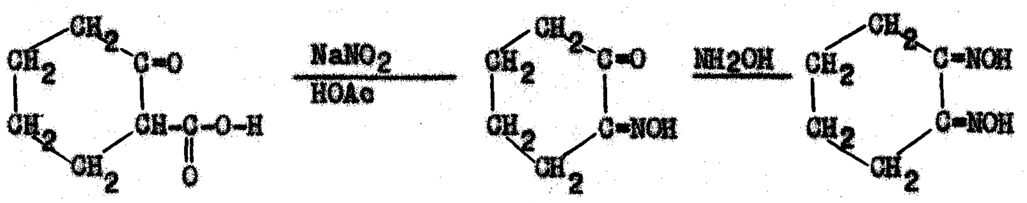
A. Review of the Literature

In 1923 Wallach and Weissenborn (143) reported that 1,2-cyclohexanedione dioxime reacted with nickel (II) ion to form a bright red precipitate. Wallach prepared this dioxime by treatment of 1,2-cyclohexanedione with hydroxylammonium chloride and potassium hydroxide. The 1,2-cyclohexanedione was synthesized by the bromination of cyclohexanone in glacial acetic acid at ice-bath temperatures and hydrolysis of the resulting mixture of dibromocyclohexanones with cold, aqueous potassium hydroxide.



This method, however, is not suitable for an economic preparation of molar quantities of the dione because of side reactions which lower the yield considerably (140, 141).

Treibs and Dinelli (127) obtained 1,2-cyclohexanedionedioxime by the treatment of cyclohexanonecarboxylic acid with sodium nitrite in cold, glacial acetic acid. The 2-hydroxyimino-1-cyclohexanone produced was then converted to the vic-dioxime by treatment with aqueous hydroxylammonium chloride and potassium hydroxide.

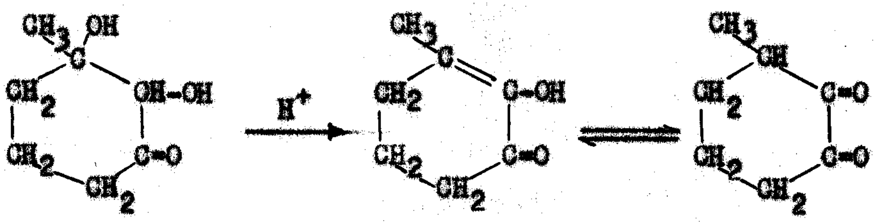


The main objection to this method is that the starting materials necessary for the synthesis of molar quantities of substituted 1,2-cyclohexanedionedioximes are not readily available at reasonable prices.

Riley, Morley, and Friend (106), Vène (132), and Rauh et al. (103) prepared 1,2-cyclohexanedionedioxime directly from cyclohexanone by oxidation with selenium dioxide in ethyl alcohol. Hach, Banks, and Diehl (45) modified this procedure and obtained the dione in a 63 per cent yield. 1,2-Cyclohexanedionedioxime was prepared in a 55 per cent yield by reaction of the dione with an aqueous solution of hydroxylammonium chloride and potassium hydroxide. This method is advantageous in that the cyclohexanone is available commercially and the yield of the dioxime is sufficient to permit laboratory preparation of molar quantities.

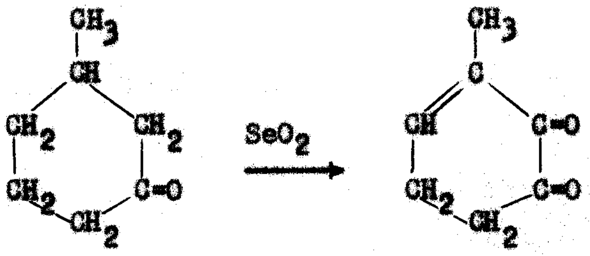
The substituted 1,2-cyclohexanedionedioximes have not been investigated as thoroughly as the parent compound. Wallach (143) described the preparation of some of the alkyl-1,2-cyclohexanedionedioximes by oximation of the corresponding vic-diones which he had prepared by the bromination method described for the preparation of 1,2-cyclohexanedionedioxime. He noted, however, that the yields were low.

Harries (49) synthesized 3-methyl-1,2-cyclohexanedione by heating 1,2-dihydroxy-1-methyl-3-cyclohexanone with a 5 per cent sulfuric acid solution for two hours.

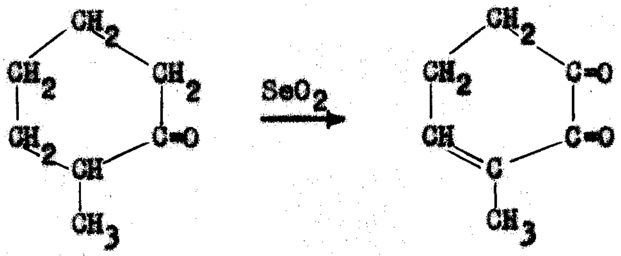


The method hardly appeared applicable to the economical synthesis of several alkylated cyclohexanediones because of the difficulty in obtaining the necessary intermediates.

Godchot and Cauquil (42) synthesized 3-methyl-1,2-cyclohexanedione and 4-methyl-1,2-cyclohexanedione by the selenium dioxide oxidation method of Riley et al. (106), but they failed to report the experimental details and the yields obtained. Godchot and Cauquil reported that 2-methylcyclohexanone and 3-methylcyclohexanone reacted with selenium dioxide to give, not the expected diones, but 3-methyl-3-cyclohexene-1,2-dione.



and



Since the selenium dioxide oxidation method had been applied to the synthesis of the methyl derivatives of 1,2-cyclohexanedione and was capable of 50 per cent yields in the case of 1,2-cyclohexanedione itself, it was decided that this reaction could be applied to the synthesis of several substituted vic-diones.

The Riley oxidation required monoketones as intermediates and while in some cases the aliphatic substituted cyclohexanones were available commercially, in others they had to be prepared in the laboratory.

Sabatier *et al.* (113) obtained cyclohexanone in high yield by passing cyclohexanol over copper oxide at 300° C. Skita and Ritter (121) employed nickel powder as a catalyst and passed oxygen along with cyclohexanol over the metal at 220° C.

A simple method for the acid dichromate oxidation of cyclohexanol to cyclohexanone has been described by Wallach (142) and Sabatier (113). Sandborn (115) employed sodium dichromate and sulfuric acid in aqueous solution for the heterogeneous oxidation of several secondary alcohols to ketones with yields of 75 per cent. Nickels (85) increased the yield of the ketone to 90 per cent by dropwise addition of the dichromate solution to an aqueous solution of the alcohol instead of the reverse procedure employed by Sandborn. Others (48, 101, 41, 85, 139, 37) have applied this method to the preparation of several alkylcyclohexanones with yields of from 70 to 90 per cent.

The dichromate oxidation procedure for the preparation of ketones appeared to be the best general method and was adopted for the synthesis of several alkylcyclohexanones. This procedure required the corresponding cycloaliphatic alcohols as starting materials and although some were obtained from commercial sources, others had to be synthesized.

From the standpoints of cost, availability, and yield of conversion to the cycloaliphatic alcohol, the best method of synthesis seemed to be catalytic hydrogenation of the corresponding phenol.

Skita (119) reported the reduction of several cresols to the methylcyclohexanols with high yields by shaking the phenol in an acetic acid-water mixture with a platinum oxide catalyst in an atmosphere of hydrogen.

Nickel powder was used as a catalyst by Sabatier and Senderens (114) for the reduction of cresols with yields of 90 per cent. They employed hydrogen at 200° C. and 100 atmospheres for several hours in order to obtain the excellent yields. This method has been applied to the preparation of several alkylcyclohexanols with similar results (82, 44, 102a). Ungrade and McLaren (129) used a Raney nickel catalyst with hydrogen at 150° C. and 100 atmospheres, and reduced several phenols with yields of better than 90 per cent.

The hydrogenation method seemed to be generally applicable and capable of good yields and, therefore, was used in this work for the synthesis of the intermediate cycloaliphatic alcohols.

It has been reported by Ipat'ev and Razuvaev (59) that high pressure hydrogenation of 4-hydroxybenzoic acid over a Raney nickel catalyst results in cyclohexanol and cyclohexanecarboxylic acid and not the expected 4-hydroxycyclohexanecarboxylic acid. Edson (22) reduced the 4-hydroxybenzoic acid directly to the saturated hydroxy-acid by employing a platinum oxide catalyst. The aromatic acid was dissolved in ethanol and a few drops of a 10 per cent potassium hydroxide solution were added along with one gram of the catalyst. Hydrogen at 43 p.s.i. was used for the reduction and the yields were near 50 per cent.

Mitsui (79) utilized a Raney nickel catalyst and hydrogen at 150° C. and 85 atmospheres for 20 hours to reduce ethyl 4-hydroxybenzoate to 4-carbethoxycyclohexanol with a yield of 78 per cent.

A 95 per cent yield for the same reduction was obtained by Martin *et al.* (75) by the use of a palladized strontium carbonate catalyst.

B. Materials and Apparatus

Activated alumina. Obtained from the Aluminum Company of America. Grade F-200. A special high purity alumina for use in chromatographic applications.

4-tert-Amylcyclohexanol. Research sample obtained from Sharples Chemical Company, Wyandotte, Michigan.

2-Methylphenol. Obtained from Eastman Kodak. White label grade.

1,4-Dioxane. Obtained from Eastman Kodak. White label grade. High purity dioxane required for the palladium catalized reductions was prepared as described in Vogel (133). One liter of dioxane was refluxed for 12 hours with 2 molar hydrochloric acid while a stream of nitrogen was bubbled through the mixture. After cooling, potassium hydroxide was added to remove the acid and the water. When the potassium hydroxide would no longer dissolve in the solution, the dioxane was decanted off the solid material and was allowed to stand over fresh potassium hydroxide pellets for 12 hours. The nearly dry dioxane was refluxed with metallic sodium for six hours and then fractionally distilled through a 50-cm. Vigreaux column. The fraction boiling from 100° to 102° C. was collected for use in the reductions.

Hydroxylammonium chloride. Obtained from Fisher Scientific Company. Certified reagent.

4-Methylcyclohexanone. Obtained from Eastman Kodak. White label grade.

Raney nickel catalyst. Raney nickel catalyst powder obtained from Central Scientific Company, Chicago, Illinois. An aluminum-nickel alloy which yields a fine nickel catalyst when treated with concentrated sodium hydroxide according to the directions given by the manufacturer or by Adkins (2).

Palladium catalyst. The catalyst was prepared by the following method. One gram of reagent-grade palladium metal was dissolved in *aqua regia* and the resulting solution was then fumed to dryness with hydrochloric acid at least two times. The palladium chloride was taken up in 10 ml. of concentrated hydrochloric acid and the solution was added to a stirred suspension of 50 g. of strontium carbonate which had been prepared by rapid mixing of strontium chloride and sodium carbonate solutions. The mixture was made basic by the addition of 10 ml. of concentrated ammonium hydroxide and while stirring, the temperature was raised to 60° C. Palladium metal was deposited on the strontium carbonate support by addition of 8 ml. of a 40 per cent formaldehyde solution while stirring vigorously. After 10 minutes, a second 8 ml. of formaldehyde was added and heating was discontinued. The liquid was decanted from the solid material and fresh water was added to and decanted from the catalyst several times. The catalyst was filtered off, washed with acetone, washed with ether, dried in a vacuum desiccator, and stored in a closed container.

Potassium dichromate. Technical grade.

Potassium hydroxide. Reagent grade.

4-iso-Propylcyclohexanol. Obtained from the Dow Chemical Company, Midland, Michigan. Boiling range 211° to 215° C.

Selenium dioxide. Obtained from the American Metals Company, Limited, New York City, New York.

Silver metal. A finely divided precipitate of silver metal was prepared by treating a solution of silver nitrate in dilute perchloric acid with zinc dust (34). The zinc dust was added in small amounts while the solution was stirred vigorously. The precipitated silver metal was washed with dilute perchloric acid and several times with water. Finally, the metal was washed with and stored under ethanol. The precipitate should not be prepared more than a day in advance of use.

Silver nitrate. Reagent grade.

4-(1,1,3,3-Tetramethylbutyl)-phenol. Obtained from Rohm and Haas Co., Philadelphia, Pennsylvania. Listed by the manufacturer as "octylphenol" and stated to be 95 per cent the para isomer. The commercial product was distilled through a 50-cm. Vigreaux column.

Zinc dust. Reagent-grade powder.

All other chemicals and mineral acids used were chemically pure or reagent grade.

The glass apparatus employed was equipped with interlocking ground glass joints which were trademarked "inter-Joint." These were obtained from the Scientific Glass Apparatus Company.

"Metro-Ware" made by Metro Industries, Long Island City, New York. This glassware was used when small quantities of material were involved.

Parr, Series 4000, High Pressure Hydrogenation Apparatus. Obtained from the Parr Instrument Company, Moline, Illinois. This apparatus was employed for all of the high pressure hydrogen reductions. The bomb had a 1000-ml. capacity and was used with the glass liner supplied with the instrument (89).

Abbe, Model 56, Temperature Regulated Refractometer. Obtained from Bausch and Lomb Optical Co., Rochester, New York. This instrument was employed for all of the refractive index measurements.

Automatic Micro and Semi-micro Cumbustion Apparatus. Obtained from Sargent and Company, Chicago, Illinois. Model S-21580 was used in all of the carbon and hydrogen analyses.

A large steambath was prepared from a 10-gallon drum in order to supply heat to the large reaction vessels required for selenium dioxide oxidations. Two holes were drilled in the side of the drum, one at the bottom and the other one third down from the top. Two iron tubes were welded into these holes and then the upper tube was connected to a steam line and the lower tube to a drain. Overlapping rings of galvanized iron were used for the top of the can to allow for the heating of various sized vessels.

C. Experimental

1. Hydrogenation of phenols to alcohols

In several cases the alkyl substituted phenol was readily available from commercial sources at low enough cost to be used as the starting material for the synthesis of the vic-dioxime. The phenols were reduced in a bomb by hydrogen under pressure over a suitable catalyst.

The procedure involved was as follows. The phenol was purified by fractional distillation through a 50-cm. Vigreaux column if it was less than Eastman white label purity or its equivalent. One mole of the pure phenol together with 2 gm. of Raney nickel catalyst were suspended in 150 ml. of ethanol. The mixture was placed in a high pressure hydrogenation bomb and hydrogen was introduced to a pressure of 1800 p.s.i. After 40 minutes the temperature of the bomb had reached approximately 150° C. and reduction started. When the hydrogen pressure had fallen to the calculated end point, the bomb was allowed to cool and the contents were removed, filtered to remove the catalyst, and fractionally distilled through a 50-cm.

Vigreaux column. Specific application of this procedure to each compound will be discussed briefly and it should be noted that in the case of the ethyl 4-hydroxybenzoate reduction, the method was modified considerably.

a. 2-Methylcyclohexanol. The 2-methylphenol was Eastman Kodak white label and no further purification was necessary. The hydrogenation proceeded when the temperature of the bomb reached 140° C. and was completed in two hours. Obtained: Yield, 91%; b.p., 163° - 165° C. (758 mm.); N_d^{20}, 1.4638. Literature: b.p., 165° C. (760 mm.); N_d^{20}, 1.4640 (119).

b. 3-Ethylcyclohexanol. Practical-grade 3-ethylphenol was obtained from Eastman Kodak and was purified by fractionation through a 50-cm. Vigreaux column. The material boiling from 212° to 216° C. at 757 mm. was collected and employed in the hydrogenation. Reduction proceeded when the temperature reached 170° C. and was complete in two and one-half hours. Obtained: Yield, 92%; b.p., 185° - 190° C. (751 mm.); N_d^{20}, 1.4650. Literature: b.p., 187° - 191° C. (760); N_d^{20}, 1.4645 (145).

c. 2,5-Dimethylcyclohexanol. 2,5-Dimethylphenol was reduced with hydrogen at 150° C. for four hours. The original pressure of the hydrogen was 1800 p.s.i. and the final pressure was 500 p.s.i. Obtained: Yield, 94%; b.p., 64° - 65° C. (12 mm.); N_d^{20}, 1.4580. Literature: b.p., 178° C. (760 mm.); N_d^{20}, 1.4585 (120).

d. *4-(1,1,3,3-Tetramethylbutyl)-cyclohexanol*. The crude 4-(1,1,3,3-tetramethylbutyl)-phenol, octylphenol, was distilled and the fraction boiling from 114° to 118° C. was employed in the hydrogenations. The reduction was carried out at 180° C. and 1800 p.s.i. of hydrogen for eight hours. Obtained: Yield, 93%; b.p., 111° - 115° C. (3 mm.); N_d^{20}, 1.4692. Literature: No report found.

e. *4-Carbethoxycyclohexanol*. Direct hydrogenation of the ethyl 4-hydroxybenzoate was carried out by use of a palladium catalyst supported on strontium carbonate. One mole of the aromatic ester and 15 gm. of the palladium catalyst were suspended in 150 ml. of very pure dioxane. The mixture was placed in a Parr Hydrogenation Apparatus and reduced at 150° C. for four hours. After removal of the catalyst by filtration the crude material was fractionated. Obtained: Yield, 80%; b.p., 115° -123° C. (4 mm.); N_d^{20}, 1.4635. Literature: b.p., 136° C. (8 mm.); N_d^{20}, 1.4698 (130).

2. Oxidation of alcohols to ketones

The general method of preparation employed was that reported by Sandborn (115) and modified by Nickels (85) with technical grade potassium dichromate in sulfuric acid solution being used as the oxidant. One mole of the purified alkylcyclohexanol was mixed with one liter of water and stirred vigorously while 100 ml. of concentrated sulfuric acid were added. Stirring was continued while a solution of 100 g. of potassium dichromate in one liter of water was added at such a rate as to keep the temperature of the oxidation mixture between 55° and 60° C. An ice bath was used to cool the reaction in order to increase the rate of addition of the oxidant. In a few cases the temperature started to rise above 60° C. and a small amount of cracked ice was added to cool the reaction. After addition of the dichromate solution was completed, the oxidation mixture was stirred and allowed to cool for one hour.

The very dark colored mixture from the completed oxidation was placed in a separatory funnel and the lighter, organic layer was separated from the lower, aqueous phase. The water fraction was returned to the funnel and extracted with three 100-ml. portions of diethyl ether. The combined ether and ketone fractions were washed with three 50-ml. volumes of aqueous, 20 per cent potassium hydroxide and two 50-ml. volumes of a saturated sodium chloride solution. The ether phase was dried with anhydrous sodium sulfate and then fractionally distilled through a 50-cm. Vigreaux column. The pure alkylcyclohexanone was collected in yields of 75 to 85 per cent. Each of the ketones that were prepared are discussed briefly in the next sections.

a. 2-Methylcyclohexanone. The 2-methylcyclohexanol was subjected to oxidation by potassium dichromate in acid solution and the crude ketone was fractionated. Obtained: Yield, 85%; b.p., 162° - 165° C. (754 mm.); N_d^{20}, 1.4494. Literature: b.p., 164° - 165° C. (760 mm.); N_d^{20}, 1.4493 (142).

b. 3-Ethylcyclohexanone. The 3-ethylcyclohexanol was oxidized with potassium dichromate in water at 55° C. Obtained: Yield, 82%; b.p., 110° - 115° C. (12 mm.); N_d^{20}, 1.4430. Literature: b.p., 112° - 116° C. (12 mm.); N_d^{20}, no report found (72).

c. 2,5-Dimethylcyclohexanone. The previously prepared 2,5-dimethylcyclohexanol was oxidized by the acid-dichromate mixture to the corresponding 2,5-dimethylcyclohexanone. Obtained: Yield, 82%; b.p., 176° - 179° C. (755 mm.); N_d^{20}, 1.4447. Literature: b.p., 175° - 177° C. (760 mm.); N_d^{20}, 1.4446 (72).

d. 4-iso-Propylcyclohexanone. The 4-iso-propylcyclohexanol was used without purification since the index of refraction was not altered significantly by fractional distillation. The ketone was obtained by fractionation of the ether extract of the oxidation mixture. Obtained: Yield, 81%; b.p., 84° - 86° C. (10 mm.); N_d^{20}, 1.4562. Literature: b.p., 85° - 86° C. (10 mm.); N_d^{20}, 1.4563 (131).

e. 4-tert-Amylcyclohexanone. The 4-tert-amylcyclohexanol was purified by fractional distillation under reduced pressure. The fraction collected from 112° to 115° C. at 12 mm. was employed in the oxidations. Obtained: Yield, 84%; b.p., 110° - 113° C. (12 mm.); m.p., 96° C. Literature: b.p., 109° - 111° C. (11 mm.); m.p., 98° C. (50).

f. 4-(1,1,3,3-Tetramethylbutyl)-cyclohexanone. 4-(1,1,3,3-Tetramethylbutyl)-cyclohexanol was subjected to oxidation by the acid-dichromate mixture and the 4-(1,1,3,3-tetramethylbutyl)-cyclohexanone was obtained by fractionation. Obtained: Yield, 85%; b.p., 91° - 95° C. (1 mm.); m.p., 102° C. Literature: No report found.

g. 4-Carbethoxycyclohexanone. 4-Carbethoxycyclohexanol was oxidized by the acid-dichromate method, but because of possible hydrolysis of the ester grouping, the usual procedure was modified.

In order to achieve maximum oxidation with minimum hydrolysis, the literature was investigated to see if kinetic data concerning the two reactions had been reported. Smith and Steele (122) studied the acid hydrolysis of several aliphatic esters including ethyl cyclohexanecarboxylate. While this was not the same compound in question, it was believed that the addition of the 4-hydroxy group would not greatly change the factors influencing the rate of hydrolysis. Smith and Steele found that the rate of hydrolysis of the ester was proportional to the hydrogen ion concentration to the first power and the log of the rate was a function of the absolute temperature. This function is expressed by the rate-temperature relationship proposed by Arrhenius, that the log of the rate was proportional to the reciprocal of the absolute temperature.

A second study by Westheimer and Novack (144) on the dichromate oxidation of iso-propyl alcohol to acetone proved that the rate of oxidation was proportional to the square of the hydrogen ion concentration. No temperature dependence of the rate could be found in the literature and it had to be assumed that the general Arrhenius equation was valid as a first approximation. It is well known that dichromate oxidations proceed rapidly at room temperatures while hydrolysis reactions require an elevated temperature.

The work of Smith and Steele reveals that the rate of hydrolysis increases slowly up to about 40° C. and then rises sharply. Therefore, it was decided that the oxidation would be carried out at room temperatures. Since the rate of oxidation was dependent on the square of the hydrogen ion concentration and the rate of hydrolysis was a function of the first power of the hydrogen ion concentration, the reaction mixture was made 4 molar in acid by adding concentrated sulfuric acid.

By employing conditions of low pH and low temperature, the 4-carbethoxycyclohexanone was expected in yields of roughly 70 per cent. Calculations indicated that under these conditions the oxidation should be at least 90 per cent complete while only about 10 per cent of the ester would be hydrolyzed. Some additional loss could be expected from side reactions.

The actual oxidiation was carried out as follows. One mole of 4-carbethoxycyclohexanol was mixed with one liter of 2 molar sulfuric acid and, while stirring vigorously, an oxidizing solution of 100 g. of potassium dichromate in 200 ml. of water was added over a period of 20 minutes. An ice bath was used to keep the temperature below 25° C. After addition of the oxidant was complete, the solution was stirred for one hour at room temperature and then extracted with three 100-ml. portions of diethyl ether. The ether phases were combined and scrubbed first with 10 per cent sodium hydroxide and then with a saturated sodium chloride solution. The base removed any chromium remaining and the salt solution removed the base and avoided the formation of an emulsion. The ether was dried with anhydrous sodium sulfate and evaporated from the keto-ester on a steam bath. The crude 4-carbethoxycyclohexanone was distilled and the pure product collected. Obtained: Yield, 65%; b.p., 112° - 118° C. (4 mm.); N_d^{25}, 1.4594. Literature: b.p., 158° C. (40 mm.); N_d^{25}, no report found (6).

3. Oxidation of ketones to vic-diones

Selenium dioxide was used as the oxidant for preparation of the vic-diones required as intermediates. The method reported by Riley *et al.* (106) and modified by Hach *et al.* (45) for the synthesis of 1,2-cyclohexanedione was employed.

The following general procedure was used. One mole of the alkylcyclohexanone was dissolved in 300 ml. of ethanol and placed in a one liter three-necked flask which was equipped with a stirrer, reflux condenser, and dropping funnel. One mole of selenium dioxide was dissolved in 200 ml. of 95 per cent ethanol and the oxidant was added dropwise to the stirred ketone solution. The addition was performed slowly to avoid a violent reaction which occurs if the oxidant is present in large excess. The temperature of the solution was maintained at 50° to 80° C. At first the solution appeared yellow and then it changed to the red-orange color of metallic selenium. Addition of the selenium dioxide was complete in about two hours, and the reaction mixture was heated on a steambath for another six hours. After allowing the mixture to stand at room temperature over night, the precipitated selenium was filtered off and the dark colored filtrate was fractionated under reduced pressure. A 50-cm. Vigreaux column was employed for the fractionations.

The different fractions were tested for dione content by formation of the highly colored ferric complex and by taking the index of refraction. The diones exist partially in the enol form and react with iron to form a colored complex. The amount of color observed was an estimation of the quantity of dione present in any one fraction. The index of refraction of a monoketone is near 1.46 while the diketone is closer to 1.50 and an estimation of the amount of dione present could be made.

In the case of the higher boiling diketones the primary distillation product was contaminated with selenium and organo-selenium by-products which distill at the higher temperatures. These contaminants were removed by stirring with freshly precipitated silver metal for one-half hour (34).

A second fractionation was carried out with a 50-cm. Vigreaux column and the diones were obtained as colorless oils or solids which upon exposure to air developed a yellow color. In the case of the higher homologs, hot water was used in the condenser to prevent clogging by the solidified dione. The lower boiling fractions were fractionated a second time to recover the unreacted monoketones.

Individual preparations are described for each dione.

a. 3-Methyl-1,2-cyclohexanedione. The 2-methylcyclohexanone was subjected to oxidation by the selenium dioxide solution and the dione obtained was recovered by fractionation. The dione was quantitatively hydrogenated over platinum oxide and it was found that two moles of hydrogen were absorbed per mole of dione. Obtained: Yield, 20%; b.p., 80° - 85° C. (12 mm.); m.p., 62° C. Literature: m.p., 62° - 65° C. (143).

b. 4-Methyl-1,2-cyclohexanedione. Selenium dioxide reacted with 4-methyl-1,2-cyclohexanone to give 4-methyl-1,2-cyclohexanedione. Obtained: Yield, 34%; b.p., 90° - 95° C. (16 mm.); m.p., 35° C. Literature: b.p., 84° - 86° C. (12 mm.); m.p., 35° - 36° C. (69).

c. 3-Ethyl-1,2-cyclohexanedione. Treatment of 3-ethylcyclohexanone with selenium dioxide in ethanol gave a dione on fractionation. The dione was hydrogenated over a platinum oxide catalyst and it was found that two moles of hydrogen were absorbed per mole of dione. Oxidation of the dione with potassium periodate gave a dibasic acid which was characterized as alpha-ethyladipic acid. Obtained: Yield, 19%; b.p., 90° - 95° C. (6 mm.); m.p., 71° C. Literature: No report found.

d. 3,6-Dimethyl-1,2-cyclohexanedione. Oxidation of 2,5-dimethylcyclohexanone with selenium dioxide afforded the corresponding dione and in addition a major quantity of a lower boiling quinone. Obtained: 2%; b.p. 85° - 90° C. (6 mm.); N_d^{20}, 1.5002. Literature: No report found.

e. 4-iso-Propyl-1,2-cyclohexanedione. Oxidation of 4-isopropylcyclohexanone gave the expected dione. Obtained: Yield, 29%; b.p., 77° - 84° C. (1 mm.); m.p., 65° - 70° C. Literature: No report found.

f. 4-tert-Amyl-1,2-cyclohexanedione. The dione was fractionated first between 100° and 125° C. at 4 mm. and the crude dione stirred with freshly precipitated silver metal in ethanol. The metal was filtered off and the dione fractionated again. Obtained: Yield, 38%; b.p., 110° - 118° C. (4 mm.); m.p., 75° - 80° C. Literature: No report found.

g. 4-(1,1,3,3-Tetramethylbutyl)-1,2-cyclohexanedione. The 4-(1,1,3,3-tetramethylbutyl)-cyclohexanone was reacted with selenium dioxide and the mixture fractionated after removal of the selenium metal by filtration. The crude dione was collected between 125° and 150° C. and was then stirred with freshly precipitated silver metal in ethanol. The pure dione was obtained by a second fractionation. Obtained: Yield, 40%; b.p., 137° - 143° C. (1 mm.); m.p., 90° - 95° C. Literature: No report found.

h. *4-Carbethoxy-1,2-cyclohexanedione*. The 4-carbethoxycyclohexanone was subjected to a selenium dioxide oxidation in dioxane in order to obtain the dione. The procedure employed was the same as with the other ketones except for the isolation of the dione. The dioxane was removed, after the oxidation was complete, by a vacuum distillation at 50 mm. and the dark residual liquid was diluted with 200 ml. of diethyl ether. The selenium metal was filtered off and the ether solution was stirred with one gram of freshly precipitated silver metal. Another 200 ml. of ether were added and the solution was extracted with 5 per cent sodium bicarbonate until no further carbon dioxide was given off. The ether phase was then cooled to 0° C. and extracted with an ice cold, 10 per cent sodium hydroxide solution. A total of 400 ml. of the base were used. The aqueous phase was separated and was neutralized with cold sulfuric acid. The temperature of the dione solution did not exceed 5° C. at any time. When the water was neutral, it was extracted with three 150-ml. portions of diethyl ether and the combined ether fractions were dried with sodium sulfate. Evaporation of the ether yielded crude 4-carbethoxy-1,2-cyclohexanedione. The dione was not purified, but was used in the next step of the synthesis as obtained from the ether extraction. Obtained: Yield, 20%. Literature: No report found.

4. Oximation of vic-diones to vic-dioximes

The vic-diones were converted into the corresponding vic-dioximes by the procedure described by Hach, Banks, and Diehl (45) which employs aqueous hydroxylamine. The yields of the dioximes were in the order of 50 per cent or better.

The procedure followed was as follows. A cold solution of 86.9 g. of hydroxylammonium chloride, 150 ml. of water and 50 g. of ice was added to a solution of 70.1 g. of potassium hydroxide and 150 g. of ice in 50 ml. of water. One tenth gram of the same dioxime, which had been prepared previously, was added to the aqueous hydroxylamine solution and then one-half gram of activated charcoal was introduced. After stirring for a minute, the charcoal was filtered off and the resulting colorless solution was mixed with one-half mole of the vic-dione to be oximated. The mixture was made homogeneous by the addition of a small amount of ethanol. After stirring the cold reaction mixture for 15 minutes, it was allowed to stand at room temperature for two hours. Then the solution was placed on a steam bath for two hours and after cooling, the white dioxime was filtered, washed thoroughly with water, and recrystallized. The solvents employed for the recrystallizations were water, water-ethanol, and benzene-petroleum ether. Analytical samples of the dioximes were recrystallized from at least two different solvents including a final crystallization from benzene-petroleum ether.

a. 3-Methyl-1,2-cyclohexanedionedioxime. The dioxime was obtained by reacting hydroxylammonium chloride with the corresponding dione and was recrystallized from boiling water. Obtained: Yield, 60%; m.p., 164° - 165° C. Literature: m.p., 166° C. (142). Analysis--For $C_7H_{12}N_2O_2$: C, 53.83; H, 7.74. Found: C, 53.93; H, 7.52.

b. 4-Methyl-1,2-cyclohexanedionedioxime. Oximation afforded the dioxime as a white solid which could be recrystallized from boiling water. Obtained: Yield, 70%; m.p., 181° - 182° C. Literature: m.p., 181° C. (142). Analysis--For $C_7H_{12}N_2O_2$: C, 53.83; H, 7.74. Found: C, 53.79; H, 7.50.

c. 3-Ethyl-1,2-cyclohexanedionedioxime. The crude dioxime was recrystallized from boiling water and a white solid resulted. Obtained: Yield, 65%; m.p., 179° - 180° C. Literature: No report found. Analysis--For $C_8H_{14}N_2O_2$: C, 56.44; H, 8.29. Found: C, 56.80; H, 8.23.

d. 3,6-Dimethyl-1,2-cyclohexanedionedioxime. The 3,6-dimethyl-1,2-cyclohexanedione was oximated and the resulting vic-dioxime was recrystallized from benzene and petroleum ether. Obtained: Yield, 52%; m.p., 160° - 161° C. Literature: No report found. Analysis--For $C_8H_{14}N_2O_2$: C, 56.44; H, 8.29. Found: C, 56.87; H, 8.11.

e. 4-iso-Propyl-1,2-cyclohexanedionedioxime. Oximation of 4-iso-propyl-1,2-cyclohexanedione was carried out in 25 per cent aqueous ethanol and the dioxime was recrystallized from a similar solvent. Obtained: 72%; m.p., 184° - 185° C. Literature: No report found. Analysis--For $C_9H_{16}N_2O_2$: C, 59.31; H, 8.85. Found: C, 59.19; H, 8.73.

f. 4-tert-Amyl-1,2-cyclohexanedionedioxime. The 4-tert-amyl-1,2-cyclohexanedionedioxime was subjected to oximation in 50 per cent aqueous ethanol and the crude dioxime was recrystallized from 25 per cent aqueous ethanol. Obtained: Yield, 80%; m.p., 202° - 204° C. Literature: No report found. Analysis--For $C_{11}H_{20}N_2O_2$: C, 62.23; H, 9.49. Found: C, 62.55; H, 9.51.

g. 4-(1,1,3,3-Tetramethylbutyl)-1,2-cyclohexanedionedioxime. The 4-octycyclohexanone was treated with hydroxylamine in 50 per cent aqueous ethanol and the corresponding dioxime was obtained. The crude dioxime was recrystallized from a 40 per cent aqueous ethanol. Obtained: Yield, 70%; m.p., 199° - 201° C. Literature: No report found. Analysis--For $C_{14}H_{26}N_2O_2$: C, 66.11; H, 10.30. Found: C, 66.37; H, 9.96.

h. 4-Carboxy-1,2-cyclohexanedionedioxime. The crude 4-carbethoxy-1,2-cyclohexanedione, obtained from the selenium dioxide reaction, was oximated with aqueous hydroxylamine. Additional base was needed since it was found the oximation was accompanied by hydrolysis of the ester. Twice the usual amount of potassium hydroxide was employed and the reaction mixture was found to be at a pH of 8 at the end of the oximation. The solution was neutralized to pH 7, extracted with three 100-ml. portions of diethyl ether, and evaporated on a steam bath. The solid material obtained was then extracted with boiling methanol and passed through a chromatographic column of activated alumina. The column was 10 cm. in diameter and 40 cm. long and it was packed with activated alumina wet with methanol. The dioxime solution in methanol was poured on the column and eluted with more methanol. After nearly two liters of methanol had passed through the column, the first dioxime was eluted. The dioxime was easily identified by testing with nickel. The column was then extruded and the sections containing the dioxime carefully separated from the rest of the alumina. The material containing the dioxime was placed in a smaller column and eluted with water until the liquid coming from the column did not contain any dioxime. The water was then evaporated on a steam bath and the crude 4-carboxy-1,2-cyclohexanedionedioxime remained in the beaker. The dioxime was recrystallized from methanol-benzene mixtures by taking as much as possible of the dioxime up in cold methanol, heating, and adding boiling benzene until the first cloudiness appeared. Obtained: Yield 5%; m.p., 189° - 191° C. Literature: No report found. Analysis--For $C_7H_{10}N_2O_4$: C, 45.43; H, 5.37. Found: C, 44.99; H, 5.32.

D. Discussion and Summary

Synthesis of the substituted 1,2-cyclohexanedionedioximes were undertaken with the basic condition that the method of preparation would have to be applicable to mole quantities at a reasonable expense. While several possible methods could have been used, only the synthesis chosen appeared to fulfill these requirements. Possibly the main objection to the preparation employed was the necessary use of selenium dioxide. This material is far from the easiest with which to work and by-products from the reaction with ketones have disagreeable odors and are toxic. However, the yields and general applicability of this type of oxidation offset any drawback because of the chemicals involved.

The substituted cyclohexanedionedioximes were synthesized roughly by the following method:

1. Reduction of the substituted phenol to the corresponding cyclohexanol.
2. Oxidation of the cyclohexanol to the cyclohexanone.
3. Oxidation of the monoketone to the vic-diketone.
4. Oximation of the vic-diketone to the vic-dioxime.

This preparation requires the substituted phenol as starting material and most of the phenols are commercially available at low cost. The hydrogenation required a high pressure bomb but gave yields of over 90 per cent for the reductions. If, however, a high pressure apparatus is not available most of the substituted cyclohexanols are available commercially at a moderate cost.

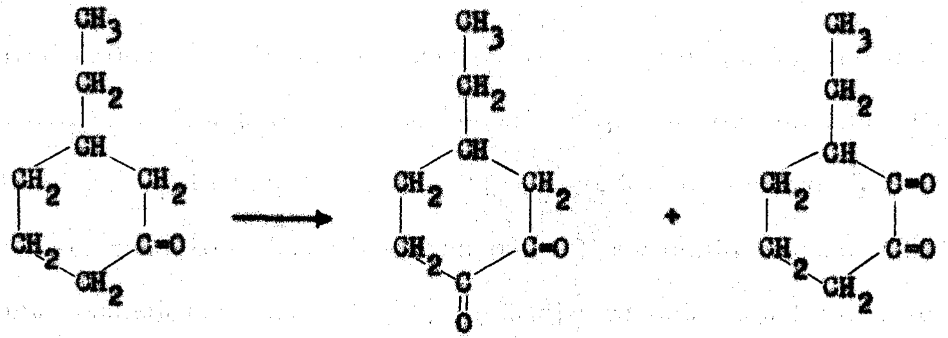
Oxidation to the monoketone did not require either special equipment or expensive chemicals. Technical-grade potassium dichromate was employed as the oxidant, since the impurities in the dichromate were of an inorganic nature and did not contaminate the final product or reduce the yield.

Most of the reactions carried out proceeded in the same manner for the various homologs, but a few of them were different in yields or products.

All of the hydrogenations proceeded as expected and yields were an average of 92 per cent. In the dichromate oxidation step, none of the compounds reacted abnormally and the average yield of the ketones was 83 per cent.

Oxidation of the monoketones with selenium dioxide gave the expected diones in yields of from 30 to 40 per cent for the cyclohexanediones substituted in the 4-position, but for 3-substituted homologs the yield was less than 20 per cent and for the 3,6-dimethyl-1,2-cyclohexanedione the yield was only 2 per cent. These results support Godchot and Cauquil (42) in their report that 2-methylcyclohexane is oxidized to 3-methyl-3-cyclohexene-1,2-dione with selenium dioxide. This would account for the reduction in yield of the non-olefinic dione. The unsaturated dione would boil at a lower temperature than the 4-methyl-1,2-cyclohexanedione and would be expected to exhibit a yellow color because of the extensive unsaturation. The lower boiling fraction, obtained by distillation of the reaction products of selenium dioxide and 2-methylcyclohexanone, was yellow in color and probably contained the unreacted monoketone and the compound reported by Godchot and Cauquil (42). They did not report the yield of 3-methyl-3-cyclohexene-1,2-dione that they observed and it could have been small. Hydrogenation of the suspected 4-methyl-1,2-cyclohexanedione over platinum oxide indicated that exactly two moles of hydrogen were absorbed per mole of dione and this indicates that the dione isolated was the 3-methyl-1,2-cyclohexanedione since 3-methyl-3-cyclohexene-1,2-dione would be expected to absorb 3 moles of hydrogen per mole of dione.

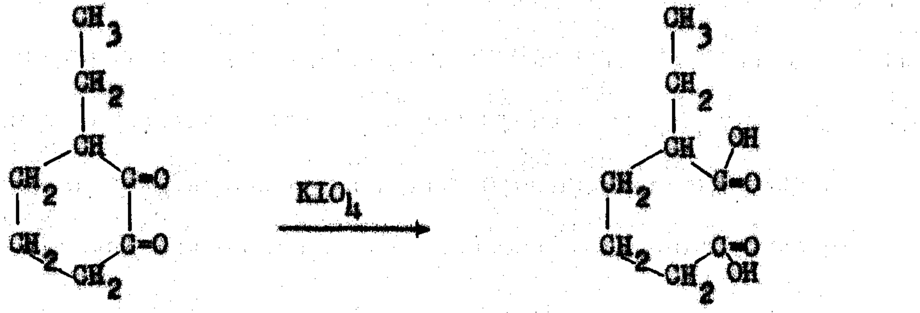
3-Ethylcyclohexanone when oxidized with selenium dioxide could possibly have yielded two diones, depending on the position of oxidation.



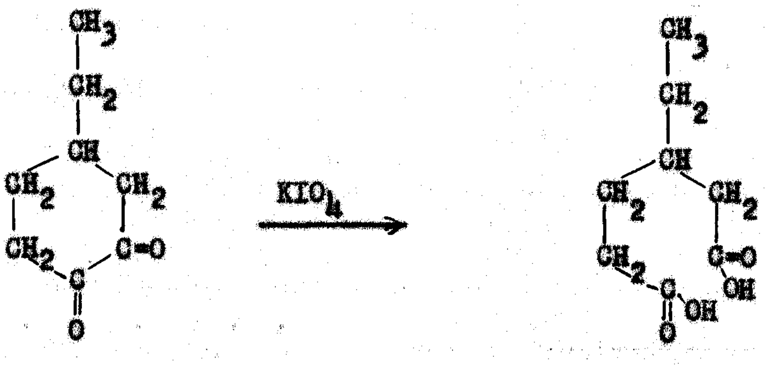
Further, Godchot and Cauquil reported that the 3-methylcyclohexanone yielded 3-methyl-3-cyclohexene-1,2-dione when oxidized with selenium dioxide. This could mean that the 3-ethylcyclohexanone might yield

3-ethyl-3-cyclohexene-1,2-dione. In order to show which of these possible products was actually formed, the dione was reduced quantitatively with hydrogen and it was found that only two moles of hydrogen were absorbed per mole of dione. This indicated that the unsaturated dione was not a likely possibility since it would be expected to react with three moles of hydrogen per mole of dione.

Potassium periodate was used to oxidize the dione and the resulting dibasic acid was characterized as alpha-ethyladipic acid. The acid melted at 49° C. and yielded a 4-phenylphenacyl derivative melting at 118° C. The alpha-ethyladipic acid is reported to melt at 49° C. by Brown et al. (13) and the beta-ethyladipic acid melts at 48° C. They also report the 4-phenylphenacyl derivatives to melt at 118° C. for the alpha-ethyladipic acid and 100° C. for the beta-ethyladipic acid. On the basis of the melting point of the derivative it was decided that the acid was alpha-ethyladipic acid. This was good evidence that the dione involved was 3-ethyl-1,2-cyclohexanedione since this compound would yield the acid found.



alpha-ethyladipic acid



beta-ethyladipic acid

Again, it must be mentioned that the yield of the saturated dione was only 19 per cent and it is probable that some of the 3-ethyl-3-cyclohexene-1,2-dione was produced thus lowering the yield of the desired product.

The 2,5-dimethylcyclohexanone reacted with selenium dioxide to form mainly a yellow product boiling at 75° to 95° C. at 12 mm. This product was most likely 1,4-dimethyl-2,3-benzoquinone. Only 2 per cent of the 3,6-dimethyl-1,2-cyclohexanedione was found indicating that the aromatic quinone was probably formed as the major product.

The final step in the synthesis of the vic-dioximes proceeded with all of the vic-diones as expected with the average yield 55 per cent.

The synthesis of 4-carboxy-1,2-cyclohexanedionedioxime required special procedures in several of the steps. Hydrogenation of 4-hydroxybenzoic acid over Raney nickel would not yield the corresponding cyclohexane compound, but by employing palladium as catalyst for reduction of ethyl 4-hydroxybenzoate, 4-carbethoxycyclohexanol was obtained.

Again, in the oxidation the 4-carbethoxycyclohexanol was special in that the danger of hydrolysis of the ester group existed. It was desirable to retain the ester in order to make isolation and purification of the subsequent intermediates easier.

The most difficult part of the synthesis of 4-carboxy-1,2-cyclohexanedionedioxime was the isolation step after the selenium dioxide oxidation. The dione is unstable to acid, base, and prolonged heating and since the isolation method requires extraction into 10 per cent potassium hydroxide, some of the dione must have been lost. The three functional groups on such a low molecular weight compound render it rather soluble in water and relatively insoluble in organic solvents. Thus, without isolation the pure dione was oximated to the dioxime which was isolated. During the oximation reaction, the ester was hydrolyzed to yield directly 4-carboxy-1,2-cyclohexanedionedioxime. Isolation of the 4-carboxy-1,2-cyclohexanedionedioxime from water was very difficult and in order to obtain the pure dioxime, it was necessary to chromatograph the material. The chromatographic procedure was easy to carry out even though the dioxime was colorless, since by simply painting a nickel chloride stripe on the inside of the glass column, the red color of the nickel-dioxime chelate would form as the dioxime passed down the column.

All of the vic-dioximes were prepared in satisfactory yields except the 3,6-dimethyl-1,2-cyclohexanedionedioxime and the

4-carboxy-1,2-cyclohexanedionedioxime. The 1,2-cyclohexanedionedioximes substituted in the 4-position were obtained in yields nearly twice that for those substituted in the 3-position.

In Table 1 the yields for the synthesis are tabulated, and it can be seen that the over-all yields for the 4-substituted compounds average 25 to 30 per cent from the phenol while the 3-substituted compounds average only 15 per cent. The 3,6-dimethyl and 4-carboxy compounds are obtained in yields of 1 to 2 per cent and can hardly be prepared in molar quantities at a moderate cost.

Table 1

Yields of the Steps in the Synthesis of Substituted 1,2-Cyclohexanedionedioximes

Substituted group	Phenol to alcohol %	Alcohol to ketone %	Ketone to vic-diketone %	Vic-diketone to vic-dioxime %
3-Methyl-	91	85	20	60
4-Methyl-	--	--	34	70
3-Ethyl-	92	82	19	65
3,6-Dimethyl-	94	82	2	52
4-iso-Propyl-	--	81	29	72
4-tert-Amyl-	--	84	38	60
4-Octyl-[a]	93	85	40	70
4-Carboxy-	80	65	20	5

[a] 4-(1,1,3,3-Tetramethylbutyl).

From the viewpoint of the preparation of the dioxime this work indicates the most promising reagents for use in analytical chemistry are the 4-methyl-, 4-iso-propyl-, 4-tert-amyl-, and 4-(1,1,3,3-tetramethylbutyl)-1,2-cyclohexanedionedioximes.

III. PROPERTIES AND STRUCTURE RELATIONSHIPS

A. Review of the Literature

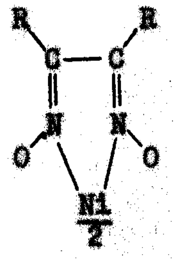
Starting with the report by Tschugaeff (128) that a compound, dimethylglyoxime, reacted with nickel to form a red, insoluble complex, dioximes have become widely used in the analysis for nickel. It was soon discovered that the functional part of the dimethylglyoxime molecule responsible for the selective precipitation of nickel was the central dioxime group, $-C(=NOH)-C(=NOH)-$. Further, it was found that the anti- form of the dioxime was the only ixomer that would precipitate the nickel selectively. Several vic-dioximes have been reported in literature. Table 2 lists a few representative compounds and their properties that have been proposed as analytical reagents.

Table 2

Some Vic-Dioximes Reported in the Literature

Compound	Melting point ° C.	Solubility in water g. per liter	Color of nickel (II) complex	Ref.
2,3-Butanedionedioxine	239	0.4	Red	(6)
1,2-Diphenylethanedionedioxime	236	<0.1	Red	(123)
1,2-Cyclohexanedionedioxime	187	8.2	Red	(103)
1,2-Cycloheptanedionedioxime	179	4.8	Yellow	(135)
1,2-Di(2-furyl)ethanedionedioxime	167	0.8	Red	(104)
1,2-Cyclopentanedionedioxime	230	1.3	Red	(134)
1,2-Cyclodecanedionedioxime	184	0.1	Yellow	(134)

The complex formed by the interaction of nickel (II) and a dioxime was thought by Pfiefer (96, 97) to be



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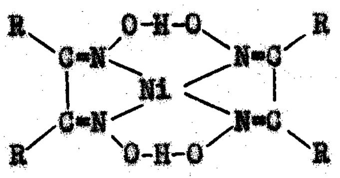
Brady (11) concluded that there were hydrogen bonds between the two dioxime groups which lie in a plane around the nickel (II). Sugden (124) proved the planer configuration of the complex by isolation of the geometric isomers of unsymmetrical vic-dioximes. Magnetic susceptibility evidence supported this planer configuration (15, 16, 67, 124) since the nickel (II) complex is diamagnetic and probably involves the dsp^2 orbitals of the nickel (II). Cavell and Sugden (16) employed dipole moment measurements to prove the planar structure of nickel-vic-dioxime complexes. They found that 4-chlorophenylbutylglyoxime complex of nickel (II) had nearly the same dipole moment as the methylbutylglyoxime complex of nickel (II) and concluded the structure must be a trans-planar type to influence the dipole moment so little.

Additional data on the hydrogen bonds between the dioxime groups have been given by Voter *et al.* (138), who gave infrared evidence to show the hydrogen bonds are very short and that the hydrogen atom is placed exactly between the two oxygen atoms.



Rundle (110) has shown by X-ray structure determinations that the nickel-2,3-butanedionedioxime complex is arranged in such a manner that the nickel atom and the four nitrogen atoms to which it is bound all lie in a plane. Further, Rundle and Godycki (111) have reported that in a crystal of the nickel-dioxime complex, all of the individual complex planes are parallel to each other with the nickel atoms directly above one another. Each plane is rotated 90° about the nickel-nickel axis from the planes immediately above and below so that the hydrogen bonds are as far apart as possible. The nickel-nickel distance was found to be 3.24 Angstroms which they thought indicated a weak metal-metal bond. Rundle *et al.* reported that this weak bond might be the factor that is responsible for the selective precipitation of the nickel complex. They also studied the palladium-2,3-butanedionedioxime complex and found its structure was quite equivalent to the corresponding nickel chelate.

Pech *et al.* (92) have proved the nickel (II), palladium (II), and platinum (II) salts of 2,3-butanedionedioxime to be isomorphous by X-ray studies of the crystals. A series of mixed crystals of the nickel and palladium complexes were prepared.

Bezzi, Bua, and Schiavinato (9) have reported the structure of the copper-2,3-butanedionedioxime complex and they found the crystal to be entirely different from the corresponding nickel complex. In particular, the copper atoms are far apart with the organic part of the molecule in between, so that no copper-copper bond seems possible.

Mellor et al. (76, 78) were able to relate the ultraviolet absorption spectra of several nickel (II) compounds with their magnetic properties. A strong absorption band was found in the 400 millimicron region of the spectrum for all of the diamagnetic complexes of nickel. In chloroform solution several of the nickel (II)-vic-dioxime complexes exhibit an absorption somewhere in the region of 350 to 425 millimicrons. Even when the nickel-dioxime complexes are not in solution, but are suspended in water, the absorption near 400 millimicrons is present although other aspects of the spectra change (134).

Yamada and Tsuchida (147) have reported the polarized spectra of the nickel-2,3-butanedionedioxime complex. With light vibrating in the direction of the nickel-nickel bond, an absorption peak occurs at 500 millimicrons while with the light vibrating in the plane of the dioxime groups, a peak is observed at 400 millimicrons. This would support the concept that nickel in a square-planar complex involves absorption near 400 millimicrons.

The absorption spectra of a material can be influenced by more than just absorption of light by bonds in the compound. If conditions are right, selective reflection of light can occur. By selective reflection it is meant that certain wavelengths of light are reflected to a greater extent than others. This usually occurs at wavelengths near strong absorption peaks (63). Substances, which show this phenomina, usually possess a metallic luster and are highly colored.

Another factor involving the interaction of light and matter, which may then affect the observed spectra of a material, is the scattering of light by small particles. Rayleigh in 1871 reported the quantitative aspects of scattering by particles of the same size as the length of the light wave. The intensity of the scattered light is proportional to $1/(\text{wavelength})^4$. This means that red light is scattered about ten times less than blue light (64).

Christiansen (17) observed that small particles in a medium of the same refractive index transmit light very well and this phenomina has been used for the preparation of selective filters for radiation in the ultraviolet and infrared regions of the spectrum. Price and Tetlow (102b) described the effect observed in slurries of organic crystals for infrared radiation. This effect in the neighborhood of an absorption band causes the absorption peak to appear shifted to the longer wavelengths.

B. Materials and Apparatus

Cary automatic recording photoelectric spectrophotometer, Model 12. This instrument was employed for scanning solutions at varying wavelengths. It is manufactured by the Applied Physics Corporation, Pasadena, California. This instrument is useful from 220 to 900 millimicrons since it has quartz optics and interchangeable tungsten and hydrogen lamps as sources. The Model 12 is equipped with a double-prism monochromater in order to obtain high dispersion and low scattering. The radiation receiver is a photomultiplier tube and the photomultiplier output is fed through an amplifier to a recorder which automatically plots absorbance as a function of wavelength. This model has a series of potential controls called a "multipot" which permits correction of unmatched cells. Cells containing the blank solution are balanced with the aid of the "multipot" and then the solution to be scanned is placed in the upper cell. The instrument is started and a plot of absorbance vs. wavelength is automatically recorded with the blank balanced out. The scanning speed for the wavelength and the recording speed of the chart are both variable and can be set for the particular type of work involved, whether it be high resolution over a narrow wavelength range or a quick scan of the ultraviolet and visible spectrum.

Beckman photoelectric spectrophotometer, Model DU. All of the absorbance readings at constant wavelength were taken with this instrument. Two of the Model DU instruments were available, one equipped with a tungsten light source for use in the visible region of the spectrum and the other with a hydrogen lamp for use in the ultraviolet. The instrument equipped for ultraviolet work had a photomultiplier attachment which gave it a greater sensitivity.

Beckman pH meter, Model G. This pH meter was used for all of the pH measurements taken. The readings with this instrument are claimed by the manufacturer to be reproducible and accurate to ± 0.02 pH units.

The melting points were all taken with the aid of a Fisher-Johns melting point apparatus. This instrument was obtained from the Fisher Scientific Company, St. Louis, Missouri. This apparatus, Model 12-143, was equipped with a variable electrical input to control the rate of heating of the melting point stage. The stage was viewed through a five power lens.

Cuvettes used to contain the solutions read on the spectrophotometers were made of silica and were calibrated to be 1.000 and 2.001 cm. in length.

The volumetric glassware used in this study was all Kimball "Exax," or "Normax" brands or their equivalent. The pipettes and burets were all calibrated to check the manufacturer's stated volume.

Chemicals necessary for the work were all C. P. or reagent-grade except for some of the organic solvents. The solvents which were not at least C. P. were distilled through a 50-cm. Vigreaux column. The dioximes were all prepared in this laboratory as described in section II of this thesis.

C. Experimental

1. Physical properties

The several vic-dioximes, the preparations of which were described in section II of this thesis, were recrystallized from water or water-alcohol mixtures at least three times and then from a petroleum ether-benzene mixture. The melting points, color, and solubility in water were determined from the pure materials (Table 3).

The solubilities were studied by suspending excess dioxime in 75 ml. of deionized water and shaking for one week at 25° C. Two methods were employed to attain equilibrium. One set of determinations was made on solutions saturated at 25° C. by shaking at 25° C., Method A, while the other set was made on solutions saturated at 90° C. and shaken at 25° C., Method B. This approached equilibrium from both sides and the true solubility could be bracketed.

Table 3

Physical Properties
of the Substituted 1,2-Cyclohexanedionedioximes

Substituted group	Solubility in water g./liter			Molarity	Melting point ° C.
	Method A	Method B	Average		
3-Methyl	3.90	4.10	4.0	0.026	164
4-Methyl	3.34	3.52	3.4	0.022	179
3-Ethyl	2.45	2.55	2.5	0.015	181
4-iso-Propyl	0.73	0.78	0.75	0.0041	184
4-tert-Amyl	0.023	0.024	0.023	0.00011	202
4-Octyl[a]	<0.0001	<0.0001	<0.0001	<0.000001	200
3,6-Dimethyl	8.0	8.1	8.0	0.048	160

[a] 4-(1,1,3,3-Tetramethylbutyl).

The excess dioxime was filtered off and an aliquot of the aqueous solution was treated with nickel. The weight of the nickel complex was determined and the solubility calculated. For the more insoluble dioximes the nickel was not weighed, but was determined colorimetrically in chloroform. These analytical methods are described in the following sections of this thesis.

The absorption spectra of the dioximes and their nickel complexes were scanned on the Cary spectrophotometer and it was found that in water solution the vic-dioximes all exhibited the same qualitative spectra and nearly the same molar absorptivity. A large peak was observed in the ultraviolet region of the spectrum with the maximum near 230 millimicrons for the dioximes studied. The molar absorptivities ranged between 7.7×10^3 and 7.9×10^3 for this maximum.

The nickel complexes of the dioximes dissolved in chloroform were scanned on the Cary spectrophotometer and the spectra were found to be very similar. Maxima were observed at 382.5 and 331.5 millimicrons for all of the nickel complexes and the molar absorptivities ranged between 2.14×10^3 and 2.20×10^3 for the former peak and between 2.79×10^3 and 2.89×10^3 for the latter peak. Table 4 indicates the wavelenth and strength of the absorption maxima for the dioximes and their nickel complexes in solution.

Fig. 1 is the absorption spectra of the 4-methyl- and the 3,6-dimethyl-1,2-cyclohexanedionedioxime-nickel (II) complexes in

Table 4

Absorption Maxima for Substituted 1,2-Cyclohexanedionedioximes and Their Nickel (II) Complexes in Chloroform

Substituted group	Molar absorptivity of dioxime 232.5 millimicrons x 10^{-3}	Molar absorptivity of Ni (II) complex 331.5 millimicrons x 10^{-3}	Molar absorptivity of Ni (II) complex 382.5 millimicrons x 10^{-3}
3-Methyl	7.8	2.79	2.14
4-Methyl	7.8	2.79	2.15
3-Ethyl	7.8	2.83	2.18
3,6-Dimethyl	7.7	2.82	2.18
4-iso-Propyl	7.8	2.79	2.18
4-tert-Amyl	7.9	2.83	2.22
4-Octyl[a]	7.9	2.89	2.20

[a] 4-(1,1,3,3-Tetramethylbutyl).

chloroform solution. It is noted that the absorption peaks are very similar.

The spectra of the nickel complexes suspended in water were scanned on the Cary spectrophotometer and two absorption peaks were observed in the visible region of the spectrum. These peaks were very different from each other with respect to their location for the different dioximes. A peak near 400 millimicrons was found for all of the dioximes, but a larger absorption peak varied from 494 to

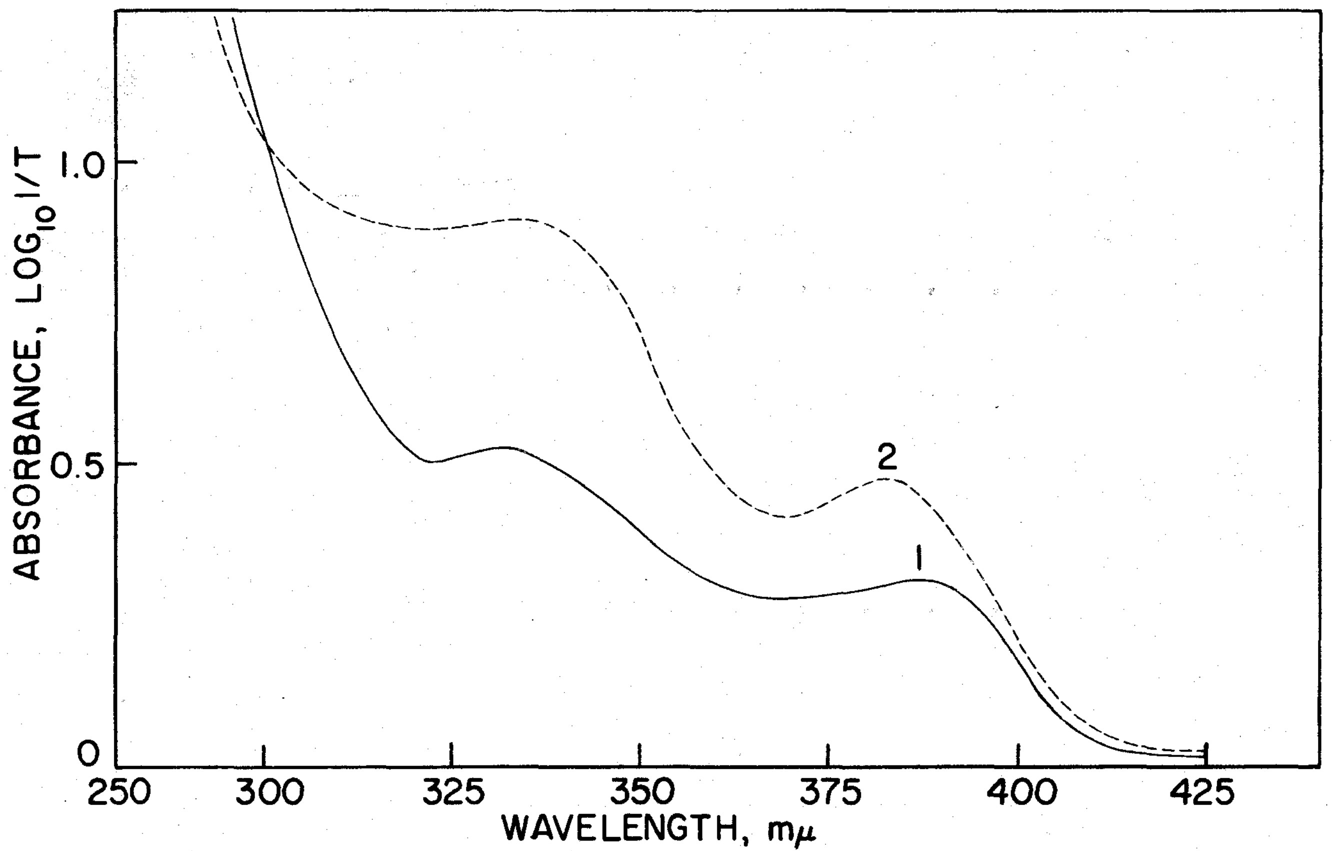


FIG. I ABSORPTION SPECTRA OF Ni(II) COMPLEXES OF 4-METHYL-, CURVE I, AND 3,6-DIMETHYL-, CURVE 2, 1,2-CYCLOHEXANEDIONE-DIOXIMES IN CHLOROFORM SOLUTION.

553 millimicrons. Table 5 indicates the wavelength of the absorption maxima for the various nickel-dioxime chelates as well as some other physical properties of the complexes. Fig. 2 is the absorption spectra of the 4-methyl- and 3,6-dimethyl-1,2-cyclohexanedionedioxime complexes of nickel (II) suspended in water.

Table 5

Physical Properties of the Nickel (II) Complexes of the Substituted 1,2-Cyclohexanedionedioximes

Substituted group	Decomposition range ° C.	Color of Ni (II) complex	Solubility in water mg. of Ni/liter	Solubility in chloroform g./liter	Absorption maxima of suspensions millimicrons
3-Methyl	230-250	Scarlet	0.18 ± 0.02	39 ± 5	547, 399
4-Methyl	230-240	Scarlet	0.056 ± 0.004	16 ± 2	549, 398
3-Ethyl	200-205	Red	1.04 ± 0.02	250 ± 25	545, 397
3,6-Dimethyl	90-120	Orange	10.0 ± 2.0	400 ± 40	494, 395
4-iso-Propyl	240-250	Violet-Red	0.009 ± 0.004	200 ± 20	553, 398
4-tert-Amyl	265-280	Scarlet	<0.004	300 ± 30	546, 398
4-Octyl[a]	270-280	Red	<0.004	400 ± 40	544, 397
4-Carboxy	145-165	Red	0.010 ± 0.005	2.6 ± 0.2	534, 398

[a] 4-(1,1,3,3-Tetramethylbutyl).

The suspensions were prepared by adding an aqueous solution of the dioxime to a dilute aqueous nickel (II) solution containing one ml. of 10 per cent gum arabic solution. These suspensions were stable for nearly two weeks.

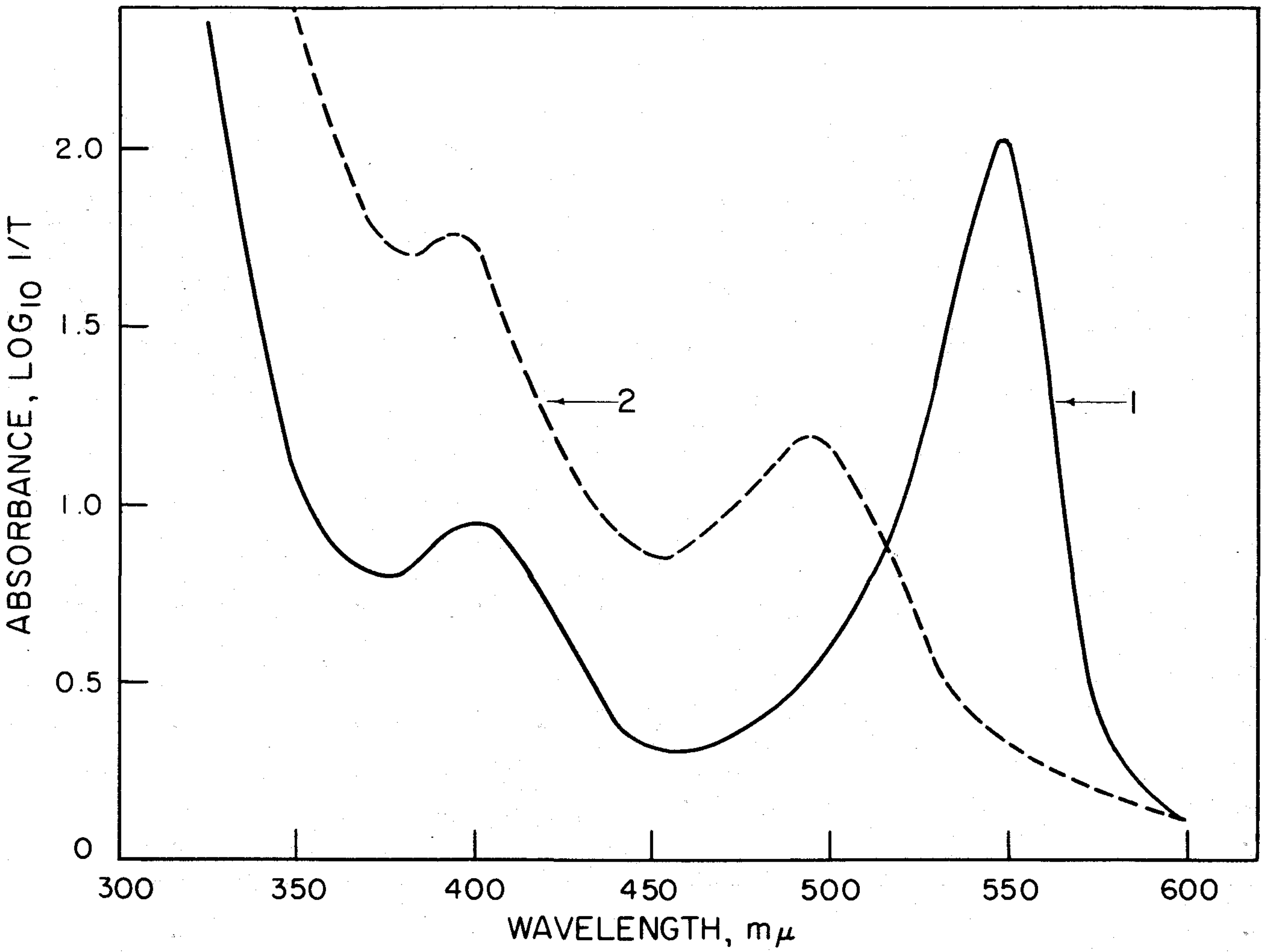


FIG. 2 ABSORPTION SPECTRA OF Ni(II)-4-METHYL-, CURVE 1, AND Ni(II)-3, 6 DIMETHYL-, CURVE 2, 1, 2-CYCLOHEXANEDIONEDIOXIMES SUSPENDED IN WATER.

In order to find out more about the peak at 550 millimicrons the spectra of several other nickel-dioxime complexes were studied and it was found that this peak was present but shifted in position. The 1,2-cycloheptanedionedioxime complex, which appears yellow in color, had peaks at 382 and 468 millimicrons; the red nickel-1,2-cyclohexanedionedioxime complex possessed maxima at 400 and 550 millimicrons; and bis(2,3-butanedionedioximato-*N*,*N'*) nickel (II) exhibited peaks at 410 and 560 millimicrons.

Aqueous suspensions of the nickel (II)-4-methyl-1,2-cyclohexanedionedioxime complex were prepared at various temperatures and it was found that the position of the 550 peak changed slightly while the 400 millimicron absorbance was unaltered. With every 10-degree increase in temperature, the peak shifted to higher wavelengths by about 1 millimicron.

Further, it was found that digestion periods at elevated temperatures caused the shift to occur. Several suspensions were prepared at room temperature and then heated at 80° to 90° C. for different lengths of time. A digestion time of one hour shifted the peak from 549 to 560 millimicrons and lesser digestion times resulted in correspondingly smaller shifts.

Several suspensions were prepared in the absence of water and it was found that the peaks at 400 were constant while the 550 millimicron maxima shifted to higher wavelengths. It was also observed that the temperature of precipitation and the digestion time were factors acting in the same manner as with aqueous suspensions.

Table 6

Absorption Maxima of the
Nickel(II)-4-methyl-1,2-cyclohexanedionedioxime Complex
in Non-aqueous Suspensions

Medium	Wavelength of "400" absorption millimicrons	Wavelength of "550" absorption millimicrons	Temperature of formation ° C.	Digestion time min.
Diethyl ether	400	551	25	10
Methyl alcohol	399	550	25	10
Toluene	399	568	60	10
Amyl alcohol	398	580	135	1
Amyl alcohol	399	580	80	3
Amyl alcohol	399	570	80	1
Amyl alcohol	399	585	135	30
Dibromoethane	398	573	70	1
Dibromoethane	399	568	60	1
Dibromoethane	399	562	25	1

The non-aqueous suspensions were prepared by dissolving the dioxime in the solvent and adding a saturated nickel chloride solution of the solvent with stirring. The digestion was controlled by heating the flasks containing the suspensions in hot water and then quenching them in ice water.

The heights of the peaks lowered with increasing wavelength of the absorption. For each millimicron increase, the absorbance decreased about 1.5 per cent and with this decreased absorbance the peaks also broadened.

The size of the particles of the nickel-dioxime complex suspended in water were determined with the aid of an electron microscope. The suspended particles, which showed an absorption maximum at 549 millimicrons, were allowed to settle out over a period of one month and then they were collected and viewed through the microscope. Photographs of the particles indicated they were needle-shaped crystals about 2 microns long and 0.02 microns wide. These were very similar in habit to the macro crystals obtained by recrystallization from bromobenzene which are needle-shaped crystals 1000 microns long and 1 micron wide.

X-ray powder diagrams were taken of the micro and macro crystals of the nickel (II)-4-methyl-1,2-cyclohexanedionedioxime complex and were found to be identical.

Since the nickel and palladium complexes of 2,3-butanedionedioxime are isomorphous, it was thought that palladium might show an absorption peak similar to the "550" peak of the nickel(II)-4-methyl-1,2-cyclohexanedionedioxime complex. A suspension of the palladium complex was prepared in water and the spectrum scanned with the Cary spectrophotometer. A large absorption peak was found at 468 millimicrons which shifted to 473 millimicrons if the solution was boiled for 10 minutes and scanned again. Fig. 3 is the absorption spectra of the palladium(II)-4-methyl-1,2-cyclohexanedionedioxime complex suspended in water and also in chloroform solution.

Several solutions of palladium and nickel mixtures were prepared and the dioxime added to form mixed crystals suspended in water. A second set of suspensions was prepared by forming the nickel and palladium dioxime complexes separately and then mixing the suspensions. These suspensions were scanned on the Cary spectrophotometer and the spectra compared.

Table 7

Absorption Spectra of Water Suspensions
of [Ni(II), Pd(II)] -4-Methyl-1,2-cyclohexanedionedioximes
and Ni(II)- and Pd(II)-4-methyl-1,2 cyclohexanedionedioximes

Ratio of Ni/Pd	Mixed crystals maxima millimicrons	Mechanical mixture maxima millimicrons
5/0	549	549
4/1	545	549, 470
3/2	534	549, 470
2/3	530	549, 470
1/4	510	549, 470
0/5	470	470

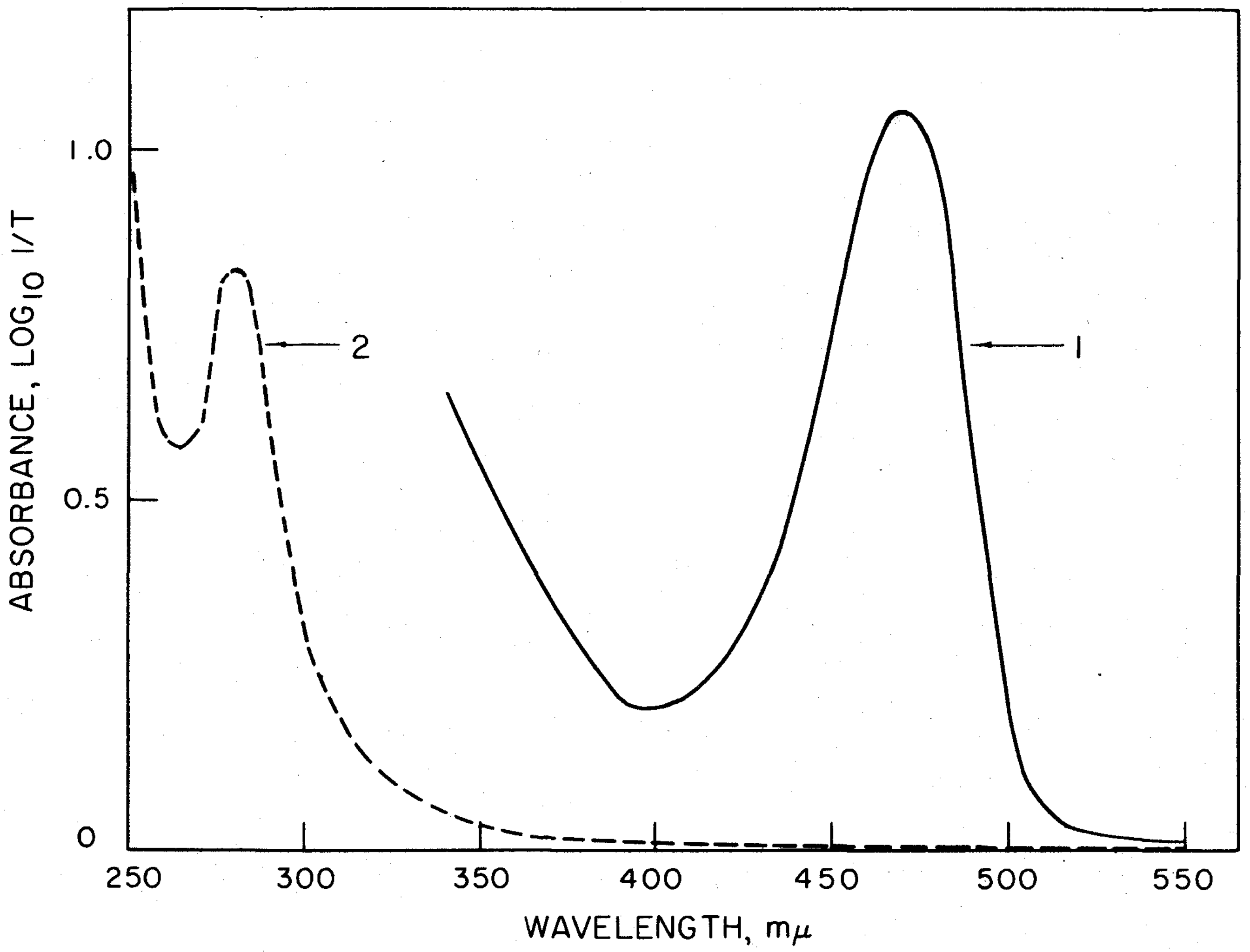


FIG. 3 ABSORPTION SPECTRA OF Pd(II)-4-METHYL-1,2-CYCLOHEXANEDIONEDIOXIME COMPLEX SUSPENDED IN WATER, CURVE 1, AND IN CHLOROFORM SOLUTION, CURVE 2.

Fig. 4 shows the absorption curves for the 2/3 ratios.

It was also found that the addition of potassium chloroplatinate in different amounts to a solution of nickel(II) perchlorate and precipitation with 4-methyl-1,2-cyclohexanedionedioxime shifted the "550" nickel peak toward 660 millimicrons which is the absorption maxima for the platinum(II)-4-methyl-1,2-cyclohexanedionedioxime complex suspended in water. The absorption spectrum of the palladium(II) complex was affected by the addition of platinum in a similar manner.

The mixed complexes with platinum(II) were prepared by mixing the metallic salts in water, adding gum arabic to stabilize the suspension, heating to solution to boiling, and forming the suspension by the addition of the dioxime. Table 8 lists the absorption maxima for different ratios of nickel, palladium, and platinum.

2. Chemical properties

The vic-dioximes prepared were tested for reactivity with metal ions and it was found that they all reacted alike. Copper, cobalt, iron, and ruthenium all formed colored complexes which appeared similar. Nickel and palladium were both precipitated by all of the dioximes from acid solution and the precipitates were highly colored.

The main difference noted was in the solubility of the metallic complexes. In water the 4-(1,1,3,3-tetramethylbutyl)-1,2-cyclo-

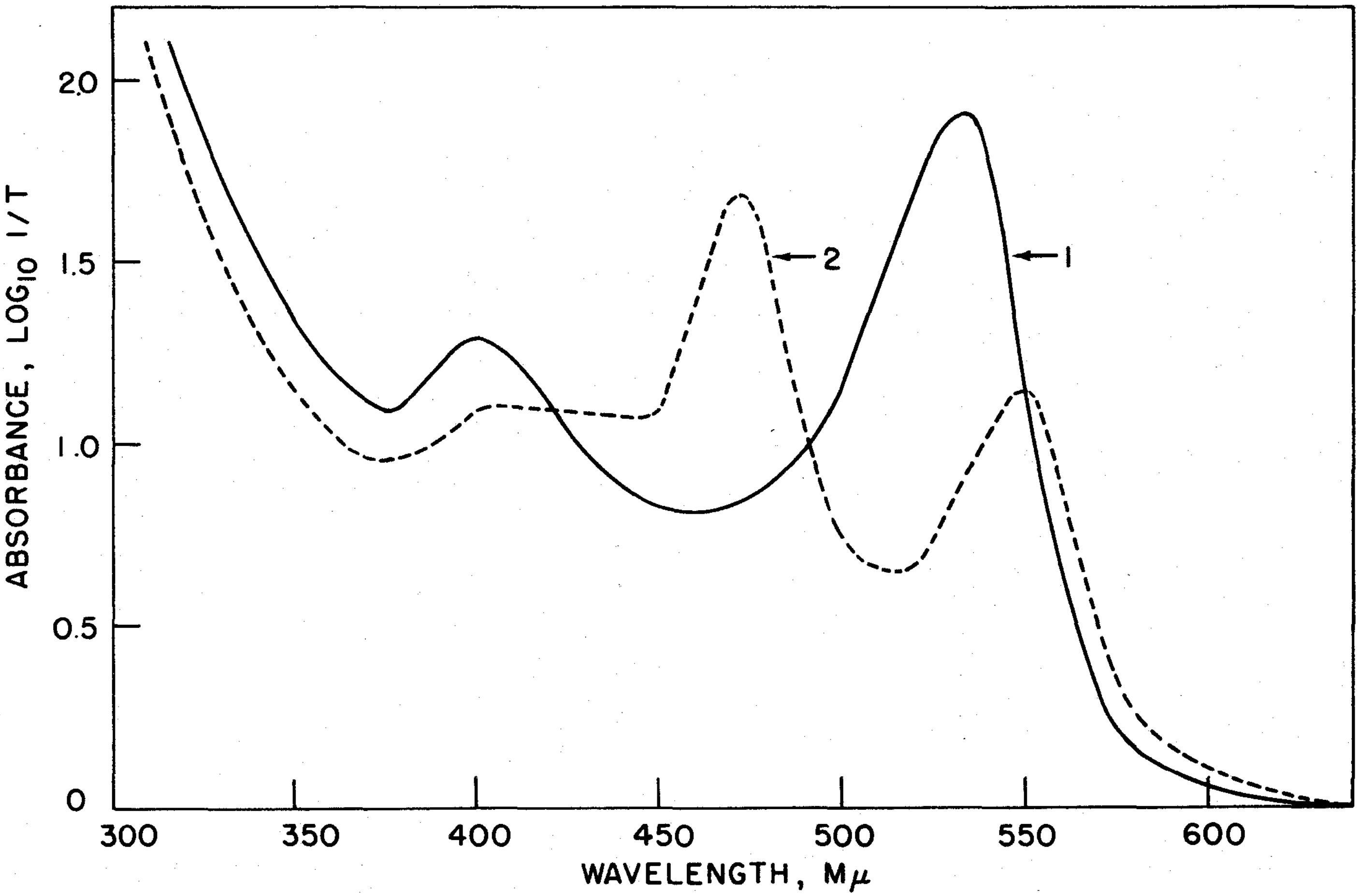


FIG. 4 ABSORPTION SPECTRA OF [Ni(II), Pd(II)]-4-METHYL-1,2-CYCLOHEXANEDIONENEDIOXIME, CURVE 1, AND A MIXTURE OF Ni(II)- AND Pd(II)-4-METHYL-1,2-CYCLOHEXANEDIONEDIOXIMES, CURVE 2, SUSPENDED IN WATER.

Table 8

Absorption Maxima for [Nickel(II), Palladium(II), Platinum(II)]-4-methyl-1,2-cyclohexanedionedioximes Suspended in Water

Ratio of Ni/Pd/Pt	Absorption maximum millimicrons
0/0/1	660
0/1/2	580
0/2/1	520
0/1/0	470
1/0/3	630
1/0/1	600
3/0/1	570
1/0/0	549
1/1/1	570-630[a]

[a] The mixture of 1/1/1, Ni/Pd/Pt did not show a sharp maximum but rather a broad band.

hexanedionedioxime formed slightly soluble complexes with the transition metals and 4-tert-amyl-1,2-cyclohexanedionedioxime formed only moderately soluble complexes. Quantitative data were not taken on the solubility of these complexes, but the dioximes become less selective as precipitants for nickel and palladium as the molecular weight increases.

D. Discussion and Summary

The physical properties of the dioximes investigated, when viewed together, offer significant information. It was noted that the melting points of the dioximes investigated differed by only 40° C. which, considering the large difference in molecular weight, is rather a narrow range and further, all of the compounds melted with decomposition. This indicates that destruction of the vic-dioxime grouping is responsible for the melting point.

It is interesting to note the effect of the same substituent in the 3- and 4-positions on the 1,2-cyclohexanedionedioxime molecule. In the case of the methyl homologs the 3-methyl compound melts 17° C. below the 4-methyl derivative. Another methyl group added to the 6-position does not alter the melting point of the 3-methyl-1,2-cyclohexanedionedioxime, but a methyl group added to the side chain to form a 3-ethyl 1,2-cyclohexanedionedioxime increases the melting point 15° C. This indicates that a substituent in the 3-position is much more influential in crystal formation than a substituent in the 4-position.

It is noted in Table 2 that all of the dioximes having free rotation of the oxime groups are less soluble in water than those restrained by ring formation. This supports the concept of extensive hydrogen bonding in the dioxime crystals since restriction on the oxime groupings would interfere with the hydrogen bond system and subsequently increase the solubility of the compound.

The solubilities of the dioximes studied in water tend to support the idea of interference in the packing of the dioximes in a crystal by 3 substituted groups. The methyl derivative in the 3 position is about 15 per cent more soluble than 4-methyl-1,2-cyclohexanedionedioxime and the 3,6-dimethyl homolog is twice as soluble as the 3-methyl-1,2-cyclohexanedionedioxime. Solubilities of the 4-substituted series decreases, as one would expect, with increasing mol. weight.

Spectra of the dioximes are all the same in the visible and ultraviolet regions which indicates that the substituted groups do not affect the dioxime functional groups to any great extent when in solution.

The spectra of the nickel complexes suspended in water were investigated and the absorption peak located near 400 millimicrons was found in each case. Mellor et al. (72) has stated that this band is characteristic of all nickel complexes that exist in the square-planar form and this, of course, would be expected of the dioxime complexes since they are of that type. A second absorption maximum was located near 550 millimicrons, but it was found to vary slightly with the particular dioxime employed. It was thought that this might involve the nickel-nickel bond and because of the interference offered by different substituted groups, the bond absorption might be altered slightly.

It can be supposed that the hindrance offered by each group would be a function of its actual volume, its "effective" volume, and its position on the cyclohexane ring. Then the hindrance to a nickel-nickel bond will increase as the alkyl group becomes larger, as a more negative group is attached, and as the substituents are shifted from 4- to the 3-position. The negative group would hinder because in the packing of nickel-dioxime crystals the substituent would be located near the oxime oxygens of the next molecule and repulsion because of electrostatic forces would result.

These effects were found in the spectra of the different nickel(II)-dioxime complexes. Substitution of a 1,1,3,3-tetramethylbutyl group in the 4-position resulted in only a 6 millimicron bathochromic shift in the position of the 550 millimicron peak of the unsubstituted 1,2-cyclohexanedionedioxime.

Intermediate bathochromic shifts were noted for the 4-tert-amyl and 4-methyl derivatives. The 4-iso-propyl-1,2-cyclohexanedionedioxime-nickel complex, however, exhibited a 3-millimicron hypsochromic shift in the "550" peak which is rather difficult to explain. It is possible that the packing of the molecules permits the iso-propyl group to fit easily in the crystal structure.

The carboxy group when substituted in the 4-position resulted in a marked increase in the solubility and a decrease in the wavelength of the "550" peak. The solubility in water could be easily explained by the addition of another hydrophilic group, but this should not affect the position of the absorption maximum unless direct interference with the nickel-nickel bond is presented by its volume and negativity.

The 4-position substituents are removed from the immediate vicinity of the nickel-nickel bond and it might be expected that a group in the 3- position would interfere to a much greater extent. It was found that a methyl group resulted in only a 2 millimicron shift depending on the position, but that a 3- ethyl group resulted in a 5 millimicron bathochromic shift. A more startling fact is that two methyl groups in the 3,6-positions shifted bathochromically the wavelength of the "550" peak by 56 millimicrons.

These facts are excellent evidence that absorption in the 550 millimicron region of the spectra involves the nickel-nickel bond or at least some sort of intermolecular interaction between the adjacent nickel-dioxime molecules.

Before the report of Yamada and Tsuchida (147) that the maximum absorption of light vibrating along the nickel-nickel axis of the crystal of bis(2,3-butanedionedioximato-N,N')nickel(II) was from 500 to 525 millimicrons, it appeared the nature of the "550" millimicron peak was strictly an absorption phenomenon. However, their maximum for a macro crystal did not coincide with the peak observed with suspensions of the micro crystals in water, since for these small crystals the peak was near 560 millimicrons. It is to be noted that they reported a maximum in the absorption spectrum at 410 millimicrons for light vibrating in the plane of the nickel-nitrogen bonds. This agrees with the data for the micro crystals and supports the concept that the square-planar nickel complexes involve absorption near the 375 to 425 millimicron region of the spectrum.

This work of Yamada and Tsuchida meant that there was a difference in the composition, habit, or interaction with light between the micro and macro crystals. It was found with the aid of an electron microscope that the micro crystals were the same in habit as the macro crystals and that they were needles 2000 by 20 millimicrons in size. An X-ray powder diagram was taken of the two types of crystals and comparison showed that the basic structure of the crystals was the same.

This meant that the difference must be with the processes involved in the interaction with light. It would be expected that crystal size alone would not affect the absorption of light to any great extent, but size would be a factor in the scattering and reflection processes. The experiments with non-aqueous solvents can all be interpreted on the basis that higher precipitation temperatures and longer digestion times tend to destroy the small crystals and form larger ones. This would effectively reduce the surface area and the number of particles. Since the peak was observed in slightly polar solvents as well as in water and alcohols, it would seem to reject the possibility of solvent absorption or interaction as the source of the "550" peak.

The explanation thus seems narrowed to some kind of scattering phenominon which is very specific for a certain wavelength band. The "Christiansen effect" seems to fit these conditions perfectly. Briefly, the "Christiansen effect" is the appearance of a rather sharp scattering peak on the long wavelength side of a strong absorption band and it is affected by the size and number of scattering particles. In the vicinity of an absorption band the refractive index changes rapidly and as the band is approached from the long wavelength side the refractive index increases until it reaches a maximum. This results in high reflectivity due to the difference in refractive indexes of the medium and the material. As the maximum of the absorption band is approached, the refractive index falls rapidly and the reflection is reduced. Coming out of the band the transmission is greatly enhanced because of the lowered refractive index and small absorption. Thus peaks are shifted to the long wavelength side of their absorption bands as a result of the scattering. Organic compounds show a sharper scattering than ionic crystals and the scattering peaks are closer to the absorption maxima.

This type of phenominon fits the observed results extremely well. The absorption band of the metal-metal bond is a factor in the location of the observed maximum, but the peak can be modified by scattering. The scattering is a function of the size of the crystals, disappearing with larger particles.

Fig. 5 illustrates the manner in which an absorption band might be modified by scattering. As the scattering losses become more important, the peak is shifted to higher wavelengths and is sharpened at the top. The dotted line, curve 1, represents the radiation lost by absorption in the crystal and the dashed line, curve 2, is the radiation lost by scattering. The solid line, curve 3, is the sum of the two other curves and represents the total radiation lost.

It is possible, by the addition of a dispersant to control the size of the particles, to alter the scattering losses and thereby sharpen the observed "550" peak. This could also shift the apparent maximum to slightly lower wavelengths as shown in the last curve in Fig. 5.

When palladium-dioxime complex exhibited the same characteristic peak in the visible spectrum, it was thought that if this peak was due to metal-metal bond absorption, the position of the maximum might be shifted by preparing a mixed crystals of nickel(II)- and palladium(II)-dioximes. This was possible since the two metall-dioxime complexes are isomorphous. This peak did shift and was located between the positions of the peaks for the individual metal-dioxime complexes. Further, it was found that platinum(II) formed isomorphous dioxime complexes with both palladium(II) and

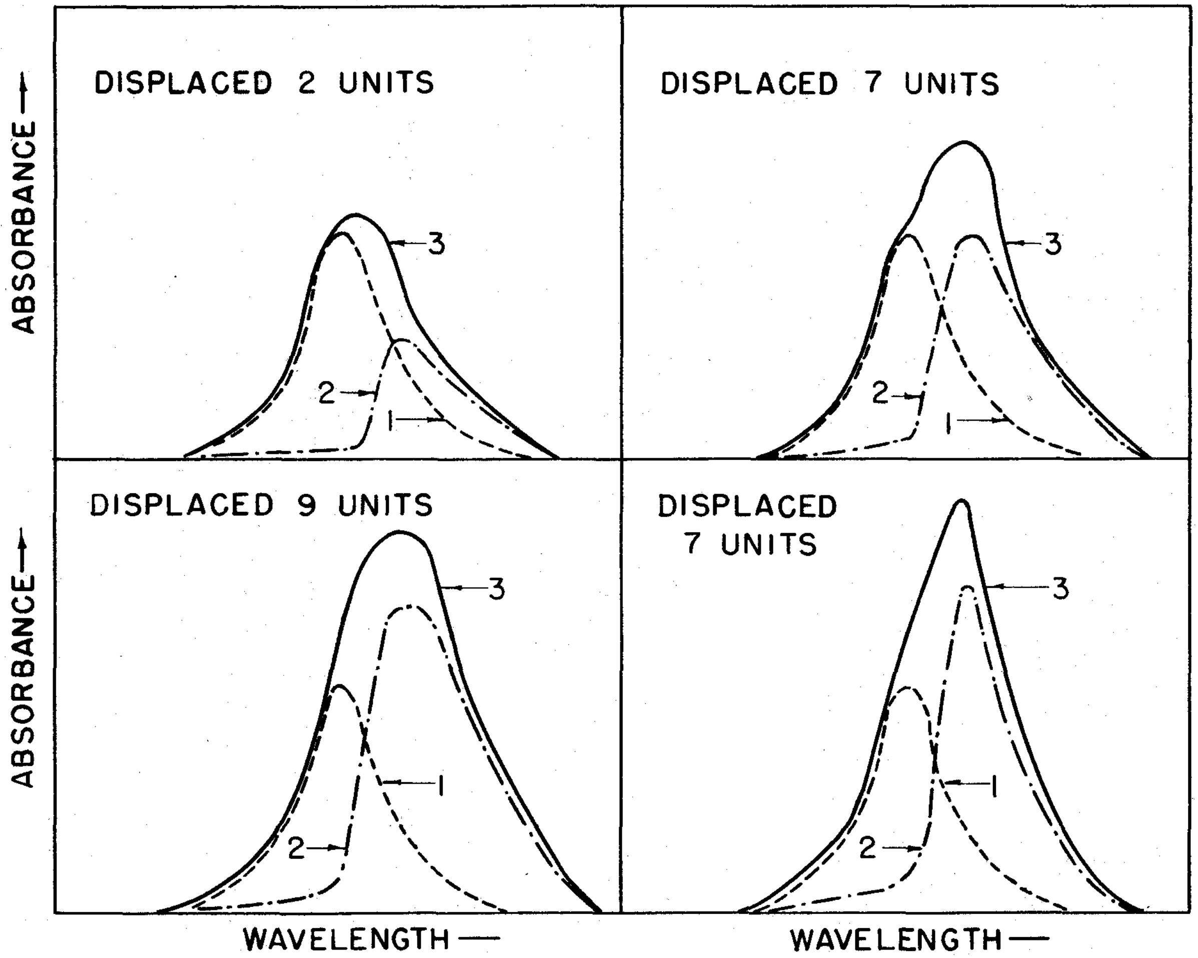


FIG.5 CHRISTIANSEN EFFECT. ABSORPTION, CURVE 1, SCATTERING, CURVE 2, AND RESULTANT, CURVE 3.

nickel(II) separately and combined. It was noticed that in the mixed crystals the peak was slightly broader than with pure crystals and that with mixed crystals involving all three metals the peak covered 50 millimicrons.

In summary, it appears the absorption at 550 millimicrons for the nickel(II)-1,2-cyclohexanedionedioxime complex in suspension is due to nickel-nickel bond absorption but the absorption peak is modified by selective scattering of the light. This peak is therefore not only a function of the amount of material present, but also of the state of subdivision.

The chemical properties of the alkylated 1,2-cyclohexanedionedioximes were almost identical as might be expected. The most outstanding thing to note is that the selective precipitation of nickel(II) and palladium(II) in water is missing with the 4-tert-amyl and 4-(1,1,3,3-tetramethylbutyl substituted compound since the metallic complexes are so organic in nature they precipitate without requiring the metal-metal bond formation.

The carboxylated 1,2-cyclohexanedionedioxime behaved chemically like a dioxime and a carboxylic acid. The nickel complex precipitated at pH 3 and redissolved as the solution was made basic, but the red color of the nickel chelate remained. The solubility of the nickel(II)-4-carboxy-1,2-cyclohexanedionedioxime in water at a pH of 9 was determined to be greater than 0.6 molar or more than 250 g. per liter.

If this material could be prepared in quantity, it would be a good water-soluble reagent for the colorimetric determination of transition elements. Also it could be used to mask several ions in aqueous solution.

This work on the properties of these vic-dioximes suggested that:

1. The 3-methyl, 4-methyl, and possibly the 4-iso-propyl-1,2-cyclohexanedionedioximes might be good water-soluble analytical reagents.

2. Since all of these vic-dioximes form colored nickel complexes which are soluble in chloroform, they could possibly be used in extraction and spectrophotometric procedures.

3. Since suspensions of the nickel(II)-, palladium(II)-, or platinum(II)-dioxime complexes in water show a strong peak in the visible which, although being a function of particle size, might be used for spectrophotometric determinations if conditions were controlled.

IV. GRAVIMETRIC APPLICATIONS

A. Review of the Literature

The vicinal-dioximes react with most of the transition metals to form a complex. However, the complexes of nickel(II) and palladium(II) are insoluble in water under the proper conditions and gravimetric determinations are possible. The compound 2,3-butanedionedioxime has been applied to the determination of nickel more than any other reagent and has been regarded as a prime example of a selective organic reagent.

2,3-Butanedioxedioxime was first reported by Tschugaeff (128) in 1905 and since then many other vic-dioximes have been suggested. Diehl (19) has reviewed some of these dioximes and has included a bibliography covering their gravimetric applications.

Voter and Banks (135) have discussed the use of water-soluble vic-dioximes in the gravimetric determination of nickel and palladium. They suggest that 1,2-cycloheptanedionedioxime, heptoxime, be employed for the determination of nickel as it possesses several properties favorable for its analytical application. Heptoxime is soluble in water to the extent of 4.8 g. per liter and is selective for the precipitation of nickel(II) in the pH range of 3 to 8. The main disadvantage of this reagent is the high cost of preparation.

Wallach (143) reported that 1,2-cyclohexanedionedioxime, nioxime, reacted with nickel(II) to give a scarlet precipitate and Feigl (26) has stated that 1,2-cyclohexanedionedioxime should be ideal as a reagent because of its solubility in water. This solubility is over 8 g. per liter.

1,2-Cyclohexanedionedioxime has been applied by Voter, Banks, and Diehl (136) to the gravimetric determination of nickel and to the gravimetric determination of palladium (137). With the nickel determination, nioxime offers several advantages over 2,3-butanedionedioxime in that it is more soluble in water, is more sensitive, quantitatively precipitates nickel down to a pH of 3, and has a more favorable gravimetric factor. These advantages are neutralized, however, by the great disadvantage that excess reagent contaminates the chelate precipitate and an empirical factor must be used. In addition, iron interferes with the determination. Voter *et al.* found that 1,2-cyclohexanedionedioxime was a good reagent for the determination of palladium as in this application excess reagent did not coprecipitate. The alicyclic vic-dioximes seem to have distinct advantages over straight or branched chain vic-dioximes. Among these advantages are a high solubility in water for corresponding molecular weights and a quantitative precipitation of the nickel(II) complex nearly 2 pH units lower. Alicyclic vic-dioximes having rings of 5 and 10 carbon atoms have been prepared and studied by Voter (134). 1,2-Cyclopentanedionedioxime was found to precipitate nickel only in the pH range of 6 to 8 and even then the complex was soluble to the extent of 100 mg. per liter. This, of course, would hardly be suitable for a quantitative gravimetric reagent. The 1,2-cyclodecanedionedioxime reacted with nickel only incompletely and because of the high molecular weight of the reagent, it was soluble in water to only 100 mg. per liter. Both of these compounds were rejected by Voter as analytical reagents for either nickel or palladium.

Since the optimum ring size for the alicyclic vic-dioximes seemed to be 6 or 7 carbon atoms, it appeared only logical to investigate the substituted 1,2-cyclohexanedionedioximes or 1,2-cycloheptanedionedioximes as possible reagents. The 7 membered ring is expensive and difficult to obtain compared to the 6 membered ring which can be obtained from reduction of benzenoid compounds.

Wallach (143) reported that 4-methyl-1,2-cyclohexanedionedioxime, 4-methylnioxime, formed a red precipitate with nickel as did the 3-methyl-1,2-cyclohexanedionedioxime, 3-methylnioxime. In fact, nearly all reports of compounds containing the vic-dioxime functional group state that they react with nickel(II) to form a red, orange, or yellow precipitate.

B. Materials and Apparatus

Generally, only chemicals of reagent grade, Eastman white label, or comparable purity were employed. The preparations of the vic-dioximes have been described in section II of this thesis.

Standard nickel perchlorate solutions. These solutions were prepared from Mond nickel obtained from the International Nickel Company, New York. An analysis supplied by the company revealed that the nickel contained 0.045 per cent iron and 0.008 per cent each of cobalt and copper. The iron content was verified by employing the 1,10-phenanthroline method for the determination of iron in nickel. The nickel was dissolved in aqua regia and the solution evaporated to dryness three times with perchloric acid. The nickel perchlorate was taken up in one liter of water and aliquot samples of the solution were analyzed for nickel by the 1,2-cycloheptanedionedioxime, heptoxime, method of Voter and Banks (135). This stock solution was used to prepare other more dilute nickel solutions. These diluted, secondary standards were also checked for nickel content by analysis.

Standard palladium perchlorate solutions. Reagent-grade palladium metal was dissolved in aqua regia and fumed to dryness three times with perchloric acid. The palladium perchlorate was dissolved in one liter of water and the solution was standardized by the 1,2-cyclohexanedionedioxime, nioxime, method for palladium suggested by Voter, Banks, and Diehl (136). More dilute solutions of palladium were prepared from this stock solution and were checked for palladium content by the nioxime method.

4-Methyl-1,2-cyclohexanedionedioxime solution. A 0.34 per cent solution of 4-methyl-1,2-cyclohexanedionedioxime, 4-methyl nioxime, in water was prepared from the dioxime synthesized in this laboratory.

4-iso-Propyl-1,2-cyclohexanedionedioxime solution. A 0.08 per cent aqueous solution of 4-iso-propyl-1,2-cyclohexanedionedioxime, 4-iso-propyl nioxime, was prepared from the dioxime synthesized in this laboratory.

The instruments and apparatus employed in this study were all obtained from commercially available stocks. The pipettes and burets used were all Kimble "Normax" or "Exax" brand. Beckman, Model G, pH meter was employed for all of the pH measurements described in section III, B of this thesis.

C. Experimental

1. 4-Methyl-1,2-cyclohexanedionedioxime

a. Determination of nickel. The 4-methyl-1,2-cyclohexanedionedioxime was investigated as to its applicability for the determination of nickel. The white, crystalline vic-dioxime was suspended in deionized water and shaken for three days at 25° C. The excess dioxime was filtered off and the solubility of the reagent in water was determined by the addition of nickel perchlorate to aliquots of the solution. The nickel-dioxime complex was filtered off, dried, and weighed and calculations of the solubility were carried out assuming the complex contained 15.90 per cent nickel. Later this assumption was proved true and the solubility of 4-methyl-1,2-cyclohexanedionedioxime in water was determined to be 3.4 g. per liter or 2.2×10^{-2} molar. A saturated solution of the dioxime was used in all of the following analytical work.

Five drops of the 4-methyl-1,2-cyclohexanedionedioxime solution were added to each of several 100-ml. flasks containing from one to 10 parts of nickel per 10,000,000 parts of water. The flasks were shaken vigorously and observations were made at three minutes, one hour, and 12 hours after addition of the dioxime. The solutions with greater than 2 parts of nickel per 10,000,000 parts of water showed a pink coloration after three minutes and a precipitate after one hour. A fine pink precipitate was observed in the flasks containing 1 and 2 parts of nickel per 10,000,000 of water after 12 hours. This precipitate was more readily seen by filtering through a small Büchner funnel onto a piece of white filter paper. The pH of these solutions was in the range 4 to 6.

The effect of pH on the quantitative precipitation of the nickel complex was studied over the range 1 to 7. Four ml. of 0.1019 molar nickel perchlorate solution were placed in a 400-ml. beaker and diluted to 125 ml. Two ml. of concentrated hydrochloric acid were added to the beakers and they were warmed to approximately 60° C. on a hot plate. Seventy ml. of the saturated dioxime solution were added and while stirring, the pH was raised slowly by the dropwise addition of a 20 per cent ammonium acetate solution. The rise in pH was followed with a pH meter to the desired value.

The nickel complex was digested at 60° C. for one-half hour and was then filtered into a weighed filter crucible of medium porosity. The precipitate was washed, dried at 105° C. for two hours, and weighed. Results showed that below pH 3 the precipitation of the nickel(II)-4-methyl-1,2-cyclohexanedionedioxime complex was incomplete.

The precipitate, obtained by the method described in the pH study, filtered easily and did not tend to creep. A study of the character of the precipitate for different methods of precipitation was made and while the accuracy of the nickel determination was not altered, rapid precipitation by direct addition of the reagent to the nickel solution at a pH greater than 3 gave a precipitate difficult to filter. The methods of precipitation investigated included slow and fast addition of reagent to a nickel solution at pH 4 to 6; slow and fast addition of ammonium acetate to a solution of the dioxime, nickel, and hydrochloric acid; cold and hot precipitations; and long and short digestion periods. The best procedure appeared to be dropwise addition of ammonium acetate to raise the pH of a solution of nickel and the dioxime, precipitation at a temperature of 60° C., and a digestion time of one-half hour at 60° C.

In another set of experiments it was found that up to a 200 per cent excess of the reagent did not affect the nickel determination. Also, it was found that the drying temperature should be kept below 115° C. and 105° C. was chosen.

Analysis of the nickel(II)-4-methyl-1,2-cyclohexanedionedioxime complex for nickel was carried out by destroying the organic material first with nitric acid and then with perchloric acid and determining the nickel with 1,2-cycloheptanedionedioxime. The theoretical percentage of nickel in $(C_7H_{11}O_2N_2)_2Ni$ is 15.90 and an average for five determinations gave the percentage of nickel as 15.91 ± 0.02.

Several solutions containing from 1 to 60 mg. of nickel were prepared and analyzed with 4-methyl-1,2-cyclohexanedionedioxime by employing the best procedure as indicated by the previous studies.

The exact procedure employed was as follows. The volume of the nickel solution was adjusted to 175 ml. and the pH of the solution was lowered to approximately 1 by the addition of hydrochloric acid. Twenty ml. of a saturated aqueous solution of 4-methyl-1,2-cyclohexanedionedioxime was introduced for every 10 mg. of nickel and the solution was warmed on a hot plate to 60° C. While stirring, enough 20 per cent ammonium acetate solution was added dropwise to raise the pH to between 3 and 5. The precipitate was digested at 60° C. for one-half hour and was then filtered off through a weighed filter crucible of medium porosity. The crucible was kept full of liquid until all of the solution had been added and then the precipitate was "sucked dry" and washed with three portions of hot water. The nickel(II)-4-methyl-1,2-cyclohexanedionedioxime complex was dried at 105° C. for two hours and weighed.

The average error for 16 determinations was 0.08 mg. which, on the average sample of 24 mg., corresponds to three parts per thousand. In Table 9 the data are tabulated for these samples and for five National Bureau of Standards steel samples.

The effect of various anions upon the determination of nickel with 4-methyl-1,2-cyclohexanedionedioxime was studied. Nickel solutions containing 1.0 g. of the foreign ions were analyzed

Table 9

Gravimetric Determination of Nickel(II) with 4-Methyl-1,2-cyclohexanedionedioxime

Sample	Number of determinations	Nickel(II) found	Nickel(II) taken
Nickel perchlorate	4	1.23 ± 0.05 mg.	1.20 mg.
Nickel perchlorate	4	5.98 ± 0.08 mg.	5.98 mg.
Nickel perchlorate	4	24.0 ± 0.08 mg.	24.0 mg.
Nickel perchlorate	4	55.8 ± 0.10 mg.	55.9 mg.
N.B.S. cast iron, No. 115[a]	3	15.85 ± 0.05 %	15.89 %
N.B.S. 18 chromium-9 nickel steel, No. 101c[a]	2	9.28 ± 0.01 %	9.27 %
N.B.S. nickel steel, No. 33c[a]	3	3.28 ± 0.00 %	3.28 %
N.B.S. nickel-molybdenum steel, No. 111a[a]	3	1.74 ± 0.00 %	1.75 %
N.B.S. chromium-nickel-molybdenum steel, No. 139[a]	3	0.567 ± 0.007%	0.563%
N.B.S. aluminum-base alloy, No. 85a[a]	2	0.412 ± 0.003%	0.410%

[a] Ten g. of citric acid added.

gravimetrically with 4-methyl-1,2-cyclohexanedionedioxime and no effect was noted from solutions containing acetate, chloride, citrate, nitrate, perchlorate, sulfate, sulfosalicylate, tartrate, and thiocyanate. The results are given in Table 10.

Table 10

Anionic Interferences in the Gravimetric Determination of Nickel(II) with 4-Methyl-1,2-cyclohexanedionedioxime

Anion added[a]	Nickel found[b] mg.	Error mg.
Acetate	15.9	+ 0.3
Chloride	15.8	+ 0.2
Citrate	15.4	- 0.2
Nitrate	15.6	0.0
Perchlorate	15.4	- 0.2
Sulfate	15.7	+ 0.1
Sulfosalicylate	15.7	+ 0.1
Tartrate	15.6	0.0
Thiocyanate	15.8	+ 0.2

[a] 1.0 g. of each anion was added.

[b] 15.6 mg. of nickel were added.

Nickel was determined with the 4-methyl-1,2-cyclohexanedionedioxime in the presence of each of the following cations: aluminmum(III), ammonium(I), barium(II), beryllium(II), bismuth(III), cadmium(II), calcium(II), cerium(III), chromium(II), cobalt(II), copper(II), iron(II), iron(III), lanthanum(III), lead(II), lithium(I), manganese(II), magnesium(II), palladium(II), potassium(I), ruthenium(IV), silver(I), sodium(I), strontium(II), thorium(IV), titanium(III), uranium(IV), vanadium(IV), and zinc(II). The results are given in Table 11.

Table 11

Cationic Interferences in the Gravimetric Determination of Nickel(II) with 4-Methyl-1,2-cyclohexanedionedioxime

Cation added	Amount of cation added g.	Nickel[f] found mg.	Error mg.
Aluminum(III)[a]	0.2	37.9	0.1
Ammonium(I)	0.2	37.7	0.1
Antimony(III)[a]	0.2	37.7	0.1
Barium(II)	0.2	37.6	0.2
Beryllium(II)	0.2	37.7	0.1
Bismuth(III)[a]	0.2	37.6	0.2
Cadmium(II)	0.2	37.8	0.0
Calcium(II)	0.2	37.8	0.0
Cerium(III)	0.2	37.9	0.1
Chromium(III)[a]	0.2	37.8	0.0

Table 11 (Continued)

Cation added	Amount of cation added g.	Nickel[f] found mg.	Error mg.
Cobalt(II)	0.02	37.9	0.1
Cobalt(III)[b]	0.2	37.9	0.1
Copper(II)	0.02	37.9	0.1
Copper(I)[c]	0.2	38.0	0.2
Iron(II)[d]	0.2	37.9	0.1
Iron(III)[a]	0.2	37.8	0.0
Lanthanum(III)	0.2	37.9	0.1
Lead(II)	0.2	37.7	0.1
Lithium(I)	0.2	37.8	0.0
Magnesium(II)	0.2	37.6	0.2
Manganese(II)	0.2	37.8	0.1
Palladium(II)[e]	0.2	37.7	0.1
Platinum(II)	0.2	37.7	0.1
Potassium(I)	0.2	37.8	0.0
Ruthenium(III)	0.2	37.9	0.1
Silver(I)	0.2	37.8	0.0
Sodium(I)	0.2	37.8	0.0
Strontium(II)	0.2	37.9	0.1
Thorium(IV)	0.2	37.9	0.1
Titanium(III)[a]	0.2	37.7	0.1

Table 11 (Continued)

Cation added	Amount of cation added g.	Nickel[f] found mg.	Error mg.
Uranium(IV)	0.2	37.8	0.0
Vanadium(III)	0.2	37.7	0.1
Zinc(II)	0.2	37.6	0.2

[a] Complexed with one g. of tartrate.

[b] Complexed as cyanide.

[c] Complexed as thiocyanate.

[d] Hydroxylamine added.

[e] Ammonium hydroxide added, pH 8 for precipitation.

[f] 37.8 mg. of nickel added.

When determining nickel in the presence of large amounts of copper or cobalt, special procedures must be followed as these ions react with the dioxime in preference to nickel even though these complexes do not precipitate. Copper can be effectively removed from the solution by adding excess thiocyanate which reduces the copper to the copper(I) and forms a soluble thiocyanate complex (146). Cobalt may be complexed as hexacyanocobaltate(III) by hydrogen peroxide and sodium cyanide. The nickel cyanide complex is then destroyed by the addition of formaldehyde (28).

b. Determination of palladium. Since 1,2-cyclohexanedionedioxime is an excellent reagent for palladium, it was thought that 4-methyl-1,2-cyclohexanedionedioxime might also be applicable to the determination of this metal. Due to the pale yellow color of the palladium(II)-vic-dioxime precipitate, the detection of palladium is not so sensitive as nickel. Ten solutions containing from 1 to 10 parts of palladium per ten million parts of water were adjusted to pH 2 and three drops of a saturated water solution of 4-methyl-1,2-cyclohexanedionedioxime were added. After three minutes a yellow color was observed in the flasks containing greater than five parts of palladium per ten million parts of water. Within one hour a pale yellow coloration could be seen in the flasks containing 4 and 5 parts of palladium per million parts of water and after 12 hours a yellow precipitate was observed in the flasks containing greater than 4 parts per ten million of palladium in water.

A study of the effect of pH on the quantitative precipitation of the palladium(II)-4-methyl-1,2-cyclohexanedionedioxime complex was made by adjusting the pH of several palladium samples and adding the dioxime solution. The precipitate was filtered off, dried, and weighed. Quantitative precipitation was found if the pH was greater than 0.7 and less than 5. Analysis of the precipitate for palladium was performed by destroying the organic material with hot nitric and perchloric acids and precipitating the palladium with 1,2-cyclohexanedionedioxime. As an average for five determinations, 25.57 ± 0.04

per cent palladium was found, which compares favorably with the theoretical 25.59 per cent palladium for $(C_7H_{11}O_2N_2)_2Pd$.

Precipitation of the complex at 60° C. and digestion for one-half hour seemed to be the best procedure to follow in determining palladium. The precipitate was difficult to filter and tended to creep if the dioxime was added to a cold palladium solution or if the precipitate was not digested. It was not necessary to raise the pH slowly after the addition of the dioxime and the reagent could be added from a pipette to the palladium solution at a pH of 1. Dropwise addition of the reagent with stirring did, however, decrease coprecipitation of other ions and make the precipitate easier to filter.

Several determinations were made on standard palladium samples and the results are given in Table 12. The average error was 0.1 mg. for 6- to 25-mg. samples or 4 to 10 parts per thousand.

Table 12

Gravimetric Determination of Palladium(II) with 4-Methyl-1,2-cyclohexanedionedioxime

Number of determinations	Palladium taken mg.	Precipitate weighed mg.	Palladium found mg.
3	6.25	24.4 ± 0.4	6.2 ± 0.1
3	12.5	49.2 ± 0.4	12.6 ± 0.1
3	25.0	98.1 ± 0.5	25.1 ± 0.1
3	50.0	194.6 ± 0.8	49.8 ± 0.2

The proper drying temperature for the precipitate was investigated by heating at 105° C. for three hours and weiging and then leaving over-night at 105° C. and reweighing. The change in weight was never greater than 0.2 mg. for ten determinations and in six cases no difference was found. If the drying temperature was 115° C., however, a loss in weight was noticed if the heating was continued over three hours.

The recommended procedure is as follows. The volume of the palladium solution is adjusted to 200 ml. for a 20-mg. sample of palladium and the pH is lowered to 1.0 with hydrochloric acid. The solution is warmed on a hot plate to 60° C. and the dioxime solution added from a pipette with stirring. Seven ml. of the saturated 4-methyl-1,2-cyclohexanedionedioxime solution are added for each 10 mg. of palladium. After digestion at 60° C. for one-half hour, the precipitate is filtered through a medium porosity filter crucible. The palladium complex is dried at 105° C. for two hours and weighed. The gravimetric factor for palladium is 0.2559.

The determination of palladium(II) in the presence of several anions was carried out and it was found that no interference resulted from acetate, chloride, nitrate, perchlorate sulfate, sulfosalicylate, or tartrate (Table 13).

Cationic interferences were studied with the following ions included: aluminum(III), antimony(III), barium(II), beryllium(II), bismuth(III), cadmium(II), calcium(II), cerium(III), chromium(III),

Table 13

Anionic Interference in the Gravimetric Determination of Palladium(II) with 4-Methyl-1,2-cyclohexanedionedioxime

Anion added	Amount of anion added g.	Palladium[a] found mg.	Error mg.
Acetate	1	12.6	+ 0.1
Chloride	1	12.8	+ 0.3
Nitrate	1	12.4	- 0.1
Perchlorate	1	12.5	0.0
Sulfate	1	12.5	0.0
Sulfosalicylate	1	12.6	+ 0.1
Tartrate	1	12.4	- 0.1

[a] 12.5 mg. of palladium were added.

cobalt(II), copper(II), iridium(III), iron(II), iron(III), lanthanum(III), lead(II), lithium(I), magnesium(II), nickel(II), platinum(II), ruthenium(III), potassium(I), rhodium(III), silver(I), sodium(I), strontium(II), thorium(IV), titanium(III), uranium(IV), vanadium(IV), zinc(II), and zirconium(IV). Table 14 lists the results of the interference study of the cations.

Gold was tested and it was found that due to reduction to the metal it interfered even in milligram amounts. Precipitation of

Table 14

Cationic Interferences in the Gravimetric Determination of Palladium(II) with 4-Methyl-1,2-cyclohexanedionedioxime

Cation added[a]	Palladium found[b] mg.	Error mg.
Aluminum(III)	25.1	+ 0.1
Ammonium(I)	25.1	+ 0.1
Antimony(III)	25.0	0.0
Barium(II)	24.9	- 0.1
Beryllium(II)	25.0	0.0
Bismuth(III)[c]	25.1	+ 0.1
Cadmium(II)	24.8	- 0.2
Calcium(II)	25.2	+ 0.2
Cerium(III)	25.0	0.0
Chromium(III)	25.1	+ 0.1
Cobalt(II)	25.0	0.0
Copper(II)	25.0	0.0
Iridium(III)	25.1	+ 0.1
Iron(II)	25.2	+ 0.2
Iron(III)[d]	25.1	+ 0.1
Lanthanum(III)	24.8	- 0.2
Lead(II)	25.1	+ 0.1
Lithium(I)	25.0	0.0
Magnesium(II)	24.8	- 0.2

Table 14 (Continued)

Cation added[a]	Palladium found[b] mg.	Error mg.
Manganese(II)	24.9	- 0.1
Nickel(II)	25.0	0.0
Platinum(II)	25.0	0.0
Potassium(I)	25.0	0.0
Rhodium(III)	25.2	+ 0.2
Ruthenium(III)	25.1	+ 0.1
Silver(I)[c]	25.0	0.0
Sodium(I)	25.0	0.0
Strontium(II)	25.1	+ 0.1
Thorium(IV)	24.9	- 0.1
Titanium(III)	24.8	- 0.2
Uranium(IV)	25.1	+ 0.1
Vanadium(IV)	25.0	0.0
Zinc(II)	24.9	- 0.1
Zirconium(IV)	25.2	+ 0.2

[a] 1.0 g. of the cation was added.

[b] 25.0 g. of the palladium were added.

[c] Chloride absent.

[d] Tartrate added.

the palladium(II)-vic-dioxime complex in the cold helped with small amounts of the gold, but no satisfactory procedure was found to remove the interference completely.

2. 4-iso-Propyl-1,2-cyclohexanedionedioxime

It was thought 4-iso-propyl-1,2-cyclohexanedionedioxime, while not too soluble in water, might be advantageously applied to the gravimetric determination of nickel and palladium due to its high molecular weight and the small solubility of its metallic complexes in water.

A saturated solution of the dioxime in water was prepared by shaking the pure, solid reagent in deionized water at 25° C. for one week. The excess reagent was filtered off and the dioxime in solution was determined by precipitation as the nickel(II) complex. This solution was used for all of the gravimetric work.

a. Determination of nickel. The sensitivity of 4-iso-propyl-1,2-cyclohexanedionedioxime in the detection of nickel was studied in the same manner as described for the 4-methyl-1,2-cyclohexanedionedioxime and it was found that 1 part in 10,000,000 was the limit of detection.

A study of the pH effect on quantitative precipitation of the nickel complex revealed that below a pH of 2.7 the weight of the precipitate was less than expected. As in the use of 4-methyl-1,2-cyclohexanedionedioxime, it was found that precipitation of the nickel(II) complex at a temperature near 60° C. and digestion of the precipitate for one-half hour afforded an easily filterable precipitate and avoided coprecipitation of foreign ions.

An advantage over the 4-methyl homolog was noted in that the reagent could be added directly to the nickel sample at a pH of 3 and it was not necessary to slowly raise the pH by the dropwise addition of ammonium acetate. One ml. of 10 per cent ammonium acetate was added, however, to buffer the pH of the solution.

Again, as with the 4-methyl-1,2-cyclohexanedionedioxime, the precipitate was dried at 105° C. for two hours for best results.

Analysis of the nickel(II)-vic-dioxime complex for nickel gave an average percentage of 13.79 ± 0.04 which corresponds to the 13.80 per cent of $(C_9H_{15}O_2N_2)_2Ni$ very well.

Small amounts of nickel were determined as follows. Several standard nickel perchlorate solutions were diluted to approximately 1 mg. of nickel per 100 ml. of water and after addition of 1 ml. of 10 per cent ammonium acetate, the pH was adjusted to 3 with dilute hydrochloric acid or ammonium hydroxide. The solution was warmed on a hot plate to nearly 70° C. and 10 ml. of the saturated 4-iso-propyl-1,2-cyclohexanedionedioxime solution were added for each milligram of nickel. The precipitate was digested at elevated temperatures for one-half hour and was filtered through a medium porosity filter crucible. After washing with three portions of hot water, the complex was dried at 105° C. for two hours and weighed. The factor used for the nickel was 0.1380. The results of the determinations are given in Table 15.

Possible interferences from several anions were investigated and it was found that no errors were caused by the presence of one g. of acetate, chloride, nitrate, perchlorate, sulfate, or tartrate. The results are given in Table 16.

Table 15

Gravimetric Determination of Nickel(II)
with 4-ixo-Propyl-1,2-cyclohexanedionedioxime

Number of determinations	Nickel taken mg.	Average nickel found mg.
2	0.52	0.47 ± 0.04
2	1.05	1.02 ± 0.04
4	2.10	2.08 ± 0.05
4	3.15	3.12 ± 0.04
2	4.20	4.24 ± 0.05
2	5.25	5.21 ± 0.05

Interferences in the determination of nickel by cations were studied and no interference was found from those ions which do not interfere with the 4-methyl-1,2-cyclohexanedionedioxime determinations. Large amounts of copper(II), cobalt(II), and iron(II)

Table 16

Anionic Interferences in the Gravimetric Determination of Nickel(II) with 4-iso-Propyl-1,2-cyclohexanedionedioxime

Anion added[a]	Nickel found[b] mg.	Error mg.
Acetate	2.04	- 0.06
Chloride	2.09	- 0.01
Nitrate	2.07	- 0.03
Perchlorate	2.12	+ 0.02
Sulfate	2.06	- 0.04
Tartrate	2.05	- 0.05

[a] 1.0 g. of anion was added.

[b] 2.10 mg. of nickel were added.

interfered unless excess dioxime was added, but the error could be lessened by complexing the foreign ions. In Table 17 the results of the study are tabulated.

The average error for all of the interference studies was ± 0.03 mg. for 2.10 mg. of nickel or 1.5 per cent. The average value for the determinations was 2.08 mg. or an error of - 0.02 mg.

Table 17

Cationic Interferences in the Gravimetric Determination of Nickel(II) with 4-iso-Propyl-1,2-cyclohexanedionedioxime

Cation added[a]	Nickel found[b] mg.	Error mg.
Aluminum(III)	2.04	- 0.06
Ammonium(I)	2.11	+ 0.01
Antimony(III)[c]	2.05	- 0.05
Barium(II)	2.13	+ 0.03
Beryllium(II)	2.06	- 0.04
Bismuth(III)[c]	2.06	- 0.04
Cadmium(II)	2.09	- 0.01
Cerium(III)	2.04	- 0.06
Chromium(III)	2.07	- 0.03
Cobalt(II)	2.29	+ 0.19
Cobalt(III)[d]	2.11	+ 0.01
Copper(II)	2.26	+ 0.16
Copper(I)[e]	2.06	- 0.04
Iron(III)	2.04	- 0.06
Lanthanum(III)	2.09	- 0.01
Lead(II)	2.13	+ 0.03
Manganese(II)	2.08	- 0.02
Platinum(II)	2.15	+ 0.05
Rhodium(III)	2.14	+ 0.04

Table 17 (Continued)

Cation added[a]	Nickel found[b] mg.	Error mg.
Ruthenium(III)	2.16	+ 0.06
Silver(I)[f]	2.06	- 0.04
Thorium(IV)	2.06	- 0.04
Uranium(IV)	2.04	- 0.06
Vanadium(IV)	2.05	- 0.05

[a] 1.0 g. of cation was added.

[b] 2.10 mg. of nickel were added.

[c] Tartrate added.

[d] As the cobalticyanide complex.

[e] As the thiocyanate complex.

[f] Chloride absent.

b. Determination of palladium. The sensitivity of 4-iso-propyl-1,2-cyclohexanedionedioxime for palladium(II) was determined to be 4 parts per 10,000,000 which is the same order as the sensitivity of the 4-methyl-1,2-cyclohexanedionedioxime.

Studies of the effects of pH, temperature of precipitation, digestion time, and drying temperature proved that the procedure employed for the determination of palladium with the 4-iso-propyl derivative should be the same as with the 4-methyl-1,2-cyclohexanedionedioxime. Smaller quantities of palladium could be determined, however, due to the higher equivalent weight and the smaller solubility of the complex in water.

Since the solubility of the reagent in water is only 0.75 g. per liter, 25 ml. of the saturated aqueous solution of 4-iso-propyl-1,2-cyclohexanedionedioxime was employed for each 4 mg. of palladium(II) present. Several milligram samples of palladium were determined with the 4-iso-propyl homolog and the results are given in Table 18. The gravimetric factor for palladium in $(C_9H_{16}O_2N_2)_2Pd$ is 0.2255.

Table 18

Gravimetric Determination of Palladium(II) with 4-iso-Propyl-1,2-cyclohexanedionedioxime

Number of determinations	Palladium taken mg.	Precipitate weighed mg.	Palladium found mg.
3	1.25	5.25 ± 0.22	1.18 ± 0.05
3	2.50	11.08 ± 0.20	2.46 ± 0.05
3	3.75	16.62 ± 0.14	3.76 ± 0.03
3	5.00	22.27 ± 0.17	5.03 ± 0.04

It appeared that the average error in the determination of milligram amounts of palladium was 0.04 mg. or a little more than one per cent for samples of 3 to 5 mg.

A study of the interferences of foreign ions revealed that all of the cations and anions that were found not to interfere with the determination of palladium with 4-methyl-1,2-cyclohexanedionedioxime do not interfere when the 4-iso-propyl derivative is used.

It was found that highly charged ions like aluminum(III) and thorium(IV) tended to yield low palladium results probably due to ionic strength effects. This error was reduced by dilution of the sample.

Table 19 lists the ions that caused some error in the method along with some that have no effect.

Table 19

Interferences in the Gravimetric Determination of Palladium(II) with 4-iso-Propyl-1,2-cyclohexanedionedioxime

Ion added	Amount added g.	Palladium[a] found mg.	Error mg.
Aluminum(III)	1	2.40	- 0.10
Ammonium(I)	1	2.46	- 0.04
Cerium(III)	1	2.41	- 0.09
Potassium(I)	1	2.48	- 0.02
Thorium(IV)	1	2.38	- 0.12
Thorium(IV)[b]	1	2.48	- 0.02
Zinc(II)	1	2.50	0.00

[a] 2.50 mg. of palladium were added.

[b] Sample diluted from 250 ml. to 500 ml.

Again, as with the 4-methyl-1,2-cyclohexanedionedioxime, gold interfered with the determination and must be absent from the solution. Gram quantities of ruthenium(III) caused error if the temperature of precipitation was too high or the digestion time more than 15 minutes, since it tended to form a stronger complex than the palladium. Excess reagent helped to avoid this error.

D. Discussion and Summary

While the literature is abundant with vic-dioximes proposed for the gravimetric determination of nickel and palladium, the need for a better reagent is always present. The 4-methyl-1,2-cyclohexanedionedioxime appears to have most of the favorable properties of the best dioximes and very few of the disadvantages.

The 4-methyl derivative is very sensitive for both nickel and palladium with the lower limit of detecting being 0.1 and 0.4 parts per million, respectively. Chemically this reagent is identical to most dioximes especially with respect to interferences. Since nickel and palladium are quantitatively precipitated at a low pH, interferences from easily hydrolyzed metal ions are removed. This is an advantage possessed by dioximes with six and seven membered alicyclic rings. However, this compound has the advantage over 1,2-cyclohexanedionedioxime of excess reagent not coprecipitating with the nickel(II) complex which requires the use of an empirical factor. In the case of palladium(II) this does not occur either with the 1,2-cyclohexanedionedioxime or its 4-methyl derivative.

While 1,2-cycloheptanedionedioxime has most of the advantages mentioned, the seven membered ring is expensive to prepare. The 4-methyl-1,2-cyclohexanedionedioxime not only has all the advantages of 1,2-cycloheptanedionedioxime, but is no more expensive to prepare than the 1,2-cyclohexanedionedioxime.

By employing the 4-methyl homolog, nickel and palladium can be determined in quantities from 5 to 50 mg. with an error of a few tenths of a milligram. Interferences are few and most interfering materials can be masked or removed. As with 1,2-cycloheptanedionedioxime, iron offered no interference if complexed with citrate or tartrate. The several determinations of nickel on National Bureau of Standards steel samples gave results accurate to 0.1 mg. In some cases up to 4 g. of iron were present, but when complexed with citrate, it offered no interference. Perhaps the most interesting interference is ruthenium(III) since the dioxime complex of this ion has never before been reported in the literature. The ruthenium complex is water soluble and will not interfere in the gravimetric determination of nickel or palladium if excess reagent is added. It was noted that the dioxime complex of ruthenium was slow to form which is consistent with known ruthenium chemistry.

Gold interfered with the determinations since the reagent reduced it to the metal. Interference is avoided simply by adding hydroquinone and filtering the precipitated gold metal before addition of the dioxime.

The 4-iso-propyl-1,2-cyclohexanedionedioxime was found to be both physically and chemically quite similar to the 4-methyl derivative except for solubility of the reagent and its complexes. These were less soluble in water as might be expected with the increased molecular weight. Two factors, the increased weight and smaller solubility, make this dioxime applicable to the determination of smaller quantities of nickel and palladium. With 1 to 4 mg. of either metal the gravimetric results are accurate to 0.04 mg. if the 4-iso-propyl homolog is employed with normal macro analysis methods. Of course, the interferences encountered are the same as with the 4-methyl-1,2-cyclohexanedionedioxime only more significant due to the smaller quantities of metal involved.

V. SPECTROPHOTOMETRIC APPLICATIONS

A. Review of the Literature

The spectrophotometric determination of materials has become one of the most widely used methods of chemical analysis due to its speed and convenience. With the presently available spectrophotometers accuracies approach that of gravimetric methods and possess the further advantage of being applicable over a broader range of concentrations. For spectrophotometric applications a colored material should conform to certain specifications. Among these are an intense color, stability, insensitivity to small changes in pH and temperature, and agreement with Beer's law (77). Beer's law states that the absorbance of a colored material at any wavelength should be proportional to the concentration of the material.

Nickel(II) is colored when hydrated and Ringbom and Sundman (107) have studied the colorimetric determination of nickel based on the color of its salts dissolved in water. Hüttner (58) has described a colorimetric method which employs concentrated hydrochloric acid to develop the color with nickel(II) by formation of the chloride complex. The yellow color of the complex was matched with a set of previously prepared standards.

Several inorganic reagents have been used to form a colored compound or complex with nickel(II). Potassium thiocarbonate (94), aqueous ammonia (32, 5), and hydrogen sulfide (62) have all been suggested and employed for the spectrophotometric determination of nickel(II) in the range of 20 to 1000 γ.

Many organic reagents react with nickel(II) to produce intensely colored complexes. The sodium salt of diethyldithiocarbamate, $(C_2H_5)_2NCSSNa$, has been proposed by Alexander et al. (3) as a colorimetric reagent for nickel(II). The metallic complex is extracted from an aqueous solution into iso-amyl alcohol to form a yellow-green organic phase. The best range for the nickel concentration is from 5 to 80 γ.

Potassium dithiooxalate, $K_2C_2O_2S_2$, is reported by Fairhill et al. (21a, 23) to form a dark red-colored complex with nickel(II) which is suitable for a colorimetric determination. Both triethanol amine, $N(C_2H_4OH)_3$ (61), and formaldoxime (35, 18) have been suggested for the colorimetric determination of nickel. These reagents are most applicable for nickel in microgram quantities. The determination of nickel and cobalt with 3-nitrososalicylic acid has been described by Perry and Serfass (94). The dark red-colored nickel complex remains in the aqueous phase while the brown cobalt compound is extracted with petroleum ether. Both phases are read with a spectrophotometer thus allowing the determination of both metallic ions in the presence of each other.

Probably the most generally used class of organic reagents for nickel(II) is the vic-dioximes. The vic-dioxime grouping, -C(=NOH)-C(=NOH)-, reacts selectively with most of the transition metals to form soluble, colored complexes and specifically with nickel(II) and palladium(II) to precipitate their chelates. The first colorimetric method involving a vic-dioxime was described by Armit and Harden (4). They employed the pink color of a suspended nickel-2,3-butanedione-dioxime complex for the colorimetric determination of nickel(II). The optimum range for the analysis was from 10 to 80 γ of nickel in a final volume of 30 ml. A rapid procedure was necessary to avoid settling out of the suspended precipitate.

Extraction of the bis(2,3-butanedionedioximato-N,N')nickel(II) into diethyl ether was suggested by Ochotin and Suichov (86b), but Hall and Young (47) preferred chloroform. The organic solution was then read on a colorimeter.

Butts *et al.* (14) took advantage of the solubility of the 1,2-cycloheptanedionedioxime complex of nickel(II) in chloroform for determination of nickel in sewage. Iron and copper, which interfere with the colorimetric determination, were removed by extraction as the cupferates and then the nickel was extracted as the dioxime complex into chloroform. The chloroform phase was stripped with hydrochloric acid and the nickel was determined by Rollet's (108) colorimetric method involving the alkaline oxidation of the nickel-2,3-butanedionedioxime chelate to form a highly colored compound which is read on a spectrophotometer at 445 millimicrons.

Gillis (40) read a chloroform solution of bis(1,2-cycloheptanedionedioximato-N,N')-nickel(II) directly without reextraction in to water. The organic solution was read at 377 millimicrons and the method was suitable for nickel in the 1- to 10-γ range.

In addition to extraction of the nickel-vic-dioxime complexes into neutral organic solvents, Passameck (90) studied pyridine solutions of the nickel-2,3-butanedionedioxime chelate. He reported that the spectrum was significantly altered from that observed in chloroform and he could determine nickel spectrophotometrically from 1 to 1000 γ.

A more commonly used colorimetric method for the determination of nickel with 2,3-butanedionedioxime was reported by Rollet (108). He modified Feigl's spot test for nickel (25) which involves oxidation of the nickel(II) complex with alkaline hypobromite. The color of the oxidized dioxime complex is nearly twice that of the nickel(II) compound and Rollet recommended the method highly. Extensive use of this method has been made in the determination of nickel in steel (20, 57, 66, 74, 83, 103), in bronze (46, 118), in aluminum (98), in magnesium (1), in calcium (1), and in many other materials.

While Rollet's method is widely employed, the reaction does not satisfy all of the requirements for an ideal method. The color is unstable and fades with time and a careful control of the procedure is necessary (39). Attempts to improve the determination have proved somewhat successful, but not completely so. Makepeace and Craft (74) studied concentration and pH effects on the analysis and different oxidants were investigated by Haim and Tarrant (46). By employing the optimum conditions as recommended by these studies, the method is fairly reliable and has been used considerably. It should be noted that the exact nature of the complex formed is still in doubt and is under current investigation (7).

Johnson and Simmons (65) suggested 1,2-cyclohexanedionedioxime (45) as a colorimetric reagent for nickel. They found Rollet's (108) oxidation procedure would apply with this vic-dioxime as well, if not better, than with 2,3-butanedionedioxime. The 1,2-cyclohexanedionedioxime complex appeared to be more stable and reproducible than when other dioximes were used.

Ferguson and Banks (30) employed an aqueous suspension of the nickel(II)-1,2-cyclohexanedionedioxime complex for the spectrophotometric determination of nickel in calcium. A sharp absorption peak at 550 millimicrons was found to be suitable for reading. The suspension was stabilized up to one week by the addition of gum arabic which is a definite advantage over the spectrophotometric method of Rollet (108). The conditions for preparation of the suspension were the same as for quantitative precipitation of the nickel complex except for the addition of gum arabic which prevented coagulation of the precipitate. The best range for the method was from 0.5 to 1.4 γ of nickel per milliliter of solution. A great many ions were studied for possible interference with the determination of nickel and only iron, ferrocyanide, cyanide, ethylenediamine tetraacetic acid, highly colored materials, strong oxidizing agents, and strong reducing agents interfered. Iron, the most serious interference, was removed by oxidizing to the ferric state and complexing with citrate. The color of the ferric citrate was compensated for in the blank. In the determination of small amounts of nickel in gram quantities of calcium an error was encountered by Ferguson and Banks which gave low results. They attributed this error to the ionic strength effects of the calcium and recommended that the calibration curve be prepared under conditions of nearly the same ionic strength as encountered in the actual determination.

The colorimetric analysis for palladium has been studied quite extensively, especially with regard to its determination in the presence of other platinum group metals. Takaki and Nagasse (125) employed 4-nitrosoresorcinol to develop a colored species with palladium which could be used in a colorimetric method.

p-Dimethylaminobenzylidene rhodamine (28, 55) has been used for the detection and estimation of palladium down to 1-γ quantities. Feigl and Frankel (27) reported that as little as 0.25 millimicrograms of palladium per milliliter can be detected and estimated by the catalytic effect of palladium on the reduction of nickel(II) by sodium hypophosphite.

Pierson (99, 100) utilized the reducing properties of mercurous chloride for the estimation of submicrogram quantities of palladium by observing the color and opaqueness of the palladium metal deposited on the mercurous chloride.

The great disadvantage of the previously cited methods for palladium is the interference by other metals of the platinum group. Since these metals nearly always accompany palladium, this is a significant drawback. A series of reagents which do not suffer from this disadvantage are the p-nitrosophenylamines. p-Nitrosophenylamine has been found to react with palladium(II) in neutral or weakly acidic solutions to form a deep red-colored complex (149). The reaction is extremely sensitive, permitting the detection of 0.005 γ of palladium(II) and the colorimetric determination of from 1 to 50 γ. Platinum, if present in amounts less than 20 parts per million, does not interfere, but gold must be removed if more than one part per million is present. The gold is easily removed by extraction as the chloride with diethyl ether and palladium is separated from large amounts of platinum by precipitation as the palladium(II) oxide with ammonium hydroxide.

Overholser and Yoe (88) studied other compounds containing the p-nitrosophenylamine functional group and found them all to form highly colored complexes with palladium. N,N-Dimethyl- and N,N-diethyl-p-nitrosophenylamine possessed several advantages as colorimetric reagents for palladium since their complexes are formed faster, are more stable, are less dependent on temperature, and follow Beer's law for palladium concentrations between zero and 0.20 γ per milliliter.

Recently Yoe and Kirkland (148) employed p-nitrosodimethylaniline for the separation and determination of palladium and platinum. While both metallic ions react with the reagent, palladium forms a complex almost immediately and platinum takes several days or elevated temperatures. The reagent is added to a mixture of the cations and the palladium complex is extracted immediately with chloroform, but the platinum, which is uncomplexed, remains in the aqueous phase. Heat applied to the water solution will cause the platinum to be complexed and it can then be extracted into chloroform. This method is good for microgram quantities of palladium, but amounts greater than 1 mg. can not be extracted successfully due to the limited solubility of the complex in chloroform.

While palladium has long been known to form a highly colored complex with vic-dioximes, only recently has the attempt to develop a spectrophotometric method involving this complex been reported. Nielsch (86a) extracted the palladium(II)-2,3-butanedionedioxime complex into chloroform and determined the amount of complex present spectrophotometrically at 366 millimicrons. The range of palladium concentrations employed was from 11 to 63 γ per milliliter.

B. Materials and Apparatus

A Beckman quartz photoelectric spectrophotometer, Model DU, manufactured by the National Technical Laboratories was used for the constant wavelength studies and for the analytical determinations. Description of the instrument is found in section III, B of this thesis.

A Cary automatic recording photoelectric spectrophotometer, Model 12, manufactured by the Applied Physics Corporation was used to obtain the spectra of complexes and reagents at various wavelengths. Description of the instrument is found in section III, B of this thesis.

A Beckman pH meter, Model G, was used for all of the pH measurements necessary for this study.

Cortex or silica cells were used for all of the absorbance measurements depending on the region of the spectrum under investigation. The cells were calibrated to be 1.001, 5.000, and 10.00 cm. in optical path length.

The volumetric glassware employed were Kimble "Exax" or "Normax" brands or their equivalent.

4-tert-Amyl-1,2-cyclohexanedionedioxime. Reagent grade. Prepared as described in section II of this thesis.

Chloroform. Chemically pure. Distilled to remove the nonvolatile materials.

Citric acid. Reagent grade.

1,2-Cyclohexanedionedioxime. Reagent grade. Prepared in this laboratory.

Diammonium citrate. Reagent grade.

Gum arabic. A 10 per cent solution was prepared from the powder and filtered to remove suspended material.

4-Methyl-1,2-cyclohexanedionedioxime. Reagent grade. Prepared as described in section II of this thesis.

Standard nickel perchlorate solutions. These solutions were prepared from Mond nickel obtained from the International Nickel Company, New York. Their preparations are described in section III, B of this thesis.

Standard palladium perchlorate solutions. Reagent grade. Prepared as described in section III, B of this thesis.

All of the other chemicals employed in this study were reagent-grade quality.

C. Experimental

The spectrophotometric methods for nickel, employing vic-dioximes, have involved determination of the oxidized complex in basic solution, determination of the nickel(II) chelate suspended in water, and determination of the nickel(II) complex in chloroform solution.

The oxidized complex has been studied rather extensively and does not appear to be the best method. Ferguson and Banks (30) have successfully applied the suspension method to nickel employing 1,2-cyclohexanedionedioxime as a reagent. They reported that the method was carried out without special precautions and since the peak they used was the 550 millimicron maximum, temperature should be a factor. As discussed in section III, D of this thesis, this peak is a function of the particle size and, therefore, the temperature of precipitation and time of digestion would influence the absorbance.

Several determinations were carried out at different temperatures of precipitation and the absorbance and position of the peak were noted. It is seen from Table 20 that if the temperature of precipitation is between 10° and 30° C., very little error results.

Table 20

Effect of Temperature on the Spectrophotometric Determination of Nickel(II) with 1,2-Cyclohexanedionedioxime in Water.

Temperature of precipitation ° C.	Absorbance observed	Position of maximum millimicrons
0	0.066	549
10	0.066	550
20	0.067	550
30	0.066	551
40	0.065	552
50	0.065	553
60	0.064	554
70	0.063	555

1. 4-Methyl-1,2-cyclohexanedionedioxime

a. Aquesous suspension. 4-Methyl-1,2-cyclohexanedionedioxime was studied for application to the spectrophotometric method of Ferguson and Banks. The absorption spectrum of the nickel-4-methyl-1,2-cyclohexanedionedioxime complex was scanned on the Cary spectrophotometer and is given in Fig. 2. The spectrum was very similar to that of the 1,2-cyclohexanedionedioxime complex in water and a sharp peak was observed at 549 millimicrons as well as a smaller peak at 398 millimicrons. Variation of the concentration of the nickel complex produced a proportional increase or decrease in the absorbance of the 549 millimicron peak without a shift in position.

The procedure adopted for the spectrophotometric determination of nickel(II) with 4-methyl-1,2-cyclohexanedionedioxime was essentially that proposed by Ferguson and Banks. In a 25-ml. volumetric flask containing the sample to be analyzed, five tenths of a milliliter of a 10 per cent gum arabic solution was added along with 2 ml. of a 20 per cent ammonium acetate solution. One ml. of a saturated aqueous solution of 4-methyl-1,2-cyclohexanedionedioxime was introduced and after dilution to the mark, the mixture was well shaken. A reading of the absorbance at 549 millimicrons was made on the suspension after two hours. The complex was read against a blank containing everything except the reagent.

It was found that 4-methyl-1,2-cyclohexanedionedioxime can be used in place of 1,2-cyclohexanedionedioxime without alteration of the procedure and the same accuracy is obtained. It must be stated, however, that no advantage was found in employing the methyl derivative. Palladium(II) was investigated as to the applicability of forming a suspension of the 4-methyl-1,2-cyclohexanedionedioxime complex and determination spectrophotometrically as with nickel(II).

A suspension of bis(4-methyl-1,2-cyclohexanedionedioximato-N,N') palladium(II) was prepared by mixing 75 ml. of a 0.00001 molar palladium(II) perchlorate solution with 1 ml. of 10 per cent aqueous gum arabic, adjusting the pH to 2 with hydrochloric acid, and adding 1 ml. of a saturated 4-methyl-1,2-cyclohexanedionedioxime solution. The absorption spectrum of the suspension was obtained with the Cary recording spectrophotometer and the curve is reproduced in Fig. 3. An absorption maximum was found at 470 millimicrons which was similar to the "550" millimicron peak of the nickel complex. The 470 millimicron region of the spectrum appeared to be suitable for an analytical determination since the reagent did not absorb to any extent. It was noted that excess reagent did not change the absorbance of the suspension indicating the reaction between palladium and the dioxime was complete.

In order to stabilize the suspension gum arabic had to be added to the solution before precipitation of the complex. A study of the optimum amount of gum arabic required was made and the results are given in Table 21. From the data it was concluded that the best quantity of gum arabic to use in the method was approximately 1 to 2 ml. of a 10 per cent solution per 100 ml. of water. With smaller

Table 21

Effect of Gum Arabic on the Suspension of the Palladium(II)-4-methyl-1,2-cyclohexanedionedioxime Complex in Water

10% Gum arabic added ml.	Absorbance after 10 min.	Absorbance after 1 hr.	Absorbance after 2 hrs.	Absorbance after 24 hrs.	Absorbance after 48 hrs.
0.1	0.060	0.067	0.068	0.066	0.062
0.5	0.060	0.067	0.068	0.067	0.066
1.0	0.060	0.067	0.067	0.067	0.067
2.0	0.060	0.066	0.067	0.068	0.068
5.0	0.058	0.064	0.067	0.067	0.068
10.0	0.053	0.062	0.065	0.066	0.067

amounts of gum arabic the suspension soon settles and with larger quantities the suspension is slow to form.

The effect of pH on formation of the suspension was investigated and as with the gravimetric determination of palladium with 4-methyl-1,2-cyclohexanedionedioxime, the quantitative range was from 0.7 to 5.

To avoid interference by transition elements and weakly basic metals, it was felt that the palladium determination should be carried out with the pH between 0.8 and 2.0.

Table 22

Effect of pH on the Formation of the Palladium(II)-4-methyl-1,2-cyclohexanedionedioxime Complex Suspension in Water

pH	Absorbance
0.0	0.004
0.3	0.012
0.7	0.069
0.8	0.072
1.0	0.073
1.5	0.073
2.0	0.072
2.5	0.072
3.0	0.073
4.0	0.071
5.0	0.069
6.0	0.067

Since the maximum to be used for the spectrophotometric determination was to be the 470 millimicron peak, it was felt that the temperature of formation of the suspension might affect the position of the peak as well as the absorbance. The effect of temperature on the absorption peak is given in Table 23 and it can be concluded that if the temperature is held between 10° C. and 30° C., no error is noted.

As the temperature of precipitation was increased above 30° C. the absorbance of the peak decreases and the peak shifts to higher wavelengths. Also, it might be mentioned that if the temperature of precipitation was at elevated temperatures and in addition the suspension was digested for any length of time, the error produced increased markedly. One would certainly expect this since digestion usually results in the formation of larger crystals.

Table 23

Effect of Temperature on the Spectrophotometric Determination of Palladium(II) with 4-Methyl-1,2-cyclohexanedionedioxime in Water

Temperature of precipitation ° C.	Absorbance observed	Position of maximum millimicrons
0	0.076	469
10	0.076	470
20	0.077	470
30	0.076	471
40	0.075	472
50	0.075	473
60	0.074	474
70	0.073	475

A calibration curve for the spectrophotometric determination of palladium was prepared by taking various amounts of a standard palladium(II) perchlorate solution and after forming the suspension, reading the absorbance. The results are listed in Table 24 and are plotted in Fig. 6. The absorptivity as determined from the average slopes of the calibration curves is 0.0542 absorbance units per microgram per milliliter per centimeter. This would give a value of 5.79×10^3 for the molar absorptivity.

The procedure followed in preparing the suspension was as follows. The sample of palladium was placed in a 100-ml. flask and diluted to nearly 80 ml. with water. One ml. of a 10 per cent solution of gum arabic was added along with sufficient concentrated hydrochloric acid to lower the pH to between one and two. One ml. of a saturated, aqueous solution of 4-methyl-1,2-cyclohexanedionedioxime was introduced and after diluting to 100.0 ml., the solution was well shaken. After two hours, the suspensions were read on the Beckman spectrophotometer in 1.001-, 5.000-, and 10.00-cm. cells at 470 millimicrons.

Interferences were studied by preparing the bis(4-methyl-1,2-cyclohexanedionedioximato-N,N')palladium(II) suspension in the presence of foreign ions. The ions added are listed in Tables 25 and 26 and it can be seen that only a few materials interfere with the method.

Table 24

Calibration Curve for the Spectrophotometric Determination of Palladium(II) as the 4-Methyl-1,2-cyclohexanedionedioxime: Suspension in Water

Palladium concentration γ per ml.	Absorbance[a]		
	1.00-cm. cell	5.00-cm. cell[b]	10.00-cm. cell[c]
5.97	0.323	1.615	-----
5.21	0.280	1.410	-----
4.47	0.242	1.210	-----
3.72	0.203	1.014	-----
2.98	0.162	0.810	1.622
2.23	0.122	0.609	1.222
1.49	0.081	0.407	0.815
0.745	0.041	0.203	0.404
0.670	0.037	0.184	0.368
0.521	0.029	0.148	0.298
0.372	0.020	0.097	0.194
0.224	0.014	0.062	0.125
0.149	0.009	0.043	0.085
0.075	0.004	0.024	0.047
0.056	0.003	0.018	0.037
0.037	0.002	0.013	0.026
0.018	0.001	0.009	0.017
0.000	0.000	0.003	0.005

[a] At 470 millimicrons.

[b] Cell correction of 0.003 should be subtracted from the 5.00-cm. cell readings.

[c] Cell correction of 0.005 should be subtracted from the 10.00-cm. cell readings.

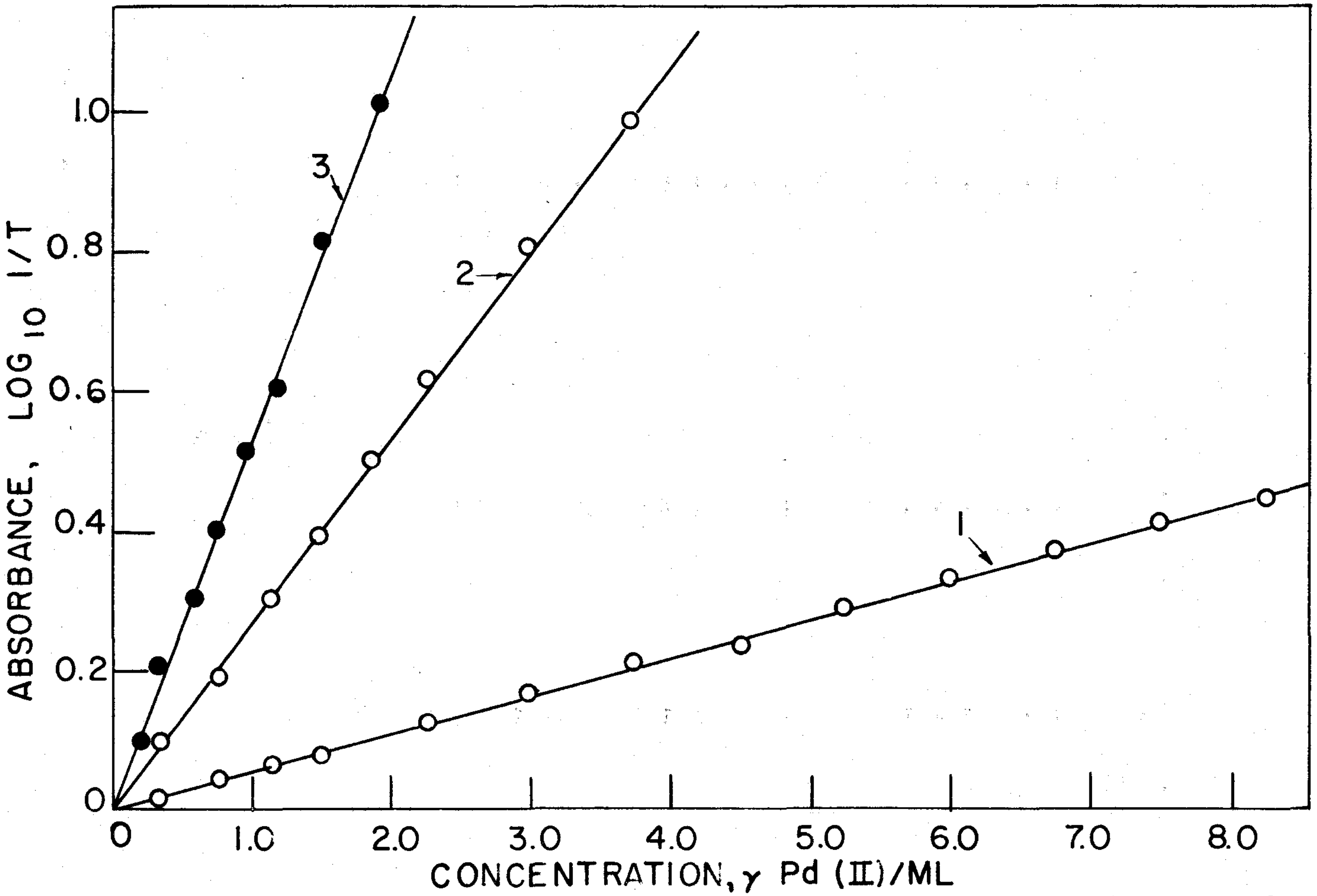


FIG. 6 SPECTROPHOTOMETRIC DETERMINATION OF Pd(II) WITH 4-METHYL-1,2-CYCLOHEXANEDIONEDIOXIME AT 470 mμ IN AQUEOUS SUSPENSION. CURVE 1, 1.000-cm. CELL, CURVE 2, 5.00-cm. CELLS, AND CURVE 3, 10.00-cm. CELLS

Table 25

Anionic Interferences in the Spectrophotometric Determination of Palladium(II) with 4-Methyl-1,2-cyclohexanedionedioxime as the Complex Suspended in Water

Ion added	Amount added mg.	Absorbance[a] observed	Error
Acetate	1000	0.099	+ 0.002
Bromate	1000	0.079	- 0.018
Bromate	100	0.097	0.000
Bromide	1000	0.096	- 0.001
Chloride	1000	0.096	- 0.001
Chromate	1000	0.101	+ 0.004
Citrate	1000	0.093	- 0.004
Citrate	100	0.099	+ 0.002
EDTA[b]	100	0.096	- 0.001
Ferrocyanide	100	0.095	- 0.002
Fluoride	1000	0.096	- 0.001
Iodide	100	0.097	0.000
Nitrate	1000	0.097	0.000
Oxalate	100	0.097	0.000
Perchlorate	1000	0.099	+ 0.002
Sulfate	1000	0.096	- 0.002
Thiosulfate	1000	0.105	+ 0.008
Thiosulfate[c]	1000	0.098	+ 0.001

Table 25 (Continued)

Ion added	Amount added mg.	Absorbance[a] observed	Error
Vanadate(V)	100	0.096	- 0.001
Uranate(VI)	100	0.098	+ 0.001

[a] Absorbance expected, 0.097.

[b] Ethylenediamine tetraacetic acid.

[c] pH adjusted to 4.5.

Table 26

Cationic Interferences in the Spectrophotometric Determination of Palladium(II) with 4-Methyl-1,2-cyclohexanedionedioxime as the Complex Suspended in Water

Cation added	Amount added mg.	Absorbance[a] observed	Error
Aluminum(III)	1000	0.092	- 0.005
Ammonium(I)	1000	0.097	0.000
Antimony(III)	100	0.095	- 0.002
Arsenic(III)	100	0.096	- 0.001
Barium(II)	100	0.098	+ 0.001
Beryllium(II)	100	0.096	- 0.001
Cadmium(II)	100	0.096	- 0.001

Table 26 (Continued)

Cation added	Amount added mg.	Absorbance[a] observed	Error
Calcium(II)	100	0.098	+ 0.001
Cerium(III)	100	0.100	+ 0.003
Chromium(III)	10	0.094	- 0.003
Cobalt(II)	1000	0.096	- 0.001
Copper(II)	1000	0.099	+ 0.002
Gold(I)	100	0.102	+ 0.005
Hafnium(IV)	100	0.087	- 0.010
Iridium(III)	100	0.102	+ 0.005
Iron(II)	100	0.083	- 0.014
Iron(III)	100	0.084	- 0.013
Iron(III)[b]	100	0.098	+ 0.001
Lanthanum(III)	100	0.091	- 0.000
Lead(II)[c]	100	0.096	- 0.001
Lithium(I)	1000	0.096	- 0.001
Magnesium(II)	100	0.097	0.000
Manganese(II)	100	0.099	+ 0.002
Mercury(II)	100	0.103	+ 0.006
Nickel(II)	1000	0.098	+ 0.001
Platinum(II)	100	0.102	+ 0.005
Potassium(I)	1000	0.098	+ 0.001
Rhodium(III)	100	0.100	+ 0.003

Table 26 (Continued)

Cation added	Amount added mg.	Absorbance[a] observed	Error
Ruthenium(III)	100	0.148	+ 0.051
Silver(I)[c]	100	0.095	- 0.002
Sodium(I)	1000	0.096	- 0.001
Strontium(II)	100	0.098	+ 0.001
Thallium(I)[c]	100	0.097	0.000
Thorium(IV)	100	0.095	- 0.002
Tin(II)	100	0.043	- 0.054
Titanium(III)	100	0.095	- 0.002
Vanadium(IV)	100	0.097	0.000
Zinc(II)	100	0.099	+ 0.002
Zirconium(IV)	100	0.090	- 0.007

[a] Absorbance expected, 0.097.

[b] Fluoride added.

[c] Chloride absent; perchloric acid used.

Colored ions were compensated for by employing a blank with very little reduction in accuracy. Chromium(III) absorbs strongly in the 470-millimicron region of the spectrum and only 0.1 mg. per milliliter can be present and still permit determination of the palladium. With greater quantities, the spectrophotometer could not be balanced.

Strong oxidizing and reducing agents interfere with the determination, but these can be eliminated. Hydroxylamine hydrochloride was added to the oxidizing agents to destroy their interference and reducing materials were removed by addition of cerium(IV) ion. Excess cerrate was destroyed by hydroxylamine.

Ruthenium(III), iron(III), and iron(II) reacted with the reagent at the pH used to form colored complexes. The iron interference was reduced by oxidation to the iron(III) state and complexation with fluoride or phosphate. Very large amounts of iron must be eliminated by an ether extraction as the chloride in 6 molar hydrochloric acid.

b. Chloroform solution. In order to prevent interference by the highly colored materials, it was thought that the palladium(II) complex might be extracted into chloroform and read in the organic phase. It was expected that the extraction would offer no difficulty since the metallic complexes of 4-methyl-1,2-cyclohexanedionedioxime were soluble in chloroform. A scan of the spectrum of the complex in chloroform revealed an absorption peak at 280 millimicrons, Fig. 3. It was decided that this peak would be satisfactory for the spectrophotometric determination of palladium since the reagent does not absorb at that wavelength.

The procedure employed for the precipitation of the palladium complex was the same as that used in preparation of the aqueous suspension except that the gum arabic was omitted. After one hour, the precipitate was extracted with three 7-ml. portions of chloroform. The chloroform was placed in a volumetric flask and diluted to volume. Water was removed by the addition of a small amount of anhydrous sodium sulfate and the organic solution was read at 280 millimicrons on a Beckman, Model DU, spectrophotometer.

A standard calibration curve was prepared with known quantities of palladium(II) and it was found that a straight line resulted from the plotting of absorbance *vs.* micrograms of palladium per milliliter. The data are tabulated in Table 27.

Table 27

Spectrophotometric Determination of Palladium(II) with 4-Methyl-1,2-cyclohexanedionedioxime in Chloroform Solution

Palladium added γ	Absorbance[a] at 280 millimicrons
0.00	0.001
3.00	0.035
4.50	0.069
7.45	0.095
14.9	0.148
16.1	0.185
22.4	0.240
37.2	0.395
55.1	0.600
74.5	0.810

[a] 2.000-cm. cells used.

The slope of the line was determined to be 0.280 and the molar absorptivity 14.9×10^3. This means the solution method is more than three times as sensitive as the suspension procedure.

All of the ions that were investigated as possible interferences in the suspension method were also studied using the extraction into chloroform. All of the interferences were the same except for the fact that colored species, such as chromium(III), offered no interference. Iron was complexed as the fluoride, phosphate, citrate, or tartrate to avoid interference. Ruthenium(III) reacted with the dioxime to form an extractable species and caused high results for palladium.

Since palladium was so easily extracted into chloroform and determined with increased sensitivity, it was obvious to attempt the same method with nickel(II). The bis(4-methyl-1,2-cyclohexanedionedioximato-N,N')nickel(II) was precipitated in a 250-ml. separatory funnel by the addition of 5 ml. of 20 per cent ammonium acetate and 1 ml. of a saturated 4-methyl-1,2-cyclohexanedionedioxime solution. After one hour the precipitate was extracted with three 7-ml. portions of chloroform. The organic phases were placed in a 25-ml. volumetric flask and diluted to volume with chloroform. After drying with 0.5 g. of anhydrous sodium sulfate, the solution was read at 383 millimicrons. A solution of the nickel complex in chloroform had been previously scanned on the Cary spectrophotometer and an absorption peak at 383 millimicrons chosen for the analytical method. The curve is reproduced in Fig. 1.

A standard calibration curve was prepared with known quantities of nickel and the data are given in Table 28. Three determinations were made for each concentration of nickel.

Table 28

Calibration Curve for the Spectrophotometric Determination of Nickel(II) with 4-Methyl-1,2-cyclohexanedionedioxime in Chloroform Solution

Nickel(II) concentration γ per ml.	Absorbance at 383 millimicrons
0.60	0.039 ± 0.002
1.20	0.082 ± 0.004
1.80	0.118 ± 0.003
2.40	0.157 ± 0.004
3.60	0.247 ± 0.004
4.80	0.327 ± 0.008
6.00	0.417 ± 0.009
7.20	0.484 ± 0.006
8.40	0.565 ± 0.007
9.60	0.632 ± 0.008

Fig. 7 is a plot of the data of Table 28 and it is seen that a straight line can be drawn with a slope of 0.0671. The average deviation of the 30 determinations of the calibration curve is 0.004 absorbance units or 0.06 γ of nickel per milliliter. The molar absorptivity calculates to be 3.94×10^3.

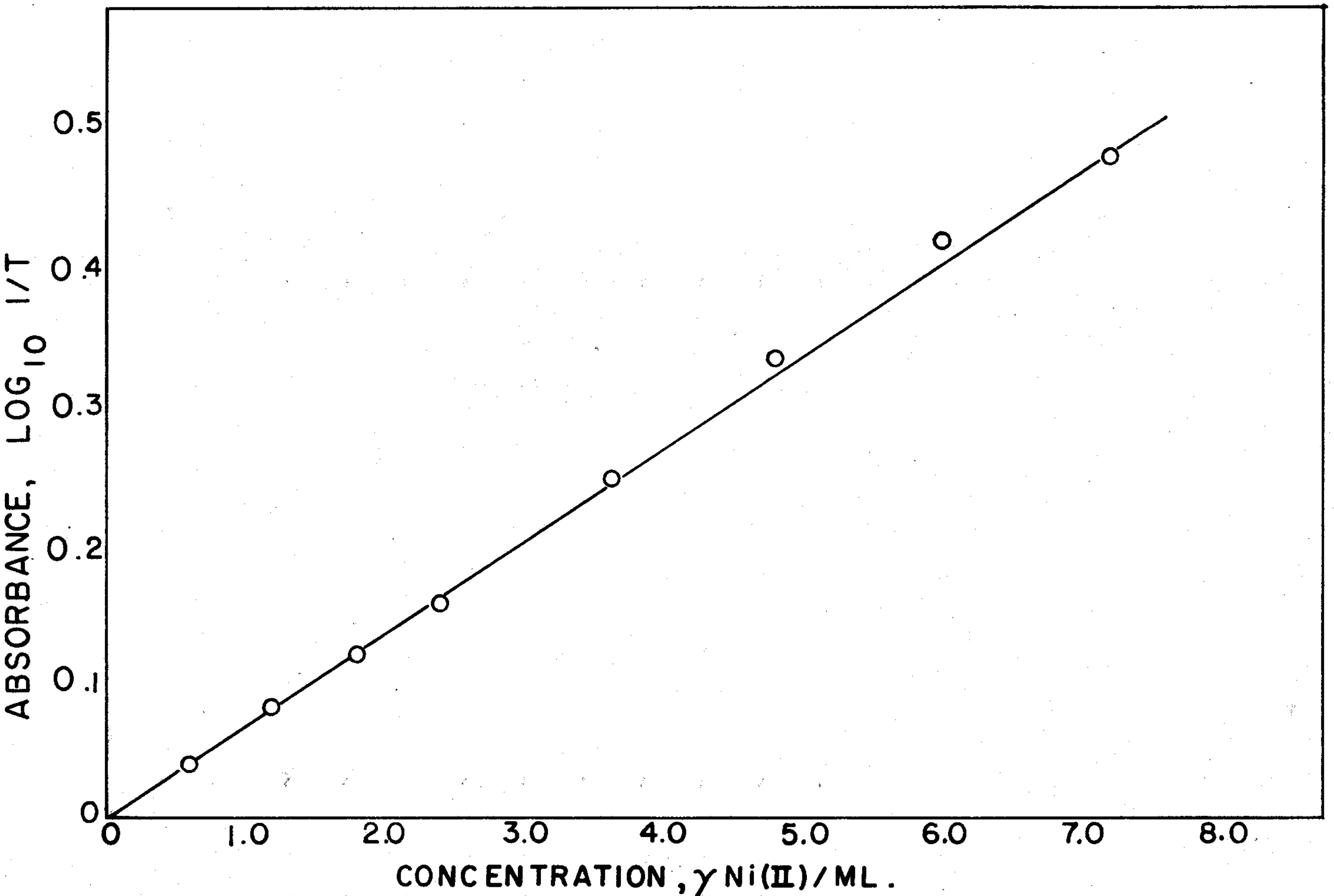


FIG. 7 SPECTROPHOTOMETRIC DETERMINATION OF Ni(II) WITH 4-METHYL-1, 2-CYCLOHEXANEDIONEDIOXIME AT 383 mμ IN CHLOROFORM SOLUTION USING 1.000 cm. CELLS.

The interferences of the method were studied (Table 29) and it was found that all of the ions that interfered with palladium also interfered with nickel. In addition copper(II), cobalt(II), and palladium caused high results if special procedures were not followed. The copper(II) was reduced and complexed with thiocyanate, the cobalt was oxidized and complexed with peroxide and cyanide, and the palladium was masked as the ammonia complex with the determination carried out at a pH of 8. Iron was removed as the cupferate (109). A National Bureau of Standards sample was determined with ± 0.5-γ accuracy or ± 1 per cent for a 41-γ sample.

Table 29

Effect of Foreign Ions on the Spectrophotometric Determination of Nickel(II) with 4-Methyl-1,2-cyclohexanedionedioxime in Chloroform Solution

Ions added	Amount of each ion mg.	Nickel[a] found γ	Error γ
Sodium(I), Potassium(I), Lithium(I), Ammonium(I)	100	15.0	0.0
Calcium(II), Strontium(II), Barium(II)	100	14.8	- 0.2
Beryllium(II), Aluminum(III), Magnesium(II)	100	15.1	+ 0.1
Lanthanum(III), Cerium(III), Thorium(IV)	100	14.7	- 0.3
Zinc(II), Cadmium(II), Manganese(II)	100	14.8	- 0.2

Table 29 (Continued)

Ions added	Amount of each ion mg.	Nickel[a] found γ	Error γ
Silver(I), Lead(II)[b]	100	14.9	- 0.1
Chromium(III)	100	15.3	+ 0.3
Cobalt(II)	100	60.9	+45.9
Copper(II)	100	70.6	+55.6
Iron(II)	100	20.1	+ 5.1
Iron(III)	100	18.1	+ 3.1
Ruthenium(III)	100	20.3	+ 5.3
Palladium(II)[c]	100	15.1	+ 0.1
Hexacyanocobaltate(III)	100	15.1	+ 0.1
Dithiocyanocuprate(I)	100	15.3	+ 0.3
Iron(III)[d]	100	15.2	+ 0.2
Chloride, Acetate, Sulfate	100	15.1	+ 0.1
Phosphate, Citrate, Tartrate	100	14.8	- 0.2
Aluminum(III)[e]	10.1 -	40.8 ± 0.5	+ 0.0

[a] 15.0 γ were added.

[b] Chloride absent.

[c] Ammonium hydroxide added, pH 8.

[d] Extracted as cupferate.

[e] N.B.S. aluminum-base alloy, No. 85a, taken 41 γ of nickel, three determinations.

2. 4-iso-Propyl-1,2-cyclohexanedionedioxime

The application of 4-iso-propyl-1,2-cyclohexanedionedioxime to the spectrophotometric determination of nickel and palladium was investigated and it was found that the same procedures employed for their determination with 4-methyl-1,2-cyclohexanedionedioxime could be applied. The accuracy and interferences by foreign ions were identical to the 4-methyl homolog, but a slight increase in the sensitivity of the method could be obtained by the more favorable distribution of the complex into the organic extractant.

By extracting large volumes of water with small volumes of chloroform, extremely small concentrations of nickel and palladium can be determined in water. Table 30 indicates the concentrations that can be determined by this method along with the error.

Table 30

Determination of Small Concentrations
of Nickel(II) and Palladium(II) in Water
with 4-iso-Propyl-1,2-cyclohexanedionedioxime

Ion and amount added γ	Concentration in aqueous phase p.p.m.	Amount found γ	Error %
Ni(II), 51.2	0.5	51.0	0.5
Ni(II), 51.2	0.1	48.9	5.0
Pd(II), 51.2	0.5	50.3	2.0
Pd(II), 51.2	0.1	44.9	12.5

Extraction of the nickel chelate proved to be even more successful than with the palladium complex. Concentrations of nickel as low as 0.1 part per 1,000,000 can be determined with only a 5 per cent error by extraction of 500 ml. of the aqueous phase with six 7-ml. portions of chloroform and dilution to 50 ml. Palladium is less sensitive by about a factor of three.

D. Discussion and Summary

The work of Voter and Banks on the spectrophotometric determination of nickel as the 1,2-cyclohexanedionedioxime complex suspended in water was checked and considered to be remarkable since the maximum they measure is not a true absorption peak but is also a function of the particle size. Their method was found to be reproducible if the procedure was followed carefully and the temperature of precipitation was maintained between 10° and 30° C. This temperature control was not mentioned by Voter and Banks, but it was found to be an important variable.

The 4-methyl-1,2-cyclohexanedionedioxime complex of nickel was suspended in water employing the same method as with the 1,2-cyclohexanedionedioxime itself, but no advantages or disadvantages were found over the unsubstituted alicyclic dioxime.

The spectrophotometric method was applied to the determination of palladium by reading the 470-millimicron peak of a suspension of bis(4-methyl-1,2-cyclohexanedionedioximato-*N*,*N'*)palladium(II) in water. Again, if the temperature of precipitation was maintained between 10° and 30° C. and the procedure was carefully followed, then from 0.5 to 150 γ of palladium can be determined with a limiting error of 0.1 γ.

The interference study revealed only a few materials that interfere with the suspension method for palladium and these are iron, ruthenium, cyanide, strong reducing and oxidizing agents, and large amounts of highly colored ions. The iron can be complexed with tartrate, cyanide removed by heating under acidic conditions, and reducing and oxidizing agents destroyed with cerium(IV) and hydroxylamine, respectively.

Ruthenium interference could not be removed and must be absent from the solution. High concentrations of colored materials were overcome by extraction of the chelates from the aqueous phase with chloroform.

The chloroform solutions of the palladium complex were read at 280 millimicrons and it was found that the sensitivity of the determination was increased several fold over the heterogeneous procedure. Both the extraction and the increased molar absorptivity contributed to this greater sensitivity.

By employing 4-methyl-1,2-cyclohexanedionedioxime in both the heterogeneous and homogeneous spectrophotometric methods, palladium can be determined in quantities from 0.5 to 1000 γ with accuracies of 1 per cent or 0.1 γ depending on which is the larger. This is a factor of 20 times more sensitive than the method reported by Nielsch (86a). The only interference found that could not be removed was ruthenium and it might be possible to distill away this metal as the tetroxide.

Nickel(II) was determined by extraction of the dioxime chelate into chloroform and the main advantages of this method over the aqueous suspension procedure are the increase in sensitivity and the removal of the interference by colored ions that are not extractable into chloroform. From 1 to 1000 γ of nickel can be determined to 1 per cent or 0.5 γ.

Interferences with the method are few with only ruthenium interfering even in the presence of masking reagents. Copper, cobalt, iron, and palladium interfere unless complexed with an appropriate anion.

The striking factor of the substituted 1,2-cyclohexanedionedioximes is the high solubility of the metal complexes in chloroform and this factor makes possible the extraction of sub-p.p.m. amounts of nickel and palladium by chloroform from large volumes of water as the 4-iso-propyl-1,2-cyclohexanedionedioxime complexes. This is perhaps the most sensitive method yet reported for the determination of nickel.

VI. TITRIMETRIC APPLICATIONS

A. Review of the Literature

Volumetric methods of analysis form a large part of the analytical picture in both academic and industrial laboratories. These methods are usually rapid, accurate, and applicable to most materials either by direct or indirect means. In order to carry out a successful volumetric determination, a solution of a reagent of known concentration is added to the substance to be determined. The reagent must react in a known manner and some method of determining the equivalence point must be available.

Nickel has been determined titrimetrically by Moore (80), who employed a standard potassium cyanide solution as the titrant and silver iodide as the indicator. The nickel was titrated with the standard cyanide solution in dilute ammonium hydroxide. When the blue color of the nickel-ammonia complex faded, a known amount of standard silver nitrate was added along with a small quantity of potassium iodide. The silver iodide formed a cloudy precipitate in the solution and by further addition of cyanide this precipitate was dissolved. When all of the silver was complexed as the cyanide, the solution became clear, indicating the end point. Kolthoff and Griffith (79) have improved on the method and eliminated the interference of iron and chromium by the addition of citrate to the solution.

Nickel has been determined indirectly by precipitation of the 8-hydroxyquinoline complex and extraction into chloroform. The 8-hydroxyquinoline was then titrated with excess standard bromine which was back titrated with thiosulfate after the addition of potassium iodide (8).

Fluck (36) has reported the indirect volumetric determination of nickel by precipitation of nickel dicyanodiamidine in ammonical tartrate solution. The precipitate is filtered, washed with alcohol, and dissolved in water. The aqueous solution is then titrated with standard hydrochloric acid to a methyl red end point. Dubsky and Haver (21b) have successfully applied this method to the microdetermination of nickel.

The use of chelating reagents as titrants for nickel has been studied by Schwarzenbach (116) and Schwarzenbach and Biedermann (117). Both ammonia triacetic acid and ethylenediamine tetraacetic acid have been employed extensively for metal ion titrations. The titrations are followed potentiometrically and a large change in potential is observed at the end point.

Several titrimetric methods, involving the use of vic-dioximes, have been reported. Direct titration of the nickel with 2,3-butanedionedioxime has been carried out by Ishibashi and Tetsumoto (60) by employing ferric sulfate as an external indicator. Excess dioxime gives a deep red color with the iron.

Since the reaction between nickel and a dioxime results in the release of two hydrogen ions, a titrimetric method based on the estimation of the acid released has been developed by Holluta (54). Before the addition of the dioxime, the solution is adjusted to a phenolphthalein end point and then after addition of the reagent, the acid is titrated with standard potassium hydroxide to the phenolphthalein end point.

An indirect method has been proposed by Tougarinoff (126) in which the nickel is first precipitated by 2,3-butanedionedioxime and then the precipitate is dissolved in hot dilute acid to form the decomposition products of the dioxime. Two moles of hydroxylamine are released per mole of dioxime present and the hydroxylamine is determined by reduction of iron(III) to iron(II) with subsequent titration of the iron(II) with permanganate. This method, although involved, is accurate to 0.1 mg. for samples up to 25 mg.

Kolthoff and Langer (71) have titrated nickel with 2,3-butanedionedioxime using a dropping-mercury electrode as an indicator electrode and 1,2-cyclohexanedionedioxime has been employed by Peshkova and Gallay (95) in the amperometric titration of nickel.

Fritz and Fulda (38) have employed a non-aqueous titrimetric method to the determination of nickel with 2,3-butanedionedioxime. The bis(2,3-butanedionedioximato-*N*,*N'*)nickel(II) was precipitated, filtered, and dissolved in glacial acetic acid. Acetonitrile was added to complex the nickel and the released acetate ions were titrated with standard perchloric acid.

Several possible methods have been suggested for the determination of equivalance points. Among those most commonly used are potentiometric, conductometric, amperometric, and visual methods. With the advent of colorimeters and spectrophotometers, several investigators attempted to improve on the visual methods with the aid of a photometric end point.

The first photoelectric measurement of a color change as a means of determining an end point was reported by Field and Baas-Becking in 1926 (33). They employed this method in conjunction with the starch-iodine reaction.

In 1928, Muller and Partaidge (81) described a photoelectric apparatus for automatic titrations employing a phototube, an amplifier, a relay, and an electomagnetic buret release. They were able to perform acidimetric, alkalimetric, permanganate, dichromate, and iodometric titrations with this apparatus. Also, the precipitation titration of chloride with silver was reported to be possible.

Several other workers during the past two decades have applied the photometric end point to many titrations (109, 112, 51). Hirano (52, 53) has been especially active in the field and has employed this method to several common titrations.

Recently Nichols and Kindt (84) applied the photometric method to the determination of fluoride with thorium. Alizarin sulfonate was used to form a colored lake with excess thorium at the end point.

Bobtelsky and Welwart (10) have carried out a photometric titration of nickel by employing 2,3-butanedionedioxime as a precipitant. They employ a photoelectric colorimeter for the end point determination and were able to analyze for milligram quantities of nickel with a few per cent error. The dioxime was added dropwise and readings were taken on the galvanometer after one minute. They were able to determine nickel in the presence of a 50-fold excess of aluminum, iron, lead, copper, cobalt, manganese, and chromium by the addition of suitable masking reagents. Citrate, tartrate, phosphate, and acetate proved to be the most useful complexing ions. Use of a photometric end point with a titration has generally been applied when a colored indicator changes, but Bricker and Sweetzer (12) have employed the method to follow the change in products or reactants of a titration that absorb light in the ultraviolet region of the spectrum. Many organic compounds that could not have been previously titrated can be determined in this manner.

Reilley and Schweitzer (105) have pointed out that with a photometric titration, when the reaction is slow near the equivalence point, extrapolation to the end point is possible and further, inert absorbing species do not interfere as their effect is canceled by the differential method involved.

Fine reviews of the photometric method, its applications, and the instruments developed for its use have been reviewed by Osborn, Elliot, and Martin (87) and Goddu and Hume (43).

B. Materials and Apparatus

Cary Recording Spectrophotometer. Described in section III, B of this thesis.

Beckman Spectrophotometer, Model DU. Described in section III, B of this thesis.

Photometric titrimeter attachment. Klingman, Hooker, and Banks (68) have constructed a photometric titration assembly for the Beckman, Model DU, spectrophotometer by modification of a Beckman Test Tube Adapter Assembly. A buret was inserted through a one-fourth-inch hole drilled in the center of the top of the compartment cover. In order to prevent the entrance of external light, the hole was fitted with a rubber grommet and the buret, below the graduations, was sprayed with optical-black paint. The test tube holder platform was removed and the two guide bars were used to position the titration cell. In order to support the buret, a three-eighth-inch rod was mounted on the back side of the assembly cover and equipped with a clamp.

A Labine "magne-stir" magnetic stirrer was modified for use with this assembly. The outside case was removed and the motor lowered to the base plate by shortening the motor support bolts and spacers. The magnetic bar mount was shortened as was the motor shaft in order to lower the magnet as far as possible. This reduced the over-all height of the stirrer to two and three-quarters inches which allowed its insertion under the titration assembly without disturbing the rest of the spectrophotometer. The stirrer controls were mounted on a utility box attached to the side of the motor base plate. This allowed the controls to be readily accessible at all times.

Titration cells. The titration cell for use in the visible region of the spectrum was a 180-ml. electrolysis beaker, the sides of which had been flattened near the bottom. This permitted the beaker to be firmly inserted between the guide bars and prevented movement during the titration. When the ultraviolet region of the spectra was used, a silica tube was employed as the titration cell. Both of these cells had an inside radius of from 3.5 to 4.0 cm.

Cuvettes. Silica cuvettes were used to investigate the absorption spectra of the complexes. These were 1.001-, 5.00-, and 10.00-cm. in length.

All burets and pipettes used were Kimble "Normax" brand and were checked before use.

The volumetric flasks were all "Exox" Kimble-ware.

Ammonium acetate. A 20 per cent solution of reagent-grade ammonium acetate was prepared by dissolving the salt in deionized water.

Chloroform. C. P.-grade chloroform was distilled to remove the non-volatile material.

Methyl alcohol. Reagent grade.

4-Methyl-1,2-cyclohexanedionedioxime. Reagent grade. Prepared in this laboratory.

4-iso-Propyl-1,2-cyclohexanedionedioxime. Reagent grade. Prepared in this laboratory.

4-tert-Amyl-1,2-cyclohexanedionedioxime. Reagent grade. Prepared in this laboratory.

Standard nickel perchlorate. Prepared as described in section IV, B of this thesis. All other chemicals used in this work were reagent-grade quality.

C. Experimental

Since the nickel complex with vic-dioximes is highly colored and the reaction virtually complete, it was thought that the equivalence point of a titration of nickel with a vic-dioxime could be located photometrically.

1. 4-Methyl-1,2-cyclohexanedionedioxime

a. Determination of nickel. To determine the possibility of a photometric titration with an aqueous suspension of the nickel-dioxime complex, 500 γ of nickel were placed in 100 ml. of water and the pH was adjusted to 4 with ammonium acetate and acetic acid. One ml. of a 10 per cent gum arabic solution was added and the entire mixture was placed in the titration cell of the spectrophotometer. With the wavelength set at 550 millimicrons, an aqueous solution of 4-methyl-1,2-cyclohexanedionedioxime was added in small increments. Absorbance readings were taken after each addition and when the absorbance ceased to increase after several additions of titrant, the titration was complete.

A plot of the absorbance *vs.* milliliters of titrant added was made and the end point easily obtained at the inflection in the graph. The expected end point of 5.21 ml. was not obtained and depending on whether the readings were made one, two, or five minutes after addition, the end points obtained were 5.51, 5.40, and 5.25 ml., respectively.

A study of the time necessary for complete color formation was made and it was found that for 99 per cent completion 20 minutes were required. The data are given in Table 31. This is too long a time for a convenient titration and it was thought that possibly the slow kinetics were due to the precipitate formation.

The solubility of the nickel-4-methyl-1,2-cyclohexanedionedioxime complex in organic solvents is such that it was soluble in a mixture of 20 per cent chloroform, 20 per cent water, and 60 per cent methanol to the extent of 0.004 g. per liter. This solubility was determined by the spectrophotometric determination of the nickel

Table 31

Kinetics of Precipitation of Nickel with 4-Methyl-1,2-cyclohexanedionedioxime[a]

Time after addition[b] min.	Absorbance observed	Fraction of reaction complete
0.50	0.019	0.10
0.75	0.028	0.15
1.00	0.037	0.20
1.50	0.053	0.29
2.00	0.066	0.37
2.50	0.077	0.43
3.00	0.088	0.49
4.00	0.104	0.59
6.00	0.127	0.72
10.00	0.161	0.91
12.00	0.166	0.94
20.00	0.176	0.99

[a] Nickel added, 20 γ in 100 ml.

[b] 1.0 ml. of 0.001 molar dioxime added.

complex at 383 millimicrons. This mixture was also found to dissolve milligram amounts of inorganic salts.

Five ml. of a 0.001 molar nickel perchlorate solution were placed in a titration cell and diluted with 50 ml. of a 75 per cent methanol-25 per cent chloroform solution. Two ml. of a 20 per cent ammonium acetate solution were introduced and the mixture was titrated with a dilute solution of 4-methyl-1,2-cyclohexanedionedioxime in water. The color development of the complex was noted to be complete within one minute after each addition which was the minimum time required for the solution to be mixed by the stirrer. The spectrophotometer was set to read the absorbance at 383 millimicrons and the slit width was adjusted to 0.05 mm. A plot of absorbance *vs.* milliliters of dioxime added gave a graph from which the end point was easily discernible. A correction for the volume of titrant added was made on the absorbance readings to give a more accurate end point.

It was observed that 4-methyl-1,2-cyclohexanedionedioxime formed a nickel complex that was only slightly soluble in the solvent mixture employed and since other substituted 1,2-cyclohexanedionedioximes are more soluble in organic solvents, further work with the photometric titration method was performed with a different dioxime.

b. *Determination of palladium.* Palladium(II) was titrated in water in the presence of gum arabic with 4-methyl-1,2-cyclohexanedionedioxime at a pH of 1.5 and it was found that the suspension was slow to form as observed with the nickel. The time required for 99 per cent color development was 20 minutes which is too long. Table 32 lists the data for the kinetics of precipitation of the palladium complex in water.

Table 32

Kinetics of Precipitation of Palladium with 4-Methyl-1,2-cyclohexanedionedioxime[a]

Time after addition[b] min.	Absorbance observed	Fraction of reaction complete
0.25	0.005	.07
0.50	0.017	.23
0.75	0.028	.38
1.25	0.040	.55
1.50	0.044	.60
2.00	0.054	.74
2.50	0.060	.81
3.00	0.062	.84
3.50	0.064	.88
4.00	0.067	.92
6.00	0.069	.95
12.00	0.071	.97
20.00	0.072	.99

[a] Palladium added, 20 γ.

[b] 1.0 ml. of dioxime added.

Attempts to titrate palladium in the mixed solvent of methanol-chloroform-water were unsuccessful. While the time required for 99 per cent color formation was reduced to six minutes, this is still too long for a good method.

2. 4-iso-Propyl-1,2-cyclohexanedionedioxime

a. Determination of nickel. It was found that the 4-iso-propyl-1,2-cyclohexanedionedioxime complex of nickel is soluble to the extent of 0.01 g. per liter in a mixture of 20 per cent chloroform, 20 per cent water, and 60 per cent methanol. This is 15 times more soluble than the 4-methyl-1,2-cyclohexanedionedioxime complex.

Titration of a sample of nickel with the 4-iso-propyl derivative proved that the reaction with nickel was fast and a photometric titration was feasible.

Several standard samples of nickel(II) were titrated using the following procedure. The nickel sample was placed in the titration cell and the volume of water brought up to 10 ml. Two ml. of 20 per cent ammonium acetate solution were added along with 75 ml. of the chloroform-methanol solvent and the stirrer was started. The spectrophotometer was balanced on the nickel solution at 383 millimicrons and afterwards the only thing changed on the instrument was the dial used to read the absorbance. The dioxime titrant was added in increments of 0.25 ml. and the absorbance readings taken after each addition. The titration was concluded when further additions of titrant failed to increase the absorbance of the solution. A typical titration curve is plotted in Fig. 8. The difference between the expected end point and the observed end point was only 0.01 ml. or a 0.5 per cent error for the titration.

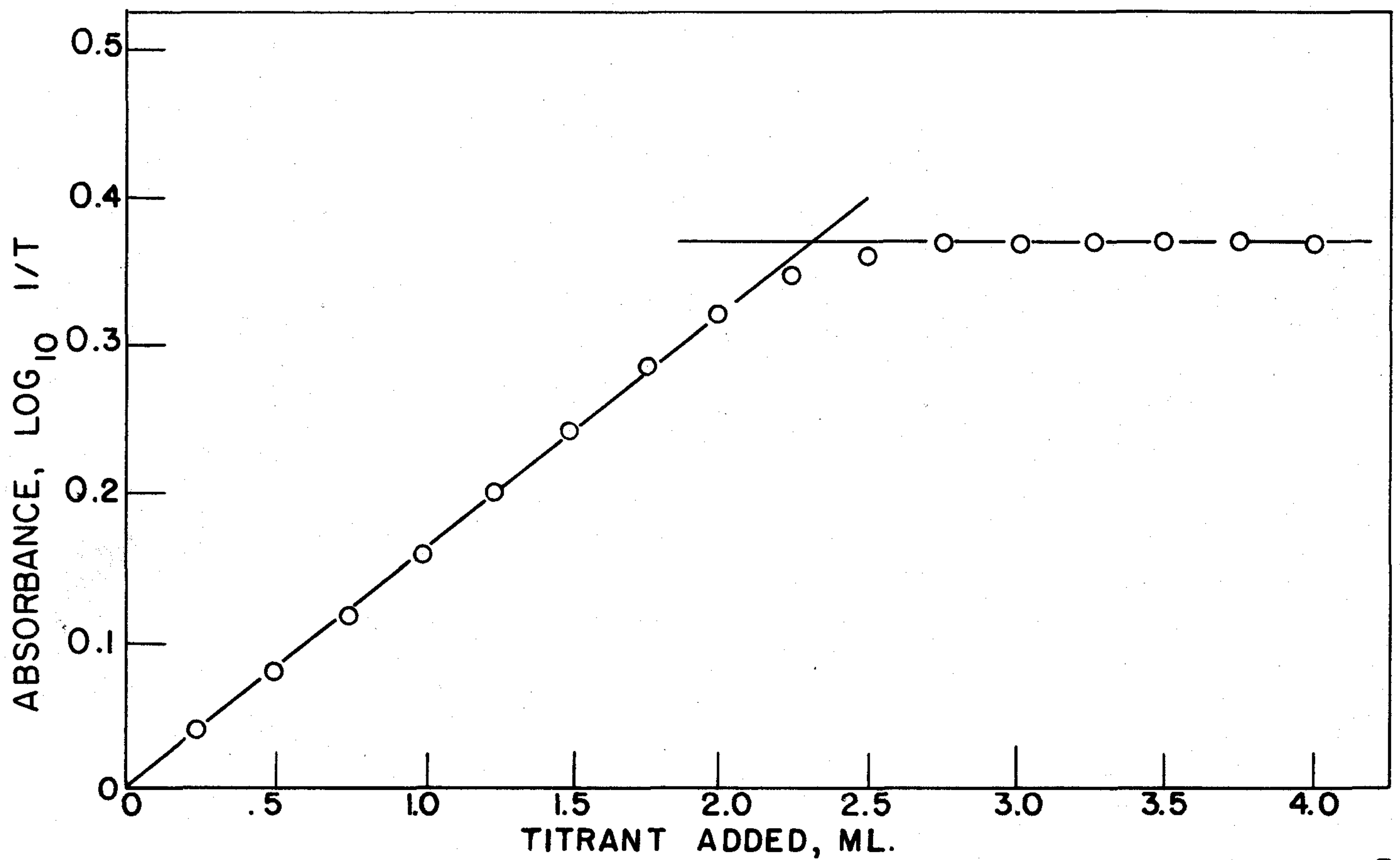


FIG.8 PHOTOMETRIC TITRATION OF 180 γ OF Ni(II) WITH 1.340×10^{-3} NORMAL 4-ISO-PROPYL-1,2-CYCLOHEXANEDIONEDIOXIME AT 383mμ. END POINT FOUND, 2.28ml.

The results of several titrations of standard nickel samples are listed in Table 33. For 10 determinations the error was ± 8 γ which was partially due to the error in delivery of the buret employed.

Table 33

Photometric Titration of Several Nickel(II) Samples

Nickel added γ	Titrant[a] added ml.	Nickel found γ	Error γ
897	3.98	891	- 6
897	4.01	900	+ 3
718	3.22	710	- 8
718	3.14	705	- 13
718	10.68 ± 0.03[b]	717 ± 2	- 1
538	2.34	525	- 13
538	2.36	530	- 8
410	6.06 ± 0.04[c]	408 ± 3	- 2
359	1.61	361	+ 2
359	1.58	356	- 3
179	.86	192	+ 13
179	.78	175	- 4

[a] 7.64×10^{-3} molar dioxime.

[b] 2.296×10^{-3} molar dioxime, three determinations.

[c] 2.296×10^{-3} molar dioxime, three determinations, N.B.S. aluminum-base alloy, No. 85a.

In two cases the titrant was diluted and a larger volume employed. One of these samples was a National Bureau of Standards sample and it was determined with an average error of ± 3 γ or 0.7 per cent for a 410-γ sample.

While vic-dioximes are very specific for the precipitation of nickel, they are not at all specific in their complexing abilities. Nearly all of the transition metals form dioxime complexes and all of these complexes are highly colored. It was, therefore, expected that several ions would interfere with the determination of nickel by the photometric titration method.

Interferences were studied by including the foreign ion in the aqueous sample of nickel and carrying out the titration as with nickel alone.

Interferences were of these kinds: one was caused by precipitation of the material in the mixed solvent used, another due to reaction with the dioxime to form a complex in preference to the nickel, and a third due to formation of a stronger complex with nickel(II) than the dioxime. Interference data are given in Table 34.

The first type of interference included the very weakly basic metals that tended to hydrolyze and precipitate as the basic salts. Most of these were held in solution with tartrate or acetate.

Table 34

Interferences in the Photometric Titration of Nickel(II) with 4-iso-Propyl-1,2-cyclohexanedionedioxime

Ion added	Amount of each ion added mg.	Nickel found[a] γ	Error γ
Sodium(I), Potassium(I), Lithium(I), Ammonium(I)	30	300	0.0
Calcium(II), Strontium(II), Barium(II), Magnesium(II), Beryllium(II)	30	302	+ 2.0
Aluminum(III), Thorium(IV), Lanthanum(III), Cerium(III)	30	290	- 10.0
Lead(II), Cadmium(II), Zinc(II), Acetate	30	301	+ 1.0
Silver(I), Gold(I)[b]	30	301	+ 1.0
Niobium(V)[c]	30	300	0.0
Chromium(II)	30	304	+ 4.0
Iron(II)	30	Interferes	
Iron(II) DPM[d]	3	302	+ 2.0
Iron(III)	30	Interferes	
Iron(III)[c]	1	301	+ 1.0
Copper(II)	30	Interferes	
Copper(II) DPM[d]	3	301	+ 1.0
Cobalt(III)[e]	30	300	0.0
Palladium(II)[f]	30	301	+ 1.0
Uranate(VI), Chromate(VI), Nitrate, Sulfate	30	299	- 1.0

Table 34 (Continued)

Ion added	Amount of each ion added mg.	Nickel found[a] γ	Error γ
Bromide, Iodide, Acetate, Chloride	30	302	+ 2.0
Citrate	30	Interferes	
Cyanide	30	Interferes	
EDTA[g]	30	Interferes	

[a] 300 γ of nickel were added.

[b] Thiocyanate added.

[c] Tartaric acid added.

[d] DPM, dipivoylmethane added.

[e] Cyanide complex.

[f] pH adjusted to 8 with ammoniumhydroxide.

[g] Ethylenediamine tetraacetic acid.

The ions that hydrolyzed and could not be complexed successfully are titanium(III), thallium(I), tin(II), bismuth(III), and arsenic(III).

The second type of interference, reaction with the reagent, was limited to copper(II), iron(II), iron(III), cobalt(II), and ruthenium(III). The cobalt interference was removed by oxidizing and complexing with cyanide and peroxide and the copper was reduced and complexed thiocyanate. A simpler method for the removal of iron and copper interferences was the addition of dipivoylmethane to the titration solution. Fig. 9 illustrates the titration of nickel with iron and dipivoylmethane present. For quantities of copper and iron over 3 mg., dipivoylmethane cannot be used since the complexes are highly colored and the spectrophotometer cannot be balanced. Ruthenium interfered and must be absent from the solution.

The third type of interference was exhibited by anions that form a strong complex with nickel(II). Cyanide, citrate, and ethylenediamine tetraacetate were all of this type and must be absent from the solution. The average error for all of the determinations, in which the foreign ion did not interfere, was 2 γ or only a 0.6 per cent error for a 300-γ determination.

3. 4-tert-Amyl-1,2-cyclohexanedionedioxime

The spectrum of the nickel chelate of 4-tert-amyl-1,2-cyclohexanedionedioxime was taken on the Cary recording spectrophotometer and found to be the same as for the 4-methyl and 4-iso-propyl derivatives.

A titration of nickel in the mixed solvent with a saturated water solution of the dioxime indicated the reaction was as fast as the titration could be carried out with a photometric end point. Because of the low solubility of the dioxime in water, the concentration of the titrant was only 0.0000242 molar and it was only feasible to titrate less than 50 γ of nickel(II) at any one time. Several determinations were made on 30-γ quantities and the average

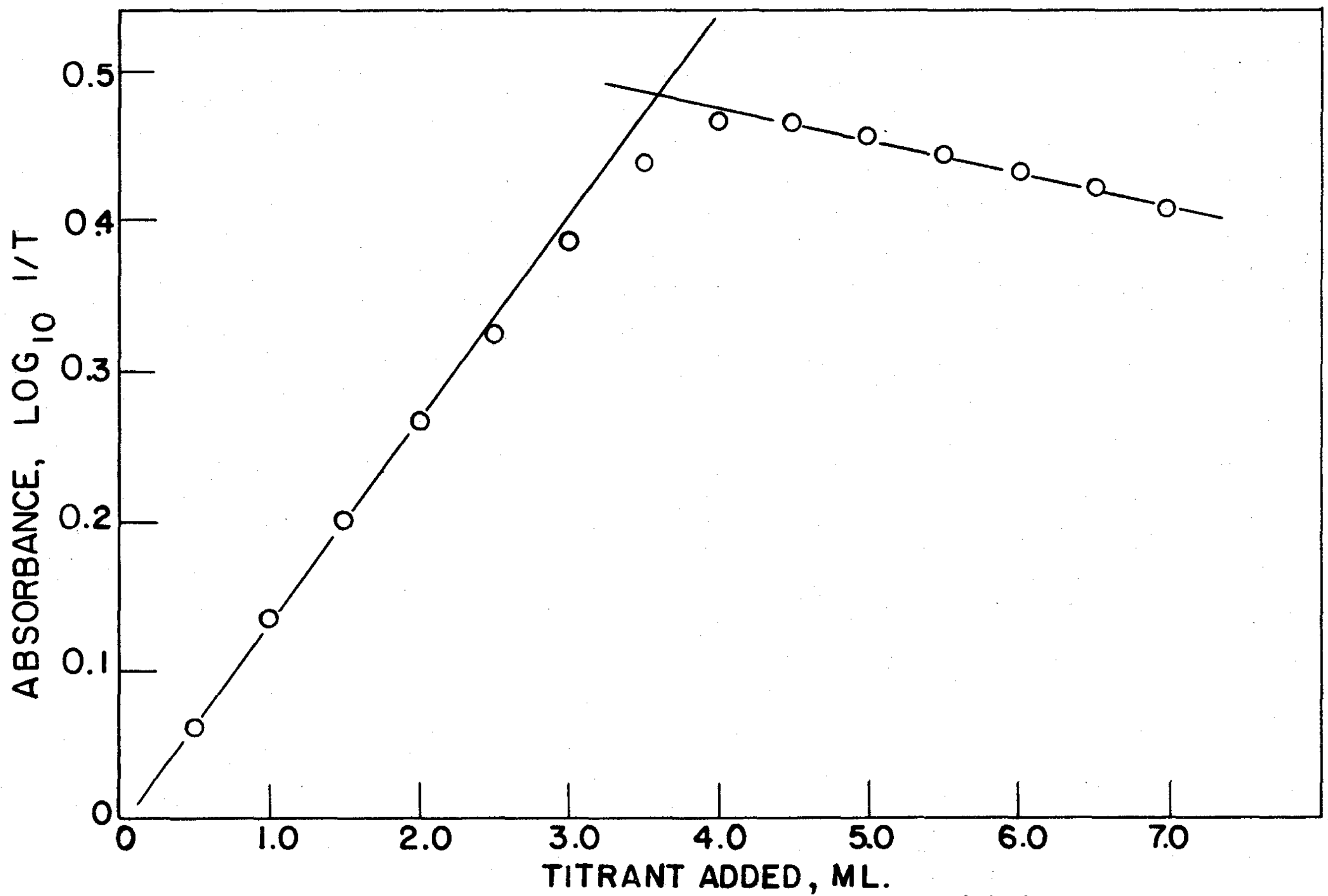


FIG. 9 PHOTOMETRIC TITRATION OF 280 γ Ni (II) WITH 1.340×10^{-3} NORMAL 4-ISO-PROPYL-1,2-CYCLOHEXANEDIONEDIOXIME AT 383 mμ IN THE PRESENCE OF 3 mg. OF Fe(III) AND DIPIVOYLMETHANE. END POINT EXPECTED, 3.55 ml.. END POINT FOUND, 3.58 ml..

of the eight titrations was 29.6 γ or an error of - 0.4 γ. The results are given in Table 35.

Interferences were studied by adding the foreign ions to the nickel sample before addition of the organic solvent. The procedure followed was the same as for titration of nickel with 4-iso-propyl-1,2-cyclohexanedionedioxime. The interferences were the same as for the iso-propyl homolog and were removed in the same manner. In the determination of 30 γ of nickel 0.3 g. or 10,000 to 1 excess of the alkali metals could be present. The alkali earths, chromium(III), manganese(II), cadmium(II), zinc(II), magnesium(II), beryllium(II), palladium(II) (as the ammonia complex), lead (as the acetate complex), cobalticyanide, uranium(VI), chromate(VI), chloride, bromide, iodide, nitrate, sulfate, acetate, and thiocyanate were found not to interfere in amounts of 0.03 g. or 1000 to 1 excess.

At a ratio of 100 to 1 (3 mg.), mercury(II), aluminum(III), thorium(IV), lanthanum(III), cerium(III), arsenic(III), fluoride, and sulfosalicylate offered no interference.

Copper, if complexed with thiocyanate, did not interfere if present in quantities less than 300 γ or 10 to 1 excess. Iron in the ferric state could be complexed with thiocyanate or phosphate and in the ferrous state with a large excess of hydroxyamine so that no interference up to 100 γ was noted.

Table 35

Photometric Titration of Nickel(II) with 4-tert-Amyl-1,2-cyclohexanedionedioxime[a]

Titrant added[b] ml.	Nickel found[c] γ	Error γ
11.61	30.0	0.0
11.32	29.1	- 0.9
11.70	30.3	+ 0.3
11.62	30.1	+ 0.1
11.59	30.0	0.0
10.98	28.4	- 1.6
11.81	30.6	- 0.6
11.44	29.6	- 0.4

[a] Wavelength was 383 millimicrons.

[b] Dioxime was 0.0000968 molar.

[c] 30.0 γ of nickel were added.

a. Determination of palladium. A photometric titration of palladium(II) with 4-iso-propyl-1,2-cyclohexanedionedioxime employing the same procedures as with the 4-methyl homolog proved to be unsuccessful due to the slow development of the color.

D. Discussion and Summary

The large absorption of light by nickel-vic-dioxime complexes affords an excellent opportunity to apply a photometric method to the determination of the end point of a titration of nickel(II) with a vic-dioxime.

The attempt to titrate in water solution was not successful due to unfavorable kinetics involved in the precipitation of the complex. The obvious thing to try then was titration in a media where the complex was soluble. Most of the previously described dioxime chelates with nickel are only slightly soluble in most solvents, but this is not the case for the aliphatic substituted 1,2-cyclohexanedionedioximes described in this thesis.

4-Methyl-1,2-cyclohexanedionedioxime was first investigated as a titrant for nickel and the photometric method proved to be applicable for locating the equivalence point. In order to keep the dioxime chelate in solution and also keep the inorganic salts from precipitating, a mixed solvent was employed. A mixture of 20 per cent chloroform, 20 per cent water and 60 per cent methanol was found to be satisfactory. The chloroform held the dioxime complex in solution, the water rendered the metallic salts soluble, and the methanol afforded a homogeneous solution.

The wavelength chosen for the photometric determination of the end point was not critical and anywhere in the range of 300 to 400 millimicrons was applicable. The main factor in determination of the wavelength setting was whether or not the spectrophotometer could be balanced on the starting solution. Some ions absorb very heavily at certain wavelengths and this region was avoided to increase the sensitivity of the end point.

While the 4-methyl-1,2-cyclohexanedionedioxime was easily applied to the titrimetric method, the nickel chelate was not sufficiently soluble in the titration mixture to permit larger than 200-γ quantities of nickel to be titrated. The nickel-4-iso-propyl- and nickel 4-tert-amyl-1,2-cyclohexanedionedioxime complexes were found to be much more soluble and are recommended.

A water solution of 4-iso-propyl-1,2-cyclohexanedionedioxime was employed as the titrant for nickel and several determinations on standard samples showed the accuracy of the method to be $\pm 8\gamma$ for 179-to 897-γ quantities. This is an error of 1 to 5 per cent which is near the limit of the accuracy for the buret used. Only 4 ml. of titrant were used on the largest sample and the limit of reading the buret employed was 0.02 ml. or a 0.5 per cent error. With the smallest sample only 0.80 ml. of titrant were necessary which meant a 3 per cent error in reading the buret. Of course, this error could be reduced if a more dilute solution of titrant were used. This was verified by the use of a 2.546-molar dioxime solution since with 10 ml. of titrant the error was reduced to $\pm 1\ \gamma$ or 0.2 per cent.

A 0.00009-molar solution of the 4-tert-amyl-1,2-cyclohexanedionedioxime was used as titrant. Eleven and six-tenths ml. were required for titration of 30 γ of nickel and in a series of eight determinations with an average error of ± 0.5 γ or less than 2 per cent.

The 4-methyl-, 4-iso-propyl-, and 4-tert-amyl-1,2-cyclohexanedionedioximes form complexes with nickel which all have the same absorption spectrum in chloroform solution and nearly the same chemical and physical properties except for solubility. Thus, the three vic-dioximes can be used for the photometric titration of small amounts of nickel. The interferences involved with the determination of nickel by this method are common to all three dioximes.

The only ions of those studied that cannot be present in any form are the ruthenium(III), cyanide, citrate, and ethylenediamine tetraacetate. Copper and iron are troublesome and must be complexed in order to avoid their interference. Thiocyanate will complex copper in small amounts as will dipivoylmethane, but gram quantities of copper must be removed from the solution. Extraction as the cupferate in acid solution proved to be satisfactory. Iron offers the same type of interference with the titration and can be disposed of in the same manner as copper.

Cobalt interfers as might be expected but can be removed by forming the cobalticyanide complex which offers no interference.

If a large amount of chromium(III) is present the solution is very highly colored and during the titration the observed absorbance decreases since the color developed by the complex is not sufficient to offset the decrease in absorbance due to dilution. The end point is still easily located, however, and chromium does not interfere.

The problem of the iron interference was investigated fully and it was found that amounts up to 50 to 1 excess over the nickel could be tolerated if a few drops of dipivoylmethane were added to the titration cell. This beta-diketone complexes iron in preference to nickel and permits the dioxime to react with the nickel first. The titration curve in Fig. 9 illustrates that the nickel is titrated first and after the nickel end point, the absorbance of the solution falls due to the destruction of the highly colored dipivoylmethane-iron complex and formation of the lesser colored dioxime-iron complex.

VII. SUGGESTIONS FOR FUTURE WORK

This study on the substituted 1,2-cyclohexanedionedioximes has suggested several possibilities for future endeavors. These are listed individually.

1. While yields of the several vic-dioximes that were prepared were 15 to 20 per cent of the theoretical in most cases, the 3,6-dimethyl-1,2-cyclohexanedionedioxime and the 4-carboxy-1,2-cyclohexanedionedioxime were obtained in 1 and 2 per cent yields. If these dioximes are to be employed in analytical methods, other means of preparing the compounds are necessary.

2. The investigations as to the nature of the nickel-dioxime complex pointed to weakening of the intermolecular attraction between the planes of the complexes in crystals by the interference of bulky groups on the cyclohexane ring of 1,2-cyclohexanedionedioxime. It might be possible by X-ray techniques to establish if the planes of the complexes are pushed apart by these groups and to correlate the physical properties of the complexes with the observed nickel-nickel distance.

3. Since the 4-carboxy-1,2-cyclohexanedionedioxime forms a nickel complex that is very soluble in basic solution, it might be possible to establish the particular nickel species present in the oxidized dioxime complex employed by Rollet for the spectrophotometric determination of nickel. This high concentration in basic

solution could make possible the determination of the magnetic susceptibility of the complex with some certainty. The exact nature of the complex is not known and it has been suggested that the nickel has an oxidation state of II, III, or IV. Most agree that it is probably III or IV and since the III state of nickel would possess one unpaired electron and the IV state would have zero or two, differentiation could probably be made on the basis of a magnetic study.

4. In all of the applications of dioximes to nickel determinations, iron is usually an interference and it seems, since nickel requires only two dioxime groups for formation of a stable complex and iron requires three, a sterically hindered dioxime might be prepared that would discourage the formation of an octahedral complex without interfering with a square-planar configuration.

5. The successful application of the photometric titration method to the determination of nickel with a dioxime suggests the application of other chelating reagents for the titration of many metals. Possibly iron could be titrated with 1,10-phenanthroline or a phenol and copper with a dioxime. Certainly with the abundance of chelating reagents available most every metallic ion could be titrated photometrically.

6. Titration of nickel(II) and palladium(II) with a dioxime in water did not prove successful and after careful consideration, it seems the kinetic problem might be due to the addition of the

gum arabic. The retardation of the gum on formation of the precipitate was established in the work on the heterogeneous spectrophotometric method. It is probable, that in the absence of the gum arabic, small amounts of these metallic ions could be determined, but larger quantities might tend to coagulate.

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