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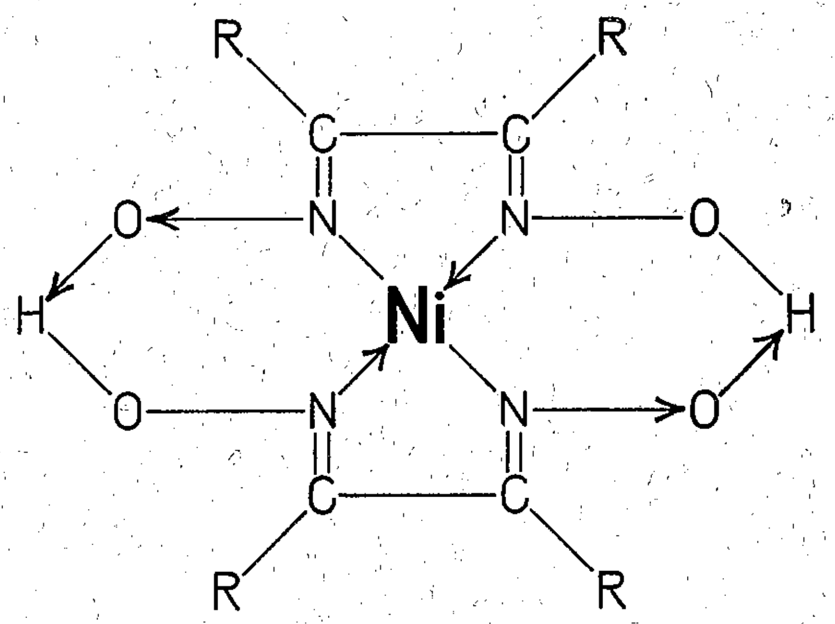
THE APPLICATIONS OF THE DIOXIMES TO ANALYTICAL CHEMISTRY



By

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IOWA STATE COLLEGE
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THE APPLICATIONS OF THE DIOXIMES TO ANALYTICAL CHEMISTRY

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ROGER ADAMS

INTRODUCTORY COMMENTARY

The appearance of this excellent critical resumé of the chemistry of the 1, 2 dioximes and their use in analytical procedures warrants a few reminiscent remarks. Although dimethyl glyoxime was used as a nickel reagent in the United States in several analytical laboratories prior to 1916, its distribution was relatively small and its value not widely recognized.

It was in 1916 that the University of Illinois first distributed to various scientific and industrial laboratories chemicals which had been cut off from importation and which had been manufactured in the University of Illinois chemical laboratories during the summer months. Among the many requests which began to pour in, there was a small but persistent demand for dimethyl glyoxime. As a consequence, a satisfactory method of synthesis was developed and the University of Illinois became the first manufacturer of this product in the United States. The demand for dimethyl glyoxime increased as the word circulated that it was available in this country. During the succeeding years hundreds of pounds were made and sold. It was not until certain industrial concerns recognized the volume of business and the growing importance of this reagent that they undertook its marketing and relieved the University of Illinois of further service in this particular chemical.

Today dimethyl glyoxime is looked upon as indispensable in every analytical laboratory. Its use in the determination of nickel is universal. Dr. Diehl is deserving of much commendation for collecting the important facts concerning this and related substances and for presenting them in such a useful form.

Roger Adams

Jan 29, 1940

PREFACE

"The Applications of the Dioximes" now comes to join the GFS booklets on varied phases of analytical chemistry. Like its predecessors it hopes to contribute its mite to the progress of analytical chemistry, and by gathering into one place the forgotten, half-noticed and quasi-familiar facts related to a rather broad topic, to make the analyst conscious that a structure now stands where formerly only isolated timbers or piles of bricks were visible. If an apology for a review article were necessary, it might be pointed out that the relevant information of a great number of journal articles is here assembled for instant reference and that the questionable has been critically culled and the worthless discarded. And where propaganda is needed for a promising but neglected method, it is here supplied. By nature the analyst is conservative and wary of change, particularly if he be a busy industrialist lacking the requisite time to confirm adequately a prospective method. To him a review will appeal as at once supplying the broad picture and summarizing the supporting evidence.

The dioximes are useful. But their story has evolved over a period of three decades and has never been adequately told as a unit. There has been much rediscovery in the unfolding of the story and the attendant waste of duplicated effort has been unfortunate. This alone would justify "The Applications of the Dioximes." But the dioximes are also instructive, for they are specific in action, and their uniqueness has few qualifications. They afford guiding principles and a constant challenge to those who would improve analytical chemistry by tapping the vast reservoir of organic compounds.

Finally, to G. F. S., himself, entrepreneur and professor, a full measure of thanks for his able and disinterested efforts in publicizing and advancing the newer analytical chemistry.

HARVEY DIEHL

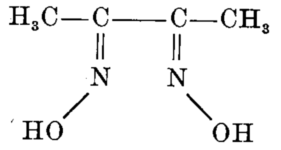
Ames, Iowa
Jan. 7, 1940.

THE APPLICATIONS OF THE DIOXIMES TO ANALYTICAL CHEMISTRY

I. GENERAL CONSIDERATIONS

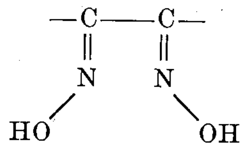
The reaction between nickel salts and the organic compound dimethylglyoxime, yielding the brilliant red insoluble nickel compound familiar to all who have studied qualitative analysis, was discovered by the Russian chemist Tschugaeff in 1905 (*1*). The striking beauty of the compound and its remarkable insolubility are frequent cause of comment. No less striking, however, is the very anomalous chemical character of the compound and the remarkable change its advent made on the analytical chemistry of the metals, particularly that of nickel. Through the latter it has effected the chemist an enormous saving in time and labor, which he has been able to divert into other channels in his pursuit of greater knowledge to serve civilization.

Dimethylglyoxime is a dioxime of an ortho-diketone, having the structural formula



More correctly the compound should be called *biacetyldioxime* which is more descriptive of the composition of the molecule than the older and more common name *dimethylglyoxime*.

The central group



of the dimethylglyoxime molecule is evidently responsible for the formation of the nickel compound, for replacement of the methyl groups by other aliphatic, aromatic or heterocyclic groups does not alter this property, nor is the color of the nickel derivative appreciably different from the characteristic scarlet red color of nickel dimethylglyoxime. The dioximes also yield yellow precipitates with palladium salts but with no other metals; and even the separation of palladium and nickel is possible by proper control of the acidity of the solution. The ortho-dioxime group may therefore be termed at once both a *nickel specific* group and a *palladium specific* group.

The unique nature of the reaction between nickel and dimethylglyoxime made it exceptionally useful in the determination of nickel, particularly in the analysis of nickel bearing metallurgical products; and one has only to consult the paper of Campbell and Smith (*2*), dealing with the accuracy of the methods of metallurgical analysis over a period of years, to appreciate the great improvement made in the method of analysis of nickel by the introduction of dimethylglyoxime.

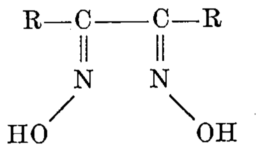
The applications of dimethylglyoxime and related ortho-dioximes to the analytical chemistry of nickel, palladium and incidentally to one or two other metals is the subject of this monograph. A short discussion of the nature of the metallic derivatives of the ortho-dioximes and a survey of the various dioximes which have been studied will precede the material dealing with the specific applications of each reagent.

B. THE NATURE OF THE METALLIC DERIVATIVES OF THE ORTHO-DIOXIMES

The nickel compound of dimethylglyoxime has the composition $Ni(C_4H_7O_2N_2)_2$, one of the hydrogen atoms of each of the molecules of dimethylglyoxime, $C_4H_8O_2N_2$, having been replaced by nickel.* The compound is a non-electrolyte and is non-polar in character rather than salt-like; it is insoluble in water, but soluble in chloroform and other organic solvents; it sublimes without decomposition at about 250° and most certainly its scarlet red color is not that of the common salts of nickel.

The anomalous character of the nickel derivative of dimethylglyoxime immediately led to the formulation of the compound as a coördination, or secondary valence, compound, in which, since two reactive groups are present in the molecule and neighboring to each other, a ring structure was present. The existence of such rings has been subsequently borne out by the results of a number of methods of attack on analogous compounds and the generic term *chelate ring* has been applied to those metallic derivatives of organic molecules in which the metal is implicated in ring structure by functional groups. Those chelate ring compounds which are also non-electrolytes have very unusual properties; because of their non-polar character they are insoluble in ionizing solvents but soluble in non-ionizing solvents; they have low melting and boiling points or sublime readily; they are highly stable and with one notable exception never occur with water of crystallization; their color depends on the structure of the molecule and departs widely from that of the normal salts of the metal. These substances, chelate non-electrolytes, are known as *inner complex* compounds and they form interesting chapters in the knowledge of such otherwise unrelated fields as analytical chemistry, mordant dyeing, biochemistry and leather tanning (*25*). Nickel dimethylglyoxime is a typical *inner complex* compound.

The symmetric dioximes, that is, those in which identical groups are attached to the central part of the molecule, should exist in three isomeric forms on the basis of the geometric isomerism first propounded by Hantzsch and Werner. In those cases where the attached groups are aromatic all three of the predicted isomeric forms are known, that is,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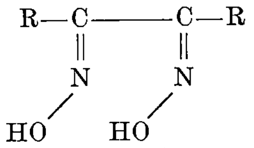
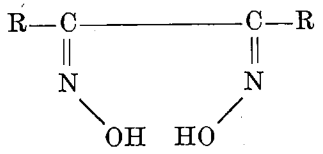

amphi-


syn-

Of the three compounds known, the α-, β-, and γ-isomeric forms, corresponding to the three configurations, the α-compound alone forms the characteristic red insoluble nickel compound, the β-form is totally incapable of reacting with metallic salts, while the γ-form gives a yellow or green-yellow compound with nickel in which one molecule of dioxime is attached to one of nickel, the hydrogens of both oxime groups being replaced by the metal (*3, 4, 15, 11, 14, 7, 6*).

The original assignment of configuration to the three isomeric forms was made on the basis of the Beckmann Rearrangement, assuming the groups which interchanged in the rearrangement were the neighboring or *cis* groups. On this basis the α-form was assigned the

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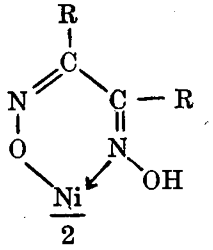
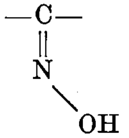
*In the literature dimethylglyoxime is frequently abbreviated to H_2D; the nickel derivative is then represented $Ni(HD)_2$.

syn-configuration and the nickel derivative was formulated as a six-membered ring (*5*)*.



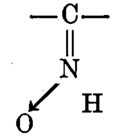
the arrow representing a secondary, or residual, valence bond and the designation $\underline{\mathrm{Ni}}$ over 2 simply indicating that two such rings are attached to the nickel atom. The work of Meisenheimer, based on the oximes formed by the ring opening of certain heterocyclic compounds, showed, however, that actually the *trans* groups are interchanged in the Beckmann Rearrangement (*20, 22*); and this has been proved also by the results of absorption spectra studies and of other lines of investigation. This necessitated a complete reassignment of the configurations given the various oximes. On the newer basis the α-form is given the *anti-*, the β-form the *syn-*, and the γ-form the *amphi*-configuration.

The difficulty with the six-membered ring formulation of the nickel compound with an *anti*-dioxime where the —OH groups are averted from each other is immediately apparent. A factor which further complicates the chemistry of the oximes, however, gives the clue to the situation. The oxime group exists in two tautomeric forms



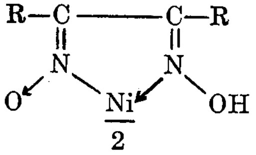
oxime form

and

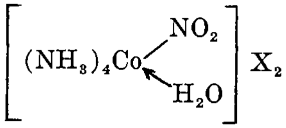


nitrone form

This tautomerism has been definitely proved by Brady and Mehta (*9*) who isolated oxygen and nitrogen ethers corresponding to each of these forms. By assuming the tautomeric nitrone form to be involved in the formation of the nickel derivative, a five-membered ring results in which the metal is attached directly to nitrogen



Pfeiffer, who proposed this formulation (*12, 16*), adduced several lines of evidence in its support, working with the simpler nickel and cobalt salts of α-benzilmonoxime and extending the reasoning to the dioximes. The metal-nitrogen linkage is well known among the coördination compounds, for example, the nitro cobalt amines, $[\mathrm{Co(NH_3)_5NO_2}]\mathrm{X_2}$ and $[\mathrm{Co(NH_3)_4(NO_2)_2}]\mathrm{X}$, both of which are yellow in contrast to the nitrito compounds, for example, $[\mathrm{(NH_3)_5Co{-}ONO}]\mathrm{X}$, which is pink in color and unstable, passing slowly into the corresponding nitro compound. Pfeiffer found that the colors of the very similar compounds



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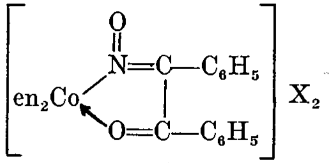
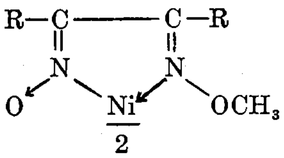
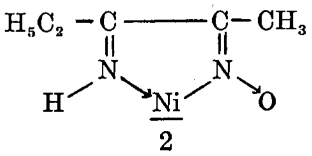


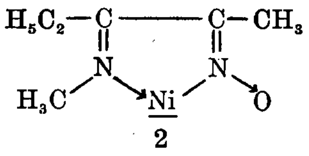
were practically identical (*17*).

That the hydroxyl group of the second oxime plays no part and the metal is not linked to oxygen is shown by the ready formation of exactly similar compounds by the mono-O-ether of benzildioxime (*18, 16*)



Pfeiffer has also found (*16*) that, when one of the oxime groups is replaced by an imino or methylimino group, complex formation occurs in identical fashion





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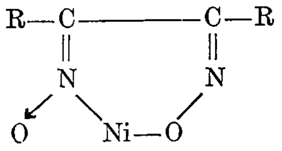
*Werner and Pfeiffer were apparently responsible for this formula; Tschugaeff never committed himself but in turn wrote the formula as a five, six, or seven membered ring or ambiguously, stating on several occasions that more work was required to settle the problem.

As mentioned, the anti-dioximes form stable, brilliant red compounds with nickel. Indeed, the tendency for such formation to occur is so great that hot aqueous or alcoholic-aqueous solutions of the dioximes will dissolve metallic nickel, copper, cobalt, or iron, liberating hydrogen (*8, 21*).

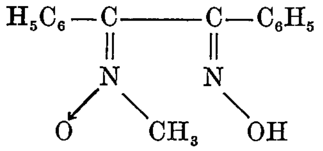
The *amphi*-dioximes (γ-form) give yellow or green-yellow compounds with nickel in which one molecule of dioxime is attached to one atom of nickel, the hydrogens of both oxime groups being replaced by the metal (*4, 15, 14*). The metal is apparently attached to one group through nitrogen and to the other through oxygen, corresponding to



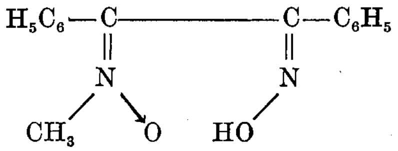
The compounds are usually amorphous, poorly defined, and difficult to purify. They are stable toward alkalies, but in contact with acids they pass rapidly into the red, stable, isomeric compounds of the α-dioxime.

The *syn*-dioximes (β-form) are completely incapable of forming compounds with the metals.

These steric factors clearly indicate that the nitrogen atom must be free on the side toward which the metal is to add. This is again borne out by the fact that neither of the mono-N-ethers of α- or β-benzildioxime



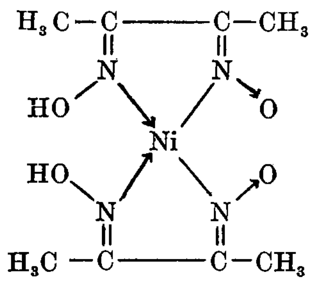
α-form

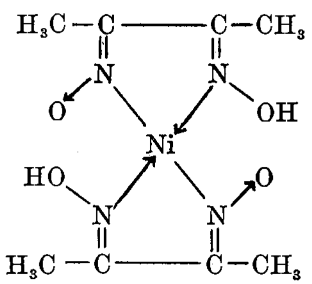


β-form

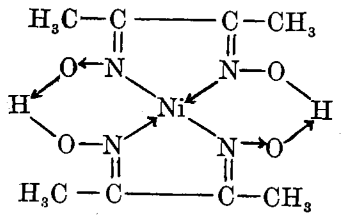
yields compounds with nickel (*18*).

A closer inspection of the structural formulas assigned the dioxime-metal compounds, e.g., nickel dimethylglyoxime, will show that if the organic molecules are disposed about the nickel in a plane, *cis-trans* isomerism may be expected depending on which of the oxime groups are united to the nickel by principal and which by secondary valence (*13*):





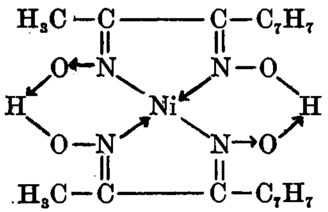
That no such isomerism has ever been observed may be explained by a tautomeric shift of the hydrogen atom (*19*), or, better, by assuming hydrogen bonding to occur between the neighboring oxygen atoms. Brady (*18*) writes the formula thus:

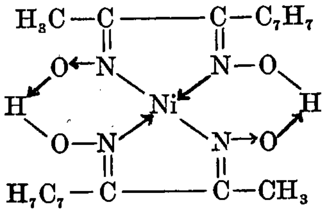


This formula also explains the lack of reactivity of the hydroxyl group in these compounds. Tschugaeff (*7*) found that nickel dimethylglyoxime would not react with phenyl isocyanate, and Barker (*10*) states that acetic anhydride has no effect on it. With methyl iodide nickel dimethylglyoxime yields an addition product from which water regenerates the original red nickel compound. Brady and Muers (*18*) report that nickel dimethylglyoxime gives no methane with methyl magnesium iodide in amyl ether.

Only one isomer of dimethylglyoxime is known, corresponding to the *anti*-configuration; the other forms apparently going over into the more stable form. It is noteworthy, however, that a temporary yellow nickel compound is first precipitated on the addition of an acetone solution of dimethylglyoxime to a dilute and very weakly acid solution of a nickel salt, the yellow compound changing to the red very rapidly.

The dioximes have been very useful in proving the planar structure of the quadricovalent nickel atom. Sugden (*19, 23*) has prepared two isomeric nickel derivatives of unsymmetrically substituted glyoximes corresponding to *cis-* and *trans*-configurations





Palladium shows the same type of isomerism (*24*).

C. SURVEY OF THE DIOXIMES AND THEIR APPLICATIONS IN ANALYSIS

The evolution of analytical chemistry has been marked by the proposal of an enormous number of methods and technics of analysis; each of these developments has been subjected to a critical scrutiny and has been rejected or retained as it met or failed to satisfy the increasing demands of accuracy, speed, and selectivity, and what has dissatisfied one generation has been discarded or modified and improved by the next. Gradually there has been established a certain set of standards that a satisfactory method should meet. These requirements may be summarized as follows:

1. The reagent should be specific or at least selective in action, that is, it should react solely with one certain ion or at most with a limited group of ions.

2. The precipitate formed should be extremely insoluble, or if a soluble colored compound is formed it should be stable indefinitely in the presence of excess reagent.

3. The precipitate should be of definite composition and stable toward drying and atmospheric moisture.

4. The precipitate should have a high molecular weight with corresponding low content of metal, or ion being determined.

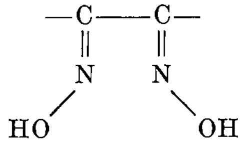
5. The precipitate or soluble compound formed should be highly colored so as to be more sensitive as a qualitative test and as a colorimetric method, and preferably the reaction should obey Beer's Law in order that it may be more adaptable as a colorimetric method.

6. The method should offer the possibility of being used alternatively as a volumetric method.

7. The reagent should be soluble in water.

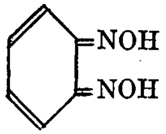
In connection with the first requirement, it should be mentioned that the use of the term *specific group*, as applied to some characteristic linkage or atomic grouping in a homologous series of organic compounds which has some particular affinity to a certain metal or group of metals, is due to Feigl, who has perhaps done more than any other in the applications of organic compounds to analytical chemistry.

A number of such specific groups are known, the ortho-dioxime,



or nickel specific group being the prototype, and from a practical viewpoint, by far the most important. Irrespective of the nature of the groups attached to the central ortho-dioxime grouping the compounds have a remarkably specific action toward nickel in weakly acid or ammoniacal solutions and toward palladium in acid solution. They react with very few other metals; notably with ferrous iron, with which they form pink soluble compounds; with copper, with which they yield a purple coloration in the presence of an oxidizing agent; with bismuth, with which they yield a yellow precipitate or coloration in ammoniacal solution; and with cobalt, with which they form a great number of soluble coördination compounds. None of these interferes seriously with the detection and determination of nickel and palladium but a number of minor points and modifications must be made in their presence as will be noted in subsequent sections of this booklet.

This specificity toward nickel and palladium vanishes when the group is part of an unsaturated ring; thus ortho-quinonedioxime and α,β-naphthquinonedioxime



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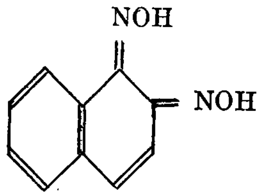
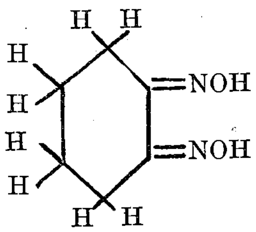
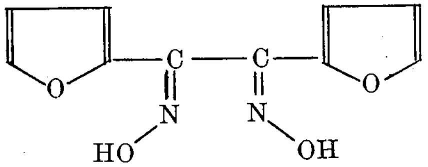


behave as dibasic acids yielding yellow precipitates with almost all metal ions in neutral solutions (*34, 31*). The aromatic ring, therefore, destroys the specific activity of the two oxime groups. The specificity toward nickel returns, however, in the saturated cyclic compound cyclohexanedionedioxime,

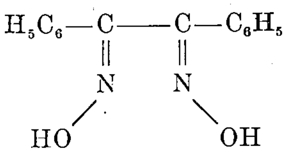


which is exactly similar to dimethylglyoxime in its behavior.

The nickel derivative of dimethylglyoxime is extremely insoluble in aqueous solution but its solubility becomes appreciable in water-alcohol and water-acetone mixtures. This is usually the situation under which the metal is precipitated since dimethylglyoxime is sparingly soluble in water and is usually added as a solution in alcohol or acetone. In this connection the reagent just mentioned, cyclohexanedionedioxime, is superior to dimethylglyoxime in being completely water soluble. Still another reagent, α-furildioxime,

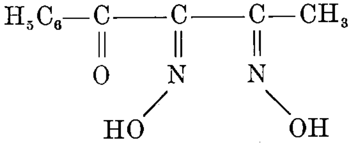


is water soluble and has the still further advantage of a considerably higher molecular weight, giving a proportionally lower content of metal in the precipitate. Alpha-benzildioxime,



$$\begin{array}{ccc} H_5C_6-C & - & C-C_6H_5 \\ \| & & \| \\ N & & N \\ / & & \backslash \\ HO & & OH \end{array}$$

While having a very high molecular weight, is completely insoluble in water. Benzoylmethylglyoxime



$$\begin{array}{ccccc} H_5C_6-C & - & C & - & C-CH_3 \\ \| & & \| & & \| \\ O & & N & & N \\ & / & & & \backslash \\ & HO & & & OH \end{array}$$

has a fairly high molecular weight but again is not soluble in water.

As qualitative tests, there is little to choose among the reagents available as the colors of the nickel compounds are about the same, although somewhat higher sensitivity is reported for the reagents having the higher molecular weights. A soluble quadrivalent nickel compound with dimethylglyoxime, having a deep orange brown color, has been found to be an extremely sensitive test and also a highly satisfactory colorimetric method for small amounts of nickel. This reaction has not been extended, however, to the other dioximes but undoubtedly it will occur with them as well as with dimethylglyoxime.

Although two methods have been proposed utilizing the dimethylglyoxime reaction as a volumetric method for the determination of nickel, little has been done in this direction. The methods are given later in this booklet in connection with dimethylglyoxime; undoubtedly they could be employed for use with the other dioximes without change in their essential features.

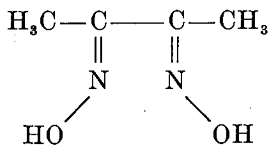
The five dioximes mentioned above are treated separately in the following pages, and a discussion of their synthesis, properties. and use in the analytical chemistry of the metals is given in detail. Their principal use is, of course, in the determination of nickel and a review of the various studies which have been made of this determination is given. The separation of palladium is equally noteworthy, however, and the methods for the colorimetric determination of iron and copper and the detection of cobalt and bismuth are sufficiently satisfactory to be in the repertory of the practicing analyst.

The detection and determination of nickel by dimethylglyoxime has, of course, found its way into the textbooks on analytical chemistry (*32, 33, 35, 36*) and the general subject has been touched in a few review articles on the general uses of organic compounds in analysis (*26, 27, 28, 29*). A number of details in connection with the reagents and their use which are essential to their successful application, particularly in more complicated problems, have been strangely overlooked, however.

It is of interest to note in passing that the organic compound biacetyl, $(CH_3CO)_2$, the flavoring matter of butter and other natural products, is assayed by conversion with hydroxylamine to dimethylglyoxime and precipitation as nickel dimethylglyoxime (*30*).

II. DIMETHYLGLYOXIME

(Biacetyldioxime)



$C_4H_8O_2N_2$ Molecular weight = 116.12

Like all of the ortho-dioximes, dimethylglyoxime yields a red insoluble nickel derivative from very weakly acid, neutral or ammoniacal solutions and a yellow palladium compound from acid solution. Being the dioxime with which these reactions were first discovered, dimethylglyoxime has been by far the most widely used of the dioximes which have been investigated.

The applications of dimethylglyoxime to the determination of nickel in a variety of materials, particularly metallurgical products, has been extensively studied and the limitations and interferences of the method are now well known. The gravimetric procedure is highly satisfactory although subject to a few limitations because of the nature of the reagent and the precipitate.

Two volumetric methods have been devised but they have not found common use. They are discussed in detail on p. I.

In the presence of an oxidizing agent and in alkaline solution, very small amounts of nickel give a brownish red coloration with dimethylglyoxime, probably due to a higher valent compound of nickel. This method has been applied to the determination of small amounts of nickel in steel and in silicate rock, and has proved to be very useful over a range of concentration not covered by the usual method.

The reaction of dimethylglyoxime with palladium has been applied to the qualitative detection and the quantitative determination of palladium and the method has practically displaced all other methods for palladium.

Gold is reduced to the metal by dimethylglyoxime, but as other reducing agents give sharper separations and are more satisfactory, this reaction is not much used.

Ferrous iron reacts with dimethylglyoxime to give an intense red soluble compound. This is a sensitive method for detecting minute amounts of iron and for determining small amounts colorimetrically; see p. II.

Cupric salts, dimethylglyoxime and an oxidizing agent yield a purple coloration which is an extremely sensitive test for copper. The nature of this reaction is still obscure and the number of variable factors which influence the intensity of the color renders the reaction not entirely suitable for the colorimetric determination of copper. This is discussed on p. III.

The methods given on pp. IV and V for the detection of bismuth and cobalt are both specific and sensitive and will undoubtedly soon find their way into the texts on qualitative analysis.

B. THE SYNTHESIS OF DIMETHYLGLYOXIME

Of the several methods by which dimethylglyoxime has been prepared, only one is suitable for the rapid and economical preparation of large amounts of the material. This involves the conversion of methylethyl ketone to biacetylmonoxime by means of an alkyl nitrite and the subsequent oximation of biacetylmonoxime to dimethylglyoxime (biacetyldioxime). The literature on this synthesis is quite extensive and will not be covered completely here as it has been very adequately treated in the two most recent studies of the method, those by Semon and Damerall (*37*) and by Slotta and Jacobi (*38*). The procedures described in these papers differ only in detail.

In both procedures biacetylmonoxime is prepared by the action of gaseous ethyl nitrite on methylethyl ketone in the presence of hydrochloric acid:

$$CH_3COC_2H_5 + C_2H_5ONO = CH_3COC(=NOH)CH_3 + C_2H_5OH.$$

Slotta and Jacobi state that a better yield is obtained if hydrogen chloride in methyl alcohol is used in place of aqueous hydrochloric acid as the condensing agent; it is then necessary, however, to slow down the reaction by the addition of ether. In either case the biacetylmonoxime is not isolated but oximated directly after removal of the major portion of the solvent and the alcohol produced.

The oximation is best done with a solution of the sodium hydroxylamine monosulfonate (or disulfonate [?]) prepared separately by the action of sulfur dioxide on sodium nitrite:

$$CH_3COC(=NOH)CH_3 + NaO_3SNHOH = \\ CH_3C(=NOH)C(=NOH)CH_3 + NaHSO_4.$$

C. PHYSICAL PROPERTIES AND PREPARATION OF REAGENT SOLUTION

Dimethylglyoxime is a white crystalline solid melting at 238 to 240° with decomposition. It should sublime on gentle heating without leaving a residue and the reagent grade material should be free from objectionable dark colored impurities.

The solubility of the compound in water is 0.40 g. per liter. Since 3.957 g. of the reagent is needed for the precipitation 1.000 g. of nickel, 0.1197 g. of reagent is required for 30 mg. of nickel, which is the maximum amount usually taken for analysis; this would require about 250 ml. of an aqueous solution. To avoid the addition of this large volume, a 1 per cent solution in alcohol is the reagent most commonly used. Even in alcohol dimethylglyoxime dissolves with some difficulty and more recently acetone has been used as a solvent for the compound. The effect of acetone on the solubility of nickel dimethylglyoxime has not been studied as has the effect of alcohol (see p. VI). Regarding the possibility of adding the solid reagent to the aqueous solution see the work of Nuka, also mentioned on p. VII. As seen from the above figures about 4 ml. of a 1 per cent solution will be required to precipitate each 10 mg. of nickel present. A definite excess of the reagent should be added but not too much because of the solubility of the precipitate in solutions containing alcohol (see p. VIII) and because of the danger of precipitating the reagent itself. From a mixture of 10 ml. of a 1 per cent solution of dimethylglyoxime in alcohol and 100 ml. of water at room temperature, dimethylglyoxime does not precipitate even on long standing; a further 5 ml. of the reagent will give a definite precipitate of reagent within an hour. Actually an even smaller excess of reagent should be added as the precipitation is generally made in hot solution from which the alcohol evaporates more rapidly, decreasing the solubility of the free reagent in the mixture.

It is also possible to use an aqueous alkaline solution of dimethylglyoxime as the reagent. Such solutions do not keep more than a week and are not so often used. Such a reagent may be made by dissolving 1 g. of dimethylglyoxime in a mixture of two parts of ammonia and one of water or by the addition of 3.5 g. of sodium hydroxide to 1 liter of water containing 10 g. of dimethylglyoxime (*39*).

D. THE QUALITATIVE DETECTION OF NICKEL

Tschugaeff was apparently the first to use dimethylglyoxime as a qualitative test for nickel (*40, 43*). The test was carried out by neutralizing the solution to be tested with ammonia, adding the solid reagent and heating for a short time. The excess reagent served as a white background upon which the scarlet red precipitate produced by even very small amounts of nickel could be clearly seen. Tschugaeff reported the sensitivity as 1 part in 400,000.

This method was subsequently checked by Kraut (*41*) who reported that he was able to detect 0.001 mg. of nickel by the method

and who applied it to the ash of a variety of natural products, by Hardin (*42*) who applied it to the ash of biological material, and by many others. The test may be carried out in the presence of iron, aluminum, chromium, and other elements which precipitate as hydroxides or basic salts on the addition of ammonia, by the addition of a soluble tartrate which prevents these metals from precipitating.

When applying the test to fats and hydrogenated vegetable products, a fleeting red color is sometimes observed on the addition of ammonia. It was first thought that this was due to some peculiar organic compound present (*44*) but is actually due to ferrous iron, derived probably from hydrogenation equipment (*51*). Dimethylglyoxime and ferrous iron produce a pink to red coloration which has been frequently mistaken for nickel (*99, 101*), see p. IX. Even small amounts of nickel yield a precipitate with dimethylglyoxime which can be filtered off for observation, while the ferrous iron color is soluble and easily eliminated by oxidation by air or boiling with nitric acid, so that no confusion should occur.

The detection of small amounts of nickel in the presence of a large amount of cobalt, as for example, the nickel in cobalt salts, is quite important. This can be done directly on the ammoniacal solution but it is necessary to add a sufficient amount of the reagent to react with all of the cobalt present and it is necessary to filter the solution as the dark color of the cobalt compounds formed, conceals the nickel precipitate. A more satisfactory procedure was devised by Middleton and Miller (*45*). By the addition of cyanide and by contact with air, the cobalt was first converted to the cobalticyanide ion. Dimethylglyoxime was added and the complex nickel cyanide ion was then decomposed by the dropwise addition of silver nitrate, which decomposes the nickel but not the cobaltic cyanide ion. The addition of silver nitrate was continued until a permanent white or pink precipitate formed. In the presence of appreciable amounts of nickel the precipitate of silver cyanide became pink immediately, with very small amounts some time was required. By this method 0.0002 mg. of nickel per ml., corresponding to about 1 part in 4,000,000 could be detected. Besides being more sensitive than the usual procedure, this method effects a great saving of reagent.

In a more recent paper Feigl and Kapulitzas (*47*) proposed a modification of the cyanide method, in that instead of decomposing the nickel cyanide complex with silver nitrate, the cyanide was destroyed by the addition of formaldehyde which also decomposes the nickel cyanide complex but again not the more stable cobalticyanide. This left a clear solution in which a much smaller amount of nickel could be detected by shaking with ether and examining the water-ether interface which collected a film of any nickel dimethylglyoxime precipitate. Iron, if present, is converted to ferricyanide which like cobalt is not decomposed by formaldehyde; the test for nickel thus also worked in the presence of iron, and of iron and cobalt together. Using this procedure, commercial so-called "nickel free" cobalt salts gave very distinct tests for nickel.

The common method of carrying out the test for nickel can be made much more sensitive by use of the spot plate and the so-called drop reaction technics of Feigl (*49, 47*).

Another qualitative test for nickel is based on the orange red color produced by the addition of dimethylglyoxime to a nickel salt which has been treated with an oxidizing agent (*75, 76, 73, 80, 48*). The nature of this reaction is discussed in connection with the colorimetric method of determining nickel, p. X.

A procedure for the detection of the minute amounts of nickel in silicate rocks by the normal reaction with dimethylglyoxime will be found in the paper of Harwood and Theobald (*50*).

Procedure for the detection of nickel. Heat the slightly acid solution to be tested to boiling, add a few drops of a 1 per cent solution of dimethylglyoxime in alcohol or acetone, and add a dilute solution of ammonia until the mixture is alkaline. Red needles indicate the presence of nickel although they may not form until the solution is cold if the amount of nickel is exceedingly small. At least 1 part of nickel in 1,000,000 can be detected in this manner. If iron or other metals precipitated by ammonia are present, add sufficient tartaric acid to prevent any precipitation on the addition of ammonia and then add the dimethylglyoxime. If a large amount of cobalt is present or if both iron and cobalt are present, the method described below must be used.

If the solution is highly colored as a consequence of the presence of foreign salts, filter the cold solution, wash well and examine the filter paper for the red precipitate.

Ferrous iron gives a ruby red color with dimethylglyoxime and ammonia and this must not be taken as indicating a small amount of nickel which will yield a precipitate; the color fades as air oxidizes the ferrous iron to ferric unless a reducing agent is present; preliminary oxidation of the iron will avoid this trouble. Bismuth yields a yellow precipitate with the reagent, unless tartaric acid is present.

In the presence of oxidizing agents, nickel and dimethylglyoxime give an orange red coloration.

Procedure for the detection of small amounts of nickel in cobalt salts (Feigl and Kapulitzas [*47*]). Dissolve a quantity of the cobalt salt to be tested, between 0.5 and 1 g. in 2 to 3 ml. of water and treat the solution dropwise with a concentrated solution of potassium cyanide until the precipitate which is produced redissolves. In order to convert the cobaltous compound into a cobaltic compound, warm the solution and add hydrogen peroxide until the solution appears honey yellow. Evaporate the solution until it becomes viscous and add an excess of solid dimethylglyoxime. Heat the solution until lukewarm (50 to 60°) and then treat dropwise with formaldehyde until the odor of the latter is perceptible. If nickel is present, finely divided nickel dimethylglyoxime separates immediately or on cooling. Shake with 1 to 2 ml. of ether; the precipitate is thus concentrated as a red film at the interface of the water and ether layers.

Procedure for the detection of small amount of nickel in the presence of large amounts of cobalt and iron (Feigl and Kapulitzas [*47*]). Like cobalt and nickel, iron is converted by potassium cyanide into the corresponding complex iron compound, which is stable toward formaldehyde and does not interfere with the nickel test.

Treat the solution to be tested for nickel, containing cobalt and iron, with a concentrated solution of potassium cyanide, and with warming add sufficient potassium cyanide to dissolve the precipitate. Boil the solution until it assumes a viscous consistency, and apply the test as above.

Procedure for the detection of nickel by dimethylglyoxime in the presence of an oxidizing agent. Treat the solution to be tested with 1 ml. of bromine water and then with ammonia until alkaline, as evidenced by the disappearance of the color of the bromine. Add dimethylglyoxime. The oxidation by the hypobromite is complete in 1 or 2 minutes and there is produced an orange red color in the presence of nickel. The sensitivity of the reaction is very great.

Procedure for the detection of nickel in fats. The following method is due to Kerr (*44*). Heat 10 g. of the fat to be tested with 10 ml. of hydrochloric acid (sp. gr. 1.12) on a steam bath for 2 to 3 hours, shaking frequently. Filter through a wet filter paper to remove the fat, collecting the filtrate in a white porcelain dish. Evaporate the filtrate to dryness in a steam bath, adding 2 to 3 ml. of concentrated nitric acid after it has been partly evaporated, to insure the destruction of all organic matter. After the evaporation is complete, dissolve the residue in a few ml. of water and add a few drops of dimethylglyoxime solution and then a few drops of ammonia. The presence of nickel is shown by the appearance of the red color or precipitate of dimethylglyoxime.

Procedure for the detection of traces of nickel in hardened fats. The following method is that of Wagenaar (*46*). In burning off a large sample of fat in order to determine traces of nickel in the residue there is apt to be some mechanical loss of nickel with the soot from the flame. This difficulty may be obviated by using a roll of quantitative filter paper for a wick. Melt a portion of the fat in a porcelain dish over a water bath or a small flame and insert vertically a strip of ashless filter paper 20 by 2.5 cm. rolled into a cylinder around a thin platinum wire. The paper soaks up the fat which burns at the top. Add the remainder of the sample at intervals. Finally ash the paper in a silica or platinum crucible, moisten with hydrochloric or nitric acid, evaporate to dryness and treat with ammonia and dimethylglyoxime. The formation of dichroic rose needles indicates the presence of nickel. By this procedure 0.03 mg. of nickel can easily be detected in 30 g. of fat, corresponding to 1 part in 1,000,000. At 1 part in 10,000,000 the test is less distinct but still positive.

E. THE GRAVIMETRIC DETERMINATION OF NICKEL WITH DIMETHYLGLYOXIME

The use of dimethylglyoxime for the separation and gravimetric determination of nickel was first advocated by Brunck, who in a series of papers (*52, 53, 54, 62, 63*) investigated the completeness of precipitation of nickel by the reagent from both ammoniacal solutions and solutions buffered with acetate, and the separation of nickel from cobalt, zinc, manganese, iron, aluminum, and chromium. The method was found to be rapid and highly satisfactory and it was quickly adopted. Numerous studies were subsequently reported confirming the results of Brunck and extending the list of separations possible (*55, 56, 57*). The gravimetric method is satisfactory in almost every detail but is limited to generally not more than 30 to 50 mg. of nickel because of the bulkiness of the precipitate. A number of problems which arise in connection with the method, due to the insolubility of dimethylglyoxime in water, to the solubility of the precipitate in alcohol-water solution, to the coprecipitation of iron and cobalt when present together, and to others, are mentioned in the following paragraphs. A number of satisfactory procedures are then given for the gravimetric determination of nickel.

The precipitation of nickel dimethylglyoxime occurs with the liberation of two hydrogen ions

$$Ni^{++} + 2\,DH_2 = Ni(DH)_2 + 2\,H^+$$

and as would be expected the precipitate is dissolved by strongly acid solutions. Precipitation is complete from solutions containing an excess of ammonia or buffered by acetate. In the latter case, however, the presence of a large amount of free acetic acid exerts a noticeable solvent action on the precipitate and it is best that the major portion of any mineral acid present be neutralized by the addition of a strong base and the remaining acid neutralized by the addition of acetate. The presence of an excess of ammonium salts is not harmful and a moderate amount of free ammonia has no effect. The precipitate is soluble in very strongly alkaline solutions giving a yellow color (*64*). It is also soluble in cyanide solutions. An excess of the reagent exerts no action on the precipitate, but a large excess should be avoided because of the possible precipitation of the dimethylglyoxime itself due to its low solubility in water and because of the increased solubility of the precipitate in water-alcohol mixtures. The precipitate must be filtered from the cold solution and should be allowed to stand at least one hour before filtering to insure complete precipitation, otherwise a further precipitation of nickel dimethylglyoxime will occur in the filtrate, although this never corresponds to more than 0.1 or 0.2 mg. of nickel (*56, 63*).

The precipitate is anhydrous and is readily dried at 110 to 120°; and it is not hygroscopic (*70*). It may be weighed as such and this is the most convenient and accurate method. The precipitate of nickel dimethylglyoxime may also, however, be ignited to the oxide, NiO, for weighing (*55, 57, 63*). As the compound begins to sublime at 250° special precautions must be taken to avoid loss, the technique which has been found suitable for this operation being to wrap the precipitate in two thicknesses of moist filter paper and to char the mass at as low temperature as possible, before burning away the filter paper. A comparison of this method with that of weighing the precipitate itself and with solution in nitric acid followed by electrodeposition has shown that it yields results slightly high by 2 to 3 mg. of nickel, probably due to the retention of carbon by the oxide (*57*).

One of the metals which is commonly associated with nickel, both naturally and in metallurgical products, is iron, and it is one of the great merits of the dimethylglyoxime method that it separates nickel from iron. The precipitation of the nickel compound can only be made from an ammoniacal solution or one buffered with acetate, and of course iron is precipitated as the hydroxide in the former solution and as the basic acetate in the latter. Three methods are available for avoiding these difficulties. The iron may be removed by the ether extraction method before precipitating the nickel and a few workers have advocated this (*55, 57*). In a more convenient method, however, the iron is retained in the solution by the addition of tartaric acid which forms a stable complex with iron from which the iron is not precipitated by ammonia or acetate. In the third method, the iron is reduced to the ferrous condition, in which form it is not precipitated from a boiling acetate solution. Both of these methods were suggested by Brunk (*53, 63*) and the former is very extensively employed in the analysis of iron and steel. It has been reported by Rothschild (*65*) that a satisfactory separation of nickel from iron cannot be obtained from an ammoniacal tartrate solution; no details are given as to the purity of the iron and nickel used and it must be assumed that cobalt was also present. This source of trouble is discussed a few paragraphs later.

Like iron, aluminum and chromium are also normally precipitated under the conditions under which nickel is precipitated with dimethylglyoxime and again fortunately the presence of tartrate will prevent this, due to the formation of extremely stable complex ions.

Small amounts of manganese, such as are present in a normal iron or steel, cause no trouble in the separation of nickel dimethylglyoxime from an ammoniacal tartrate solution; but when larger amounts are present the precipitation must be made from an acetate solution.

In weakly ammoniacal solutions copper yields a green precipitate which dissolves easily in an excess of ammonia; when coprecipitated with nickel, however, not all of the copper is dissolved by the excess of ammonia and the results are unreliable (*64, 66*). Precipitation from an acetate solution apparently gives a satisfactory separation (*66*) but this conclusion is based on only one analysis. The situation is much better when tartrate is present although while Balz (*72*) reports the method to be satisfactory, Grossmann and Mannheim (*64*) state that some copper is always carried down mechanically and that a reprecipitation of the nickel dimethylglyoxime is necessary. In any case, if the copper is first reduced to the univalent state by a sulfite and the precipitation then made by the addition of tartrate, dimethylglyoxime and acetate, a satisfactory separation can be achieved (*72, 71*). Precipitation with ammonia cannot be used here as cuprous oxide or metallic copper are formed by reduction.

The separation of nickel from zinc by precipitation with dimethylglyoxime from an ammoniacal solution is entirely satisfactory (*53*).

The precipitation of nickel by dimethylglyoxime in the presence of a large number of foreign metals was studied by Weeldenberg (*66*). The separation from lead was found to be satisfactory if the precipitation was made from an acetate solution with a large amount of acetate present to hold the lead in solution. Amounts of bismuth up to 0.2 g. did not interfere if tartrate was present while as much as 0.5 g. of arsenic and antimony did not affect the results. Amounts of tin above 50 mg. caused the results to be high. Cadmium, zinc, aluminum, and magnesium were without effect.

The precipitation of nickel may also be made in the presence of vanadium, for example, in ferrovanadium, after the latter has been oxidized to vanadic acid by boiling with nitric acid (*58*).

The separation of nickel from cobalt can very conveniently be made by dimethylglyoxime. An orange or brown colored soluble cobalt compound containing dimethylglyoxime is formed and it is necessary to add sufficient dimethylglyoxime to combine with all of the cobalt to insure complete precipitation of the nickel. On long standing a cobalt compound containing dimethylglyoxime and ammonia may settle out but it is readily soluble in hot water. The small amounts of nickel in cobalt compounds may be separated and determined by dimethylglyoxime but the precipitation must be made from a solution buffered with acetate as not all the nickel is precipitated from an ammoniacal solution containing large amounts of cobalt. A better method of attacking the latter problem is to convert the cobalt to the stable cobalticyanide ion before the addition of the dimethylglyoxime (*47*). Nickel dimethylglyoxime is not precipitated in the presence of cyanide but the nickel cyanide complex is decomposed, while cobalticyanide is not, by the addition of formaldehyde. The precipitation of the nickel compound is then carried out in the normal manner and as only a slight excess of dimethylglyoxime over that necessary to combine with the nickel is required a great saving of reagent is effected. Details of this procedure are given later.

Still another method of separating nickel from large amounts of cobalt involves the conversion of the latter to the trivalent state in ammoniacal solution, soluble cobaltic amines being formed; the solution is boiled to destroy the excess oxidizing agent and the nickel is then precipitated by dimethylglyoxime (*32, 33*).

The separations of nickel from iron and from cobalt are satisfactory as mentioned above; when iron and cobalt are present together, there is produced, even in the presence of tartaric acid, a voluminous, amorphous, red brown precipitate (*59, 60, 61, 62, 63*). This rapidly plugs up the filter because of its slimy character and cannot be removed by washing. It consists of an iron and cobalt compound, containing three molecules of dimethylglyoxime, and has the formula $FeCoC_{12}H_{19}N_6O_6$ (*63, 67*). If the iron is present in the ferrous condition no such precipitate is formed, so that this difficulty is very easily overcome by reducing the iron prior to the precipitation of the nickel. This can be conveniently done by sulfur dioxide or a sulfite and the precipitation can be carried out either by the addition of tartrate and ammonia or by acetate (*63, 67*).

Because of the importance of the determination of nickel in steels which contain cobalt, also cobalt and aluminum, and cobalt, aluminum and copper, the newer magnetic alloys, this subject was further investigated by Balz (*72*). Reduction of the iron to the bivalent state was found to be the only satisfactory method; but with copper present the precipitation must be made from an acetate solution for the tartrate ammonia solution is in effect a Fehling's solution and with sulfite present, cuprous oxide or copper is precipitated. If copper but no cobalt is present the precipitation can be made without the preliminary reduction of iron.

The determination of nickel in a tungsten steel by the dimethylglyoxime method, keeping the tungsten in solution with tartrate, is reported to give slightly high results (*68*) although not many details are given.

The disturbing effect of nitrates on the precipitation of nickel appears to be an unsettled problem. Definitely, nitrate does prevent the precipitation of small amounts of nickel (Harwood and Theobald

[*50*]) and this may account for the results of Jones who found that precipitation of nickel was incomplete when present in steel in amounts less than 0.06 per cent. On the other hand nitrate is commonly present during the determination of nickel in steel. Further, however, if this loss is due to the formation of quadrivalent nickel, as seems probable (see p. XI), the presence of tartrate or citrate, which is also present during the determination may act as a reducing agent and counteract the effect of the oxidizing action of the nitrate. However, tartrate was also present in the determinations made by Jones.

The gravimetric method should be used with some circumspection when applied to the determination of small amounts of nickel. Jones (*77*) found that frequently amounts of nickel in steel as high as 0.1 per cent were reported as "traces." When the amount of nickel is less than 0.06 per cent some nickel very definitely is not precipitated even on prolonged standing and it is questionable whether the determination is accurate when working on the usual size of sample. Jones took various amounts of nickel and carried out the precipitation as usual in a slightly ammoniacal solution in a volume of 100 ml. After standing overnight, the precipitate was filtered through a close pulp filter, was not washed, and the nickel in the filtrate was determined by the colorimetric method described a few pages later in this booklet.

Weight of nickel taken, g.:	0.0001	0.0002	0.0003	0.00075	0.0010	0.0015	0.0020	0.0025
Percentage of nickel in filtrate:	35.0	7.5	5.0	2.0	2.25	1.0	0.25	negligible

The colorimetric method appears definitely superior to the gravimetric for amounts of nickel in this range.

The determination of the very small amounts of nickel in silicate rock is also best made by means of the colorimetric method, although a procedure for this determination by the usual gravimetric reaction has been devised by Harwood and Theobald (*50*).

The solubility of nickel dimethylglyoxime was studied by Nuka (*70*) who found that as much as 0.6 mg. of the nickel compound dissolved per 100 ml. of hot water, while in cold water less than 0.1 mg. dissolved per 100 ml. If the precipitate is filtered from the hot solution, the loss of nickel may thus be appreciable and may be a considerable percentage of the total amount of nickel present, which is usually not more than 30 mg. Further, the solubility is not sensibly decreased by a large excess of dimethylglyoxime. Even more important, however, is the increased solubility in solutions containing alcohol which is the common condition since the reagent is usually added as a solution in alcohol.

Composition of solution total volume 500 ml.	Solubility of nickel dimethylglyoxime per 100 ml.
Cold water	< 0.1 mg.
Hot water + 0.2 g. dimethylglyoxime	0.6
Hot water + 0.5 g. dimethylglyoxime	0.5
Hot water + 0.2 g. dimethylglyoxime + 150 ml. hot alcohol	1.5
Hot water + 0.2 g. dimethylglyoxime + 100 ml. hot alcohol	1.1
Hot water + 0.2 g. dimethylglyoxime + 50 ml. hot alcohol	0.8
Cold water + 0.2 g. dimethylglyoxime + 100 ml. hot alcohol	< 0.1

It is definitely necessary then to cool the solution before filtering and Nuka recommended that the solution cool at least one hour and that cold water be used to transfer and wash the precipitate.

While from the above table it appears that in the cold the presence of alcohol does not increase the solubility, Nuka devised a modified procedure whereby solid dimethylglyoxime was added to the cold nickel solution, the solution heated to boiling, the precipitation made by the addition of ammonia, and the solution cooled before filtration. It is stated that the presence of solid dimethylglyoxime in the precipitate causes no difficulty as its solubility in cold water is 0.04 g. per 100 ml. and also because the reagent sublimes at a temperature of 120° which may be used to dry the precipitate.

On the other hand, it is amazing how much bad treatment this method will stand. In order to hasten the determination Dick (*69*) filtered the precipitate hot, without standing, washed with hot water, then five times with 95 per cent alcohol and finally washed well with ether. The precipitate was then dried by aspirating air through it for 2 or 3 minutes and then weighed. This technic was tested on known amounts of nickel sulfate, $NiSO_4 \cdot 7H_2O$, and five analyses gave results not only agreeing among themselves by 0.03 per cent but the average deviated only 0.03 per cent below the theoretical content of nickel sulfate. No statement is given as to the purity of the nickel sufate or even a murmur made as to the actual content of nickel as determined by other methods; nor is any mention made of the amount of reagent added in excess or of the volume of the solution which would have something to do with the amount of reagent which accompanied the precipitate. Such fortuitous compensations of errors will probably shock most thoroughgoing analysts but may hold some attraction for those who like to have their results in a hurry.

Procedure for the gravimetric determination of nickel. The following procedure is used for the determination of nickel when present alone. If interfering metals are present, the procedure must be modified according to the preceding discussion, as in the procedures for the determination of nickel in iron and steel which follow later.

The determination of nickel in the nickel dimethylglyoxime precipitate is most conveniently and commonly made by direct weighing of the precipitate. Ignition of the precipitate to the oxide is also given, however, although it yields slightly high results. Still another method, possibly somewhat more rapid than the others, involves decomposition of the precipitate and the titration of the nickel with cyanide.

The following procedure is the standard one, which has been checked numerous times since first proposed by Brunck.

Heat the slightly acid solution, containing not more than about 0.050 g. of nickel and having a volume of 100 to 150 ml., to boiling. Add a 1 per cent solution of dimethylglyoxime in alcohol or acetone, adding 4 ml. for each 10 mg. of nickel present and a 5 ml. excess. Precipitate the nickel by adding ammonia until the solution is slightly alkaline. Allow the precipitate to stand for 1 hour, cooling at the same time. Filter on a Gooch crucible, wash well with cold water, dry at 120° for 1 hour and weigh. Multiply the weight of the precipitate by 0.2032 to obtain the weight of nickel.

If the precipitate is to be ignited to the oxide for weighing, filter on paper and wash well with cold water. Wrap the precipitate and place in a weighed porcelain crucible. Char the paper at as low temperature as possible without burning, examining the escaping gases to make sure that the red finely divided precipitate is not being carried along mechanically. Burn away the charred paper and ignite the precipitate with free access to air. Cool and weigh as nickel oxide, NiO, containing 78.58 per cent nickel.

If the determination is to be concluded by the cyanide titration, filter the precipitate on paper and wash well with water. Dissolve the precipitate of nickel dimethylglyoxime on the paper with hot dilute nitric acid (5 : 1) and wash the paper with water. Add a few drops of concentrated hydrochloric acid, and boil 5 minutes to destroy the dimethylglyoxime, and expel chlorine and oxides of nitrogen. Cool, dilute, neutralize with ammonia and carry out the cyanide titration as usual employing the silver iodide end point (*33,85*) or following the titration potentiometrically using a silver or silver sulfide indicator electrode (*72*).

If iron, aluminum, chromium, zinc, or small amounts of manganese are present, add 4 to 5 g. of tartaric acid for each g. of foreign metal, neutralize with ammonia and add more tartaric acid if a precipitate is present. Acidify slightly, add dimethylglyoxime and precipitate the nickel by the addition of ammonia. In case large amounts of manganese are present, barely neutralize the solution with ammonia, add 0.5 ml. of concentrated hydrochloric acid, add the dimethylglyoxime, and precipitate the nickel by adding 4 to 5 g. of sodium acetate.

Procedure for the determination of nickel in iron and steel. The size of the sample taken should be such that not more than about 30 mg. of nickel will be present because of the great bulk of the precipitate; thus for a steel containing

up to 1 per-cent nickel	use a 3 g. sample
1 to 3 per cent nickel	use a 1 g. sample
3 to 6 per cent nickel	use a 0.5 g. sample
above 6 per cent nickel	use a 0.25 g. sample

Weigh the sample into a 400 ml. beaker and treat with 30 ml. of hydrochloric acid and heat to dissolve the steel. Add 10 ml. of nitric acid to decompose any carbides remaining and oxidize the ferrous salts; boil for 15 minutes and dilute to 200 ml. Add 40 ml. of 20 per cent solution of tartaric acid, neutralize with ammonia and add 1 ml. in excess. Filter off any silica or insoluble matter present and wash with hot water containing a little ammonia. Make slightly acid with acetic acid, heat to 60° and add 20 ml. of a 1 per cent solution of dimethylglyoxime in alcohol, or acetone. Add ammonia until slightly alkaline and digest for 30 minutes at 60°. If copper is present an additional amount of dimethylglyoxime should be added and the solution allowed to stand several hours. After standing at least 1 hour filter the cold solution on a Gooch or fritted glass crucible keeping the crucible filled with liquid. Wash with cold water and dry at 110 to 120° and weigh as nickel dimethylglyoxime, containing 20.32 per cent nickel.

Or conclude the determination by one of the two alternative methods mentioned above.

Procedure for the determination of nickel in a steel containing cobalt or cobalt and copper. The following procedure is taken from the work of Balz (*72*). Copper and iron in the sample are first reduced to the univalent and bivalent states by sulfite and the nickel is then precipitated from a solution containing tartrate; the precipitation may be made from an ammoniacal solution if copper is absent but must be made in a solution buffered with acetate if copper is present.

The method was tested on two steels:

Composition	Nickel found
1. Nickel.......................23.6 per cent	23.57 per cent (from acetate solution)
Aluminum............... 5.8 per cent	23.59 per cent (from acetate solution)
Cobalt...................... 3.5 per cent	23.58 per cent (from ammoniacal solution)
Iron..........................remainder	23.56 per cent (from ammoniacal solution)
2. Nickel.......................20.3 per cent	20.29 per cent (from acetate solution)
Cobalt.......................10.8 per cent	20.26 per cent (from acetate solution)
Aluminum............... 7.3 per cent	20.28 per cent (from acetate solution)
Copper..................... 5.8 per cent	
Iron..........................remainder	

These results were obtained by weighing the precipitate as such. The nickel in the precipitate may also be determined by one of the alternative methods mentioned above.

Weigh a sample of the steel of such size that it will contain about 30 mg. of nickel. Dissolve the sample in dilute nitric acid (1 : 1, about 50 ml. for each 1 g. of sample). Boil to expel oxides of nitrogen and filter off the silica which has separated. Reduce all of the iron to the ferrous state by the addition of sodium sulfite or a saturated solution of sulfur dioxide (10 g. of sodium sulfite or 20 ml. of saturated solution of sulfur dioxide per 1 g. of sample). Add 4 g. of tartaric acid for each 1 g. of sample, just neutralize with ammonia, acidify slightly by the addition of 1 ml. of hydrochloric acid and dilute to 300 ml. Heat to incipient boiling, add 6 to 8 ml. of a 1 per cent alcohol or acetone solution of dimethylglyoxime for each 10 mg. of nickel present and precipitate the nickel by the addition of 4 g. of sodium acetate. Heat gently for a few minutes, test for completeness of precipitation by the further addition of sodium acetate and dimethylglyoxime. Cool for 1 hour making certain that a reducing solution is maintained, adding more sulfite if necessary. Filter the precipitate on a weighed Gooch crucible, wash with cold water, dry at 120° and weigh.

If copper is absent the precipitation may be made from an ammoniacal solution, but the precipitation from the acetate solution gives the correct results in any case.

Procedure for the determination of nickel in the presence of large amounts of cobalt and in cobalt salts. The following method is taken from the work of Feigl and Kapulitzas (*47*). Cobalt is first converted to potassium cobalticyanide by the action of potassium cyanide and hydrogen peroxide which oxidizes the cobalt to the trivalent state. The excess cyanide and the nickel cyanide complex, but not the cobalticyanide, are then destroyed by formaldehyde, which forms the nitrile of glycolic acid with cyanide. The nickel is then precipitated with dimethylglyoxime. The authors recommend the addition of solid dimethylglyoxime and in order to remove the solid reagent which necessarily accompanies the precipitate, dissolve in acid and reprecipitate in the customary manner. No reason was given for this but the addition of alcohol probably causes the precipitation of potassium cobalticyanide.

The method is equally applicable to the determination of nickel in the presence of large amounts of both cobalt and iron, for the latter is converted to ferricyanide which is not decomposed by formaldehyde.

The method was tested on known mixtures of nickel and cobalt, the extreme ratio of nickel to cobalt being 1 to 200, the amount of nickel taken being 11 mg.; the greatest error in the nickel determined was 0.06 mg. The nickel in four samples of "nickel free" cobalt salts was determined by this method and nickel was found in each, for example, in a 25 g. sample of cobalt chloride, 1.6 mg. of nickel was found. Two determinations of nickel in the presence of 100 times as much of both iron and cobalt gave 11.66, 11.58 mg. nickel found, 11.62 mg. nickel taken.

Treat the solution containing the cobalt and nickel with a saturated solution of potassium cyanide until the precipitate first produced is redissolved. Add 3 per cent hydrogen peroxide and heat for a few minutes. If the solution does not appear honey yellow in color, add a further amount of hydrogen peroxide. In order to remove the excess hydrogen peroxide, heat and evaporate the solution to about one-fourth of its original volume. If a small amount of precipitate forms which is not dissolved by the further addition of potassium cyanide, filter it off. Dilute the clear solution to 200 to 300 ml. Add an excess of solid dimethylglyoxime, warm the solution to 50 to 60° and add formaldehyde until the odor of the latter is present. Allow the mixture to stand 1.5 hours and filter off the precipitate of nickel dimethylglyoxime which also contains some solid dimethylglyoxime. In order to remove the latter, dissolve the precipitate in dilute hydrochloric acid, filter, and precipitate the nickel in the clear solution in the usual manner with a 1 per cent solution of dimethylglyoxime in alcohol or acetone.

For the determination of the nickel content of pure cobalt salts the following modification of the above procedure is used. Dissolve 15 to 20 g. of the pure cobalt salt in the least amount of water possible, treat with hydrogen peroxide and formaldehyde as given above, but continue the heating until the solution has evaporated to a thick syrupy consistency. Add an excess of solid dimethylglyoxime, formaldehyde and continue as above.

F. THE VOLUMETRIC DETERMINATION OF NICKEL BY DIMETHYLGLYOXIME

The formation of nickel dimethylglyoxime is accompanied by the liberation of two hydrogen ions and a volumetric method for the determination of nickel based on the titration of the acid liberated in this reaction was devised by Holluta (*73*). Dimethylglyoxime itself is practically undissociated in water or alcohol and is stable toward alkali, going to dimethylfurazan to a slight extent only after long boiling with strong caustic. By preparing a water-alcohol solution of dimethylglyoxime and potassium hydroxide it is possible to add the reagent and the standard base at the same time, more than one molecule of dimethylglyoxime being present for each molecule of potassium hydroxide. The solution containing the nickel is neutralized to methyl red and the standard solution added. After the addition of a few ml. of the standard solution, the solution is warmed somewhat which serves to coagulate the precipitate into balls which adhere to the walls of the flask or float on the surface. On further addition of the standard solution, the precipitate coagulates rapidly and the color change of methyl red, indicating the end-point, is clearly discernable. The end-point is better with dilute solutions but the interference by carbon dioxide becomes serious. In practice the upper limit of the nickel which can be conveniently determined is about 10 mg., above that the amount of precipitate being so great as to interfere with the end-point. The method was checked against known amounts of nickel and a large number of results were reported;

those obtained with 0.01 N solutions being of the order of accuracy of 0.02 to 0.03 mg. of nickel on a 10 mg. sample. No study was made of the interference of other metals such as iron or cobalt.

A second method which has been devised (Tougarinoff, *74*) for the volumetric determination of nickel is indirect in that it measures the hydroxylamine resulting from the decomposition of the nickel dimethylglyoxime precipitate. After filtration, the precipitate is dissolved in acids, the dimethylglyoxime liberated hydrolyzed, and the hydroxylamine produced, oxidized by ferric iron; the resulting ferrous iron is finally titrated with permanganate. The final reactions are

$$CH_3C(NOH)C(NOH)CH_3 + 2\,H_2O + H_2SO_4 = CH_3COCOCH_3 + (NH_2OH)_2H_2SO_4$$

$$2\,NH_2OH + 2\,Fe_2(SO_4)_3 = N_2O + 4\,FeSO_4 + H_2O + 2\,H_2SO_4$$

$$10\,FeSO_4 + 2\,KMnO_4 + 8\,H_2SO_4 = 5\,Fe_2(SO_4)_3 + 2\,MnSO_4 + K_2SO_4 + 8\,H_2O.$$

The method was tested on known amounts of pure nickel, on German silver, coinage metal and a synthetic nickel steel. The results compared very favorably with those obtained by electrodeposition of the nickel, the quantities of nickel taken and found agreeing within less than 0.1 mg. on amounts of nickel as high as 25 mg.

Procedure for the volumetric determination of nickel dimethylglyoxime (Tougarinoff Method). Precipitate the nickel in a steel or non-ferrous alloy, as nickel dimethylglyoxime by the usual procedure; see gravimetric methods for details. The sample taken should be of such size that not more than 25 mg. of nickel is present. Filter the precipitate and wash well but do not attempt to transfer the last traces of precipitate. Pour 15 ml. of approximately 12 N sulfuric acid into the flask in which the precipitation was made and heat to boiling; the precipitate which remains in the flask dissolves immediately on contact with the acid. Pour the hot acid on the precipitate and stir with a rod to promote the solution of the precipitate, collecting the filtrate in a 300 ml. Kjeldahl flask. When the precipitate has dissolved, pierce the filter (the fibers of filter paper which are carried through have no effect on the determination) and rinse the flask and filter with boiling water, bringing the volume of the filtrate to about 75 ml. Heat the filtrate and boil vigorously to reduce the volume to about 25 ml., which should require about 10 minutes. Without interrupting the boiling add 50 ml. of a solution of 40 g. of ferric sulfate per liter and continue the boiling for 5 minutes. Cool the solution under the tap, dilute with 150 ml. of water, add 3 ml. of phosphoric acid (sp. gr. 1.7) and titrate with 0.1 N potassium permanganate to the appearance of a permanent pink color.

G. THE COLORIMETRIC DETERMINATION OF NICKEL BY DIMETHYLGLYOXIME

THE NICKELIC COMPOUND OF DIMETHYLGLYOXIME

During the early investigation of the precipitation of nickel by dimethylglyoxime, Brunck found that the presence of a large amount of nitrate in the solution had an adverse effect on the determination of nickel.* Feigl (*75*) investigated this effect further and found that ferricyanide, higher oxides, permanganate, and in general all oxidizing agents, gave the same effect, an intense red solution forming which contained the unprecipitated nickel. In a strongly alkaline solution in contact with lead dioxide a large amount of the normal nickel dimethylglyoxime compound could be dissolved. After the lead dioxide was removed by filtration, the solution had strong oxidizing properties; it liberated iodine from iodide in acid solution, and oxidized benzidine to benzidine blue. Ammonium sulfide had no effect on the solution but the compound was decomposed on acidification. By careful neutralization a dark red powder was isolated which was insoluble in water and alcohol, soluble in alkalies, but decomposed by acids. It exploded on heating. Analysis for nickel and nitrogen indicated the composition to be $Ni(C_4H_7O_2N_2)_2O$. A determination of the oxidizing power by its ability to free iodine from iodide in acid solution gave a ratio of nickel to iodine of 1 to 2, indicating that the compound was a quadrivalent nickel compound.

Feigl also showed that the reaction could be used as a qualitative test for very small amounts of nickel, reporting that the sensitivity of the test was 1 part in 1,666,000 as compared with 1 part in 400,000 in the normal reaction of nickel with dimethylglyoxime.

The reaction is an excellent method for the colorimetric determination of small amounts of nickel. The first work in this direction was done by Rollet (*76*) who used bromine followed by ammonia as the oxidizing agent; no data confirming the accuracy of the method was reported, however, and the effects of interfering ions was not studied.

Jones (*77*) applied the method to the determination of small amounts of nickel in steel, finding the colorimetric method far more satisfactory than the usual gravimetric procedure where precipitation is incomplete in case the nickel is less than 0.06 per cent. Details of the procedure are given later.

The method has also been applied to the determination of amounts of nickel up to 15 per cent in steel, using the Leifo photometer (*78*)

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Weigh a sample of the steel of such size that it will contain about 30 mg. of nickel. Dissolve the sample in dilute nitric acid (1 : 1, about 50 ml. for each 1 g. of sample). Boil to expel oxides of nitrogen and filter off the silica which has separated. Reduce all of the iron to the ferrous state by the addition of sodium sulfite or a saturated solution of sulfur dioxide (10 g. of sodium sulfite or 20 ml. of saturated solution of sulfur dioxide per 1 g. of sample). Add 4 g. of tartaric acid for each 1 g. of sample, just neutralize with ammonia, acidify slightly by the addition of 1 ml. of hydrochloric acid and dilute to 300 ml. Heat to incipient boiling, add 6 to 8 ml. of a 1 per cent alcohol or acetone solution of dimethylglyoxime for each 10 mg. of nickel present and precipitate the nickel by the addition of 4 g. of sodium acetate. Heat gently for a few minutes, test for completeness of precipitation by the further addition of sodium acetate and dimethylglyoxime. Cool for 1 hour making certain that a reducing solution is maintained, adding more sulfite if necessary. Filter the precipitate on a weighed Gooch crucible, wash with cold water, dry at 120° and weigh.

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and the Zeiss Pulfrich step photometer (*79*). The actual determinations, of course, were made on aliquot portions of large samples, e.g., 5 ml. of a 1 g. sample diluted to one liter. The results are surprisingly good considering that any error in the determination is multiplied by the dilution factor, 200 in this case, and this attests the sensitivity and reliability of the method and the accuracy of photo-electric instruments. The principal merit of these methods is the speed with which they can be carried out and where the highest order of accuracy is not necessary they are very useful. Details of these procedures will be found in the original papers.

The colorimetric method has also been applied to the determination of the nickel in silicate rock (*80*). Details of the method are given later.

Procedure for the colorimetric determination of small amounts of nickel in steel. The following procedure is taken from the work of Jones (*77*). The iron is first separated from the nickel by precipitation with ammonia in the presence of cyanide, the nickel remaining in solution as the stable potassium nickelo-cyanide ion. This gives a sharper separation than the basic acetate or zinc oxide methods. Sodium hypochlorite is used as the oxidizing agent. Ammonium salts and cyanide decomposition product affect the color and must be removed in accurate work. A fairly good approximate determination can be made, however, as indicated in the procedure. The sensitivity of the reaction is 1 part in 10,000,000 and amounts of nickel between 0.01 and 0.1 mg. can be determined by the method. Copper and cobalt, if present in the steel, accompany the nickel and cause some trouble because of the color of their ions when present in appreciable quantity. Large amounts of copper are removed in the procedure given but large amounts of cobalt must be compensated for by the addition of cobalt to the standards. Amounts of manganese up to 2 per cent do not interfere; higher amounts interfere owing to the formation of a brown colloidal peroxide. In the latter case it is necessary to remove the manganese by precipitation as the dioxide from a strong nitric acid solution with chloric acid.

The method was tested on mixtures of various samples of pure, electrolytically deposited iron, the nickel content of which was found by blank runs, and pure nickel. In a typical run 0.00020 g. of nickel was added to 4 g. of iron, corresponding to 0.0050 per cent nickel, and the method indicated that 0.00019 g. of nickel was present corresponding to 0.0047 per cent. A number of determinations indicated about this same order of accuracy. The nickel in a number of plain carbon steels was determined by this method and by the gravimetric

method followed by the cyanide titration; the results by the colorimetric method were always considerably higher when the nickel content was below 0.06 per cent but agreed well with the results by the gravimetric method for percentages of nickel above that.

Separation of nickel and iron. Dissolve a 1 g. sample in 10 ml. of hydrochloric acid, and oxidize by the addition of 5 ml. of nitric acid. Boil the solution for a few minutes and dilute somewhat with cold water. Transfer to a 200 ml. volumetric flask, and add dilute ammonia (1 part of ammonia sp. gr. 0.88 to 1 part of water) from a buret or dropping bottle until a slight precipitate of hydroxide is formed which just fails to redissolve in the ferric chloride. Add 2 ml. of a 1 per cent solution of potassium cyanide, shake the flask well, add 10 ml. of the dilute ammonia, and dilute the flask to the mark. No allowance is made for the volume of precipitate. Pour the entire mixture back into the original flask and mix the contents thoroughly. Allow the precipitate to settle a little and filter through a large fluted 41 Whatman filter paper. Use 100 ml. of the filtrate for qualitative purposes, this being desirable inasmuch as all plain carbon steels which are assumed to be almost free from nickel contain quantities far in excess of the amount for which the method was designed. The above method of separating nickel from iron is to be preferred to the one recommended in some text books, of pouring the acid solution into ammonia containing cyanide, as it permits the nickel to react more readily with the excess of cyanide, and also keeps the excess ammonia more under control. A large excess of ammonia should be avoided, as it is apt to interfere with the formation of potassium nickel-cyanide and has a detrimental effect on the qualitative test.

Approximate determination of nickel. Transfer the 50.0 ml. of filtrate to a 100 ml. Nessler tube and dilute to the mark with water. Add 2 ml. of a clear solution of dimethylglyoxime in alcohol (just short of saturation), stir the contents with a glass rod, add 1 ml. of commercial sodium hypochlorite solution, and stir again. On standing the solution will develop a reddish-brown color if nickel is present. Fill a similar Nessler tube to the mark with water, add 6 drops of dilute ammonia (1 : 1) and 2 ml. of dimethylglyoxime solution; stir the mixture, add 1 ml. of sodium hypochlorite solution and stir again. Add 3 drops of a standard nickel solution containing 0.00005 g. nickel per ml. from a buret and mix well. Compare the colors of the sample and standard and continue the addition of standard nickel solution until the colors match, stirring well after each addition and allowing several minutes to elapse before making further additions. The colors of the two solutions may not be of exactly the same tint, owing to the interference of ammonium salts and decomposition products from the excess of cyanide added, which impart a brownish tint, but the amount of nickel registered by taking the reading when the intensity of color of the solutions is identical is nevertheless near the truth. The tint of the test solution improves on standing, and in some cases the qualitative figure is identical with the one finally obtained, although sometimes higher when the copper content is fairly large, but the interference of copper in the test is almost negligible when present in amounts usually found in steels, as any color given is discharged by the potassium cyanide present in the filtrate.

Final determination of nickel. While the qualitative test is being carried out, make the main 100.0 ml. sample of the filtrate just acid with hydrochloric acid, then add 5 per cent of concentrated acid in excess, and pass hydrogen sulfide into the warm solution in a rapid stream for 15 minutes. Allow any copper sulfide (mixed with a little sulfur) to settle out on the water bath and when the precipitate has coagulated filter through a pulp filter into a 600 ml. wide mouth beaker and wash with a dilute solution of an electrolyte, such as a 5 per cent ammonium chloride. Long standing is not necessary to remove the whole of the copper, as traces not precipitated have no effect on the determination; if it is known that only traces are present, this stage may be omitted. Boil the filtrate down to a low volume, remove from the heat, and add 50 ml. of concentrated nitric acid to destroy ammonium salts. Brisk ebullition occurs at this stage and further heat must be applied cautiously. Evaporate completely to dryness, but do not bake for any length of time; add more nitric acid to complete the destruction of ammonium salts if necessary. Take up the residue with hot water, heat until all has dissolved, filter if necessary, and cool.

The solution is now ready for the colorimetric determination, either on the whole solution, or after being made up to a known volume and a suitable fraction taken which will be indicated by the qualitative test. For colorimetric measurement the solution should not contain more than 0.1 mg. of nickel, i.e., equivalent to 2 ml. of standard solution, or results will tend to be inexact, as it is difficult to determine the changes of tint with more concentrated solutions. If the nickel content is very minute as shown by the qualitative test, another determination may be made *de novo*, starting with a 4 g. sample, making the solution up to 500 ml., and using half for the determination. A good working idea of the nickel content of the sample is obtained in about 45 minutes from the commencement of the experiment. The color comparison is finally made as described in the qualitative test.

Procedure for the determination of nickel in silicate rocks. The following procedure is taken directly from the work of Sandell and Perlich (*80*). The method is based on the extraction of nickel dimethylglyoxime with chloroform from the ammoniacal citrate solution of the rock sample. By shaking the chloroform extract with dilute hydrochloric acid the dimethylglyoxime compound is decomposed and nickel is brought into the aqueous phase, in which it is then determined colorimetrically by Rollet's method (*76*).

This method is particularly designed for rocks of such low nickel content that the nickel cannot well be determined by the gravimetric method of Harwood and Theobald (*50*).

The authors tested the method on a series of synthetically prepared rocks having nickel contents ranging from 0.0003 to 0.04 per cent. The sensitivity of the method is great enough to allow the detection of less than 0.0001 per cent of nickel when a 0.5 g. sample is taken.

Copper, cobalt, manganese, chromium, and vanadium in the amounts that are likely to be encountered in most igneous rocks do not interfere. It may be expected that much copper and cobalt will lead to high results. One-tenth mg. of cobalt carried through the procedure gave a color corresponding to about 0.0015 mg. of nickel, and 0.100 mg. of copper gave no color. Manganese in large quantities may cause trouble by oxidizing nickel to the nickelic condition in the ammoniacal solution during shaking, and the results for nickel will then be low, because nickelic dimethylglyoxime is not extracted by chloroform.

Under the conditions specified for the final determination of nickel, Beer's law is closely followed up to a concentration of about 0.006 mg. of nickel per ml. Above this concentration a precipitate may separate.

The solubility of nickel dimethylglyoxime in chloroform at room temperature corresponds to approximately 0.050 mg. of nickel per ml.

Weigh 0.25 g. of finely powdered basic rock (0.01 to 0.05 per cent nickel), or 0.5 g. or more of acidic rock, into a platinum dish, add a few ml. of water, 0.5 ml. of 70 per cent perchloric acid, and 2.5 ml. of hydrofluoric acid (for a sample greater than 0.25 g. these amounts should be correspondingly increased). Evaporate the mixture to dryness, take up the residue in 0.5 ml. of perchloric acid and 2 or 3 ml. of water, and again evaporate to dryness. To the residue add 0.5 to 1 ml. of concentrated hydrochloric acid and 5 ml. of water. Heat to bring all soluble material into solution, add 5 ml. of 10 per cent sodium citrate solution, neutralize the cold solution with concentrated ammonium hydroxide using litmus paper, and add a few drops in excess. If there is an appreciable amount of precipitate or residue in the solution at this point, filter through a small paper, wash with small portions of water, and ignite the paper and its contents. Fuse the residue with approximately 0.1 g. of sodium carbonate, add an excess of dilute hydrochloric acid to the cooled melt, and heat to effect as complete solution as possible. Add 2 or 3 ml. of 10 per cent sodium citrate solution, make slightly ammoniacal, and reserve the solution.

To the main solution (filtrate from any insoluble material) add 2 ml. of 1 per cent alcoholic dimethylglyoxime solution, and shake vigorously for one-half minute with two or three portions of reagent quality chloroform, each having a volume of 2 or 3 ml. In a similar manner extract the ammoniacal solution of the sodium carbonate melt. Combine all the chloroform extracts and shake vigorously with 10 ml. of 1 to 50 ammonium hydroxide solution. Draw off the chloroform, taking care that no drops of the aqueous phase accompany it, and shake the water layer with a ml. or two of chloroform to recover any suspended drops of chloroform solution.

Shake the chloroform solution of nickel dimethylglyoxime vigorously for 1 minute with two portions of 0.5 N hydrochloric acid, each having a volume of 0.5 ml. (or slightly less if the solution is finally to be made up to 10 ml.). Transfer the hydrochloric acid solutions to a volumetric flask of suitable size or a flat-bottomed color comparison tube (1.8 x 15 cm.), taking care that no appreciable amount of chloroform is carried over. For color comparison in a colorimeter the nickel concentration of the final solution should be at least 0.001 mg. per ml. For most acidic rocks the standard series method of color comparison will usually have to be applied because of the low nickel content. A suitable series of standards for a silicic rock is 0.000, 0.001, 0.002 . . . . . . 0.010 mg. of nickel for a 0.5 g. sample. Whether a colorimeter or tubes are used, the final nickel concentration should not exceed 0.005 mg. per ml. or else a precipitate of nickel dimethylglyoxime may be produced.

The unknown nickel solution and the standard nickel solution, diluted to about 10 ml. with 0.5 N hydrochloric acid, are treated simultaneously as follows: Add 5 drops of freshly prepared saturated bromine water, mix, and then add concentrated ammonium hydroxide dropwise with shaking until the color of bromine disappears; finally add an excess of 3 or 4 drops. Next add 0.5 ml. of 1 per cent solution of dimethylglyoxime in alcohol, mix, and dilute to volume with water if a volumetric flask is used. The color comparison may be made immediately. The color intensity of the solution increases slowly on standing; the unknown and standard solutions should therefore be treated with the reagents at the same time.

If necessary apply a correction for nickel in the reagents.

H. THE DETECTION AND GRAVIMETRIC DETERMINATION OF PALLADIUM

The reaction of dimethylglyoxime with palladium salts was first observed by Tschugaeff (*1*) and was applied to the separation and determination of palladium by Wunder and Thüringer (*83*). The precipitate of palladium is yellow in color, being variously described as a bright yellow, a lemon yellow, and a canary yellow. It is insoluble in dilute mineral acids from which the palladium is precipitated quantitatively by a slight excess of the reagent, and appears to be completely insoluble in hot water. It dissolves readily in ammonia and cyanide solutions. The composition of the precipitate is $(C_4H_7O_2N_2)_2Pd$ and the structure of the compound is undoubtedly the same as that of nickel dimethylglyoxime, p. XIII.

Since dimethylglyoxime precipitates nickel only from a weakly acid or ammoniacal solution, but precipitates palladium from a dilute mineral acid solution, it is almost a specific reagent for palladium. Gold is reduced to the metal by the reagent and platinum is partially precipitated, either as the metal or as a greenish complex compound, on boiling the solution.

Precipitation with dimethylglyoxime serves to separate palladium from iron (*83, 85*), copper (*83, 85*), tin (*86*), nickel (*81*) and undoubtedly from all of the common metals. Palladium is readily and completely separated from rhodium and iridium, in a chloride solution, by a single precipitation (*84, 94, 95*). The method is not a separation from gold which is precipitated as the metal, nor from large amounts of platinum (*82, 84, 90*). By carrying out the precipitation in the cold and making a reprecipitation, palladium may be separated from small amounts of platinum (*88, 92, 89, 96*).

The solubility of the precipitate is such that little attention must be paid to the solution as long as only dilute mineral acid, either hydrochloric or sulfuric, is present. The solubility of the precipitate under various conditions was investigated by Wunder and Thüringer (*84*) who reported the following figures:

Solubility in water	0.002 per cent
Solubility in 2 per cent hydrochloric acid	0.0013 per cent
Solubility in 20 per cent acetic acid	0.0021 per cent
Solubility in 50 per cent alcohol	0.0018 per cent

The presence of nitrates in the solution prevents the complete precipitation of palladium.

The precipitate may be dried at 115° and weighed as such, containing 31.67 per cent palladium. This is an entirely satisfactory procedure and the most convenient one (*87, 94, 95*). The precipitate may also, however, be wrapped in an extra layer of filter paper, carefully charred, the filter paper burned away, then the palladium reduced to the metal by ignition in hydrogen, and finally the metal ignited and cooled in an atmosphere of carbon dioxide. Palladium possesses the property of absorbing a considerable quantity of hydrogen, so that it is difficult to obtain constant weight. If the absorbed hydrogen is eliminated by igniting the metal so obtained in an inert gas, no difficulty is encountered. Strong ignition in air is sufficient to decompose all oxides of palladium, without resort to hydrogen, but the gray metal tarnishes as it cools unless an inert gas protects it; the error, however, amounts to only 0.1 mg. with quantities of palladium weighing 100 mg. (*95*).

Procedure for the detection of palladium. Make the solution slightly acid with a few drops of hydrochloric or sulfuric acid. Add a few ml. of dimethylglyoxime solution. Warm gently to precipitate the palladium and coagulate the precipitate. A bright yellow precipitate indicates palladium. If the precipitate is a dirty yellow, gold or platinum is also present.

Procedure for the determination of palladium (as carried out by Gilchrist [*94, 95*]). Dilute the solution containing the palladium, which should be weakly acid with either hydrochloric or sulfuric acid, to a volume of about 400 ml. Add sufficient volume of a 1 per cent solution of dimethylglyoxime in 95 per cent alcohol to precipitate all of the palladium, adding 2.2 ml. of the reagent for each 10 mg. of palladium present and an excess of about 10 per cent to insure complete precipitation. Let the solution stand for one hour and then filter it, the manner of filtration depending on the form in which the palladium is to be weighed.

If, for any reason, it is desired to reprecipitate the palladium, filter on paper, wash the precipitate with dilute hydrochloric acid (1 : 99), and then with hot water. The precipitate can be washed with a considerable volume of water without a trace of it dissolving. Transfer the washed filter and precipitate to a conical flask, closed with a short-stemmed funnel and decompose with a mixture of sulfuric and nitric acids. Heat the solution until fumes of sulfuric acid are evolved, dilute it somewhat and filter. Precipitate the palladium in the diluted solution with dimethylglyoxime.

If the palladium is to be weighed as palladium dimethylglyoxime, filter the precipitate on a porcelain or glass filtering crucible, using suction. Wash the precipitate as previously directed and dry at 110° for one hour. Calculate the quantity of palladium, using the theoretical factor 0.3167.

If the palladium is to be weighed as the metal, filter the precipitate on paper. Wash the precipitate as previously directed. Wipe the inner walls of the beaker and also the glass rod with a small piece of paper. Wrap the filter and the precipitate in a second filter and place them in a porcelain crucible. Dry and ignite carefully in air. Only sufficient heat should be supplied to keep the papers smoking gently. Ignite the charred residue strongly in air, and then in hydrogen. Ignite the metallic palladium in carbon dioxide for two minutes and cool in carbon dioxide. Weight the residue as metallic palladium.

I. THE DETECTION AND COLORIMETRIC DETERMINATION OF FERROUS IRON

That ferrous iron reacted with the α-orthodioximes in the presence of ammonia, pyridine or aliphatic amines yielding soluble compounds, red or violet in color, was reported by Tschugaeff in the very first of the papers (*1*) dealing with the metallic derivatives of the dioximes. Some effort was made by Tschugaeff to elucidate the nature of these compounds but no one else has evidently further interested himself in this problem. Apparently the compounds correspond to the general composition $Fe(DH_2)_2A_2$, where DH_2 represents one molecule of dioxime and A a molecule of ammonia, pyridine or amine.

The first application of the reaction to the qualitative analysis of iron was made by Slawik (*97*) who rediscovered the reaction by noting the changing color of the filtrate from the determination of nickel in steel; on standing in sunlight the dimethylglyoxime, or perhaps the tartrate, reduced the iron to the ferrous state producing a characteristic ruby red color. By a series of tests Slawik confirmed that the reaction was due to ferrous iron and discovered that it could be used as an extremely sensitive test for iron. The reaction was also rediscovered subsequently by others and the error which is occasionally made of mistaking the color for nickel publicized (*99, 100, 101*).

Without ammonia, pyridine or some amine present, a weak yellow color is produced by ferrous iron and dimethylglyoxime. Hydrazine also brings forth the red color and is a convenient base to use since it also will reduce the iron to the ferrous condition which is essential to the test. Ferric iron does not produce such a color with dimethylglyoxime and may be kept in solution during the test for ferrous iron by the addition of tartrate which does not interfere with the test for ferrous iron. If no excess reducing agent, such as hydrazine, is present the color fades in contact with air as the iron is oxidized to the ferric state.

The sensitivity of the reaction as a test for iron is very great. It is reported (*98*) that it is possible to detect 0.00005 mg. of iron, corresponding to 1 part in 20,000,000, by the test.

Tschugaeff and Orelkin (*98*) later applied the reaction to colorimetric determination of iron. Alkali and alkaline earth metals, and magnesium have no effect on the determination.

Procedure for the detection of ferrous iron and total iron. To the solution to be tested add a few drops of a solution of dimethylglyoxime in alcohol and then a slight excess of ammonia. Heat the solution for a few minutes. A rose red color, which is more easily observed against a white background, indicates ferrous iron. A blank should be run on the reagent. If ferric iron is also present add tartaric acid before making the solution ammoniacal in order to prevent ferric hydroxide from precipitating.

To detect iron in either form, add hydrazine sulfate which will reduce ferric iron to ferrous, before making the solution ammoniacal.

Procedure for the colorimetric determination of iron. Treat 50 to 70 ml. of the solution with 1 g. of hydrazine sulfate and with 5 ml. of a saturated solution of dimethylglyoxime in alcohol; heat to boiling, add 10 ml. of concentrated ammonia and continue the boiling 30 seconds longer. Cool the solution quickly under running water and dilute to 100 ml. Without delay transfer to a colorimeter vessel and compare with a standard freshly prepared in a similar way. Amounts of iron in the order of hundredths to tenths of a mg. may be determined in this manner.

J. THE DETECTION AND THE COLORIMETRIC DETERMINATION OF COPPER

Certain oxidizing agents, when added to very dilute feebly alkaline solutions of a cupric salt containing dimethylglyoxime, produce an intense reddish-violet color resembling that of permanganate. This was first noticed by Clarke and Jones (*102*) and subsequently studied by Kolthoff (*103*) and Hurd and Chambers (*104*). The color produced by sodium hypochlorite or bromine water is rather fugitive, partly due to the sensitiveness of the color to acid and excess alkali, and to the difficulties of adjusting the pH value when using these oxidizing agents. Ammonium persulfate produces a weak reddish color, but on the addition of silver nitrate, an immediate development of the intense permanganate color occurs, especially when pyridine is used as the means of obtaining a slight alkalinity. Potassium periodate is also a suitable oxidizing agent.

The nature of this reaction is unknown. In the presence of considerable periodate, the red color of the compound fades fairly rapidly but may be brought back by the addition of more dimethylglyoxime. From this it is inferred (*103*) that the dimethylglyoxime is oxidized to some product which gives a red color with copper, an excess of the oxidizing agent further oxidizing this compound to a colorless product. It would be of great interest to know the nature of the oxidation product of dimethylglyoxime as it would probably be a valuable reagent for the detection of copper.

Chloride must be absent from the solution to be examined and this somewhat limits the applicability of the test, which is otherwise highly sensitive and specific for copper.

Procedure for the detection and determination of copper (Clarke and Jones [102] as modified by Hurd and Chambers [104]). Neutralize the solution, which must be free from chloride, and render it very faintly acid by the addition of 2.0 ml. of 0.4 N sulfuric acid. Place the solution in a 100 ml. Nessler tube, dilute to the mark and dissolve 1 g. of ammonium persulfate in the solution. Add 1 ml. of saturated solution of dimethylglyoxime in alcohol, 0.5 ml. of a 0.5 per cent solution of silver nitrate, and 2 ml. of 10 per cent aqueous pyridine and stir. The color may be compared by running a standard solution of copper sulfate (1 ml. = 0.0001 g. of Cu) into a similar Nessler tube containing the same amounts of reagents. Carry out the comparison without undue delay, as the color shows some tendency to fade on standing.

The intensity of the color produced depends on the amount of pyridine used and exactly the quantity specified should be added. The color reaches its maximum intensity at about 5 minutes when the amount of copper present is less than 0.030 mg.; above this amount, the color reaches a maximum immediately and fades rapidly. If the initial sulfuric acid concentration greatly exceeds 0.008 N the coloration is very faint and fugitive and the addition of a corresponding amount of pyridine does not stabilize the color. Silver nitrate greatly in excess of the amount given tends to promote rapid fading and introduces a yellow coloration which interferes with the accurate estimation of the copper present. Significant increase in the initial concentration of ammonium persulfate causes rapid fading.

As little as 0.01 mg. of copper yields a distinct reddish-violet color; the method is not suitable for determining more than 0.1 mg. One part of copper can be readily detected in 10,000,000 parts of water. Small amounts of certain other heavy metals give yellow or brown colorations under the conditions of the test, but the reddish-violet color appears to be specific for copper. Sulfates and nitrates appear to be without effect on the determination. Sodium sulfate, magnesium sulfate, calcium sulfate, and potassium nitrate in concentrations as high as 2 mg. per ml. do not appreciably affect the intensity or stability of the color. Although the turbidity produced by silver chloride, formed because of the presence of chloride in the water, may be discharged with an excess of pyridine as recommended by the original authors, the color intensity for a given amount of copper is greatly reduced. If the chloride content exceeds 0.0005 mg. per ml., the method is not reliable and should be used with caution. Iron in amounts greater than 0.002 mg. per ml. introduces serious error. Cobalt in concentrations greater than 0.00002 mg. per ml. likewise renders the determination unreliable.

Procedure for the detection of copper (Kolthoff modification [103]). Prepare a buffer solution consisting of 100 ml. of N sodium acetate and 7 ml. of N acetic acid. To 10 ml. of the solution to be tested add 1 ml. of the buffer solution, 0.2 to 0.3 ml. of a 0.1 per cent solution of dimethylglyoxime and 1 ml. of saturated potassium periodate solution. Observe the color after standing 3 to 5 minutes. A violet-red color shows the presence of copper; the sensitivity is about 0.1 mg. of copper per liter.

This procedure can be applied to the detection of copper in tap water if not more than traces of zinc or lead are present; 10 mg. of zinc or lead per liter have very little influence, the color being somewhat weaker than in a blank without zinc or lead. In the presence of larger amounts, zinc or lead periodate precipitates and the sensitivity of the test decreases very much. Ferric iron also interferes, although 1 mg. of copper per liter in the presence of 10 mg. of iron per liter gives a distinct reaction. The addition of 1 to 2 drops of N disodium phosphate improves the situation to such an extent that 1 mg. of copper in the presence of 20 mg. of iron per liter can be detected. Other cations, such as cadmium or manganese, interfere, as they precipitate with periodate.

K. THE DETECTION OF BISMUTH

The reaction of bismuth with dimethylglyoxime was first observed by Kubina and Plicta (105). A solution of the chloride or nitrate of bismuth when treated with dimethylglyoxime and the hot solution made strongly alkaline with ammonia, produces an intense yellow, very voluminous precipitate, the supernatant liquid appearing clear. A yellow white precipitate, which is apparently a mixture of the basic salt and the yellow compound, is produced if the solution is made only weakly ammoniacal. If the precipitation is carried out in the cold only the white basic salt is precipitated but the yellow compound is formed on standing.

Sulfate solutions do not give the test, only a white precipitate being produced, which is not changed on heating; if chloride or nitrate is added to the solution, however, and the solution heated the yellow compound is quickly formed.

Small amounts of bismuth produce only a yellow color on the addition of ammonia, and only after some standing does the yellow precipitate form; the precipitate is more easily observed if collected on a filter paper in this case. The sensitivity of the test is given in the following table:

Bismuth in g.	
$4.7 \cdot 10^3$	Heavy yellow precipitate
$4.7 \cdot 10^4$	Intense yellow color, then immediate precipitation
$1.4 \cdot 10^4$	Definite yellow color, precipitation after a few minutes
$2.4 \cdot 10^5$	Light yellow color, later precipitation of a yellow film
$1.4 \cdot 10^5$	Very weak yellow color, later precipitation of yellow film
$9.5 \cdot 10^6$	Undetectable

The yellow compound is decomposed by acetic acid with the formation of the basic salt, and ammonium sulfide converts it to bismuth sulfide. Tartrates prevent the precipitation of the compound; this makes possible the detection of nickel in the presence of large amounts of bismuth by means of dimethylglyoxime.

Arsenic, antimony, tin, cobalt, ferric iron, and manganese interfere with the test. Copper, which forms a dark brown soluble compound with dimethylglyoxime, does not interfere if not present in too large amounts. It is necessary, however, to dilute the solution before carrying out the test and the solution must be filtered in order to detect the precipitate of the yellow bismuth compound.

The precipitate apparently cannot be used for the gravimetric determination of bismuth.

L. THE DETECTION OF COBALT

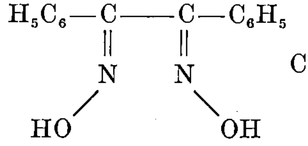
Tschugaeff (*4*) prepared and studied a number of compounds of cobalt containing dimethylglyoxime and ammonia or pyridine. The first attempt to use the brown color of these compounds as a qualitative test for cobalt was made by Braley and Hobart in 1921 (*106*). The brown color is stable in an acetic acid solution and 0.0005 mg. of cobalt per ml. gives a very distinct color. Considerable quantities of iron and copper mask the color. The reaction is fairly satisfactory as colorimetric method for cobalt if the acidity of the solution is controlled by the addition of sodium acetate. Nickel, if present, precipitates and is filtered off before observing the solution.

The reaction was later shown to be far more sensitive if other amines, particularly aromatic amines were substituted for ammonia (*107, 108*). Of these, benzidine is very satisfactory. A neutral cobalt salt solution, treated with acetate and then with alcoholic solutions of dimethylglyoxime and of benzidine, gives an orange red coloration, by means of which 0.01 mg. of cobalt may be detected. Chromium and copper interfere by giving precipitates. The test is particularly well adapted to the examination of the cobalt-nickel precipitate in the usual scheme of qualitative analysis (*109*).

Procedure for the detection of cobalt in a mixture of cobalt and nickel sulfides (Chiarottino procedure according to Scott). Dissolve the precipitate of cobalt and nickel sulfides, after separation from the rest of the Group 3 precipitate, in hydrochloric acid containing a little nitric acid. Filter the solution and evaporate practically to dryness. Dissolve the residue in a few ml. of water containing 1 ml. of dilute acetic acid. To this solution add 1 g. of solid sodium acetate, 0.5 ml. of a 0.5 per cent solution of benzidine in alcohol and an excess of a solution of dimethylglyoxime in alcohol. If nickel is present as indicated by a precipitate of nickel dimethylglyoxime, filter the solution. In the absence of cobalt the filtrate will be colorless to yellow. If cobalt is present the filtrate will have a red coloration. Should the concentration of cobalt be so small that the red color is not very pronounced, it may be intensified by adding solid sodium acetate and allowing the solution to stand for several hours.

III. ALPHA-BENZILDIOXIME

(Alpha-Diphenylglyoxime)



$C_{14}H_{12}O_2N_2$ Molecular weight: 240.26.

The nickel derivative of α-benzildioxime was described by Tschugaeff (*1*) but first applied as a qualitative test and as a gravimetric method for the determination of nickel by Atack (*110, 111*). Like the nickel derivatives of other α-ortho-dioximes, nickel α-benzildioxime consists of two molecules of oxime and one atom of nickel, $(C_{14}H_{11}O_2N_2)_2Ni$; it is a non-electrolyte, and since it is also a chelate compound, it is a true *inner complex* compound. It is red in color, and insoluble in neutral and ammoniacal solutions, but soluble in mineral acids and in cyanide solutions.

As an analytical reagent α-benzildioxime is superior to dimethylglyoxime in that the nickel compound is less soluble and therefore more sensitive as a qualitative test, and having a greater molecular weight, the percentage of nickel in the precipitate is smaller and the conversion factor more favorable. It suffers the disadvantage of being very insoluble in water and only slightly soluble in alcohol, so that extreme care is necessary to avoid the addition of much excess reagent since the compound itself is precipitated as the alcohol is diluted by water.

The palladium compound of α-benzildioxime apparently decomposes rapidly.

The Synthesis of Alpha-Benzildioxime

Dissolve 10 g. of benzil in 50 ml. of methyl alcohol, add 8 g. of hydroxylamine hydrochloride and boil for three hours. Filter off the precipitate of the dioxime, wash with hot water and then with a small amount of 50 per cent ethyl alcohol. Because of its low solubility it is difficult to recrystallize the material from alcohol; it is very soluble in acetone, however, from which it is obtained in small leaves. After drying the product melts sharply at 237°. A further yield can be obtained by boiling the filtrate with hydroxylamine hydrochloride.

Preparation of Reagent Solution

The reagent commonly used is a 0.05 per cent solution of α-benzildioxime in alcohol or acetone. It is not very soluble in alcohol but dissolves somewhat more easily if about 5 per cent ammonia is added. This ammoniacal solution is quite stable and keeps for some time. The acetone solution is very easily prepared.

The Qualitative Detection of Nickel

In the absence of interfering elements, α-benzildioxime gives an immediate precipitate with as little as 0.002 mg. of nickel per 5 ml., corresponding to less than 1 part in 2,000,000. Large amounts of nitrate interfere with the precipitation.

For the detection of nickel in the presence of cobalt, α-benzildioxime is definitely superior to dimethylglyoxime in that the color it gives with cobalt is only a faint yellow in contrast to dark brown, and in that the nickel precipitates immediately, no solvent effect of the cobalt salts being exerted as in the case of dimethylglyoxime. In the presence of 100 times as much cobalt, 1 part of nickel in 1,000,000 parts of an ammoniacal solution gives an immediate precipitate with α-benzildioxime. Larger amounts of cobalt must be oxidized before carrying out the test.

Alpha-benzildioxime gives a violet color with ferrous salts but this does not mask the reaction with nickel. In the presence of ferric iron, citrate or tartrate is added to prevent the precipitation of the iron, and nickel may be detected in the presence of 1000 times as much iron. Large amounts of silver, magnesium, chromium, zinc, or manganese do not interfere with the test for nickel.

The Gravimetric Determination of Nickel

Because of the bulkiness of the precipitate it is best to limit the amount of nickel to be precipitated to about 25 mg. The precipitation is made in an ammoniacal solution by the addition of the reagent, care being taken to avoid the addition of more than a slight excess as the reagent is not soluble in water.

The precipitate is extremely insoluble and may be washed with hot water and water-alcohol mixtures safely.

The method is affected by the presence of nitrates which must therefore be removed by evaporation with sulfuric acid before making the precipitation.

The presence of cobalt requires that sufficient of the reagent be added to combine with both it and the nickel but does not otherwise interfere with the determination of nickel. The separation of nickel from iron by precipitation in an ammoniacal citrate or tartrate solution is satisfactory. Neither zinc or magnesium interfere with the precipitation of nickel if sufficient ammonium salts are present to keep them in solution. In the presence of chromium, tartrate must be added as with iron. In the presence of manganese precipitation must be effected from a slightly acid solution containing acetic acid. Care must be used, however, as α-benzildioxime is changed by acids to its β-isomer which does not give the nickel reaction.

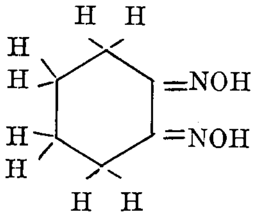
The gravimetric method was tested by Atack (*110, 111*) on known amounts of pure nickel salts up to 25 mg., alone and in the presence of cobalt and of iron; the results were uniformly good, the error always being less than 0.1 mg. of nickel. Strebinger, who further tested the method (*112*) obtained consistently high results when the precipitate was weighed as such. The error was somewhat less when an acetone solution of the reagent was used but still of the order of 0.1 to 0.2 mg. of nickel. This was undoubtedly due to contamination of the precipitate by the reagent, for the correct results were obtained when the precipitate was ignited to the oxide for weighing. Strebinger strongly recommended the latter procedure, although Atack reported that ignition of the precipitate failed to yield satisfactory results.

Procedure for the gravimetric determination of nickel. Make the solution, which should contain not more than 25 mg. of nickel, slightly ammoniacal, and add with stirring a slight excess of the reagent in solution in alcohol or acetone. Heat for a few moments to coagulate the precipitate.

If the precipitate is to be weighed as such, filter on a Gooch crucible using suction. Wash with warm 50 per cent alcohol, then with hot water and dry at 110°. Weigh as nickel benzildioxime, containing 10.92 per cent nickel.

If the precipitate is to be ignited to the oxide, filter the precipitate on paper, wash well with hot water, transfer to a porcelain crucible, moisten with nitric acid and ash. Cool, treat with 2 or 3 drops of nitric acid, evaporate away the acid and ignite. Finally weigh as nickel oxide.

IV. CYCLOHEXANEDIONEDIOXIME



$C_6H_{10}O_2N_2$ Molecular weight: 142.16.

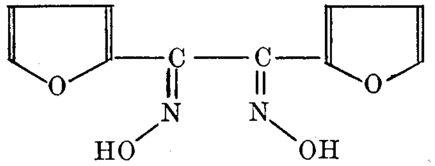
Cyclohexanedionedioxime (Wallach, *113*) is the cyclic analogue of dimethylglyoxime, and like it, it yields an intense red nickel compound, insoluble in neutral and ammoniacal solutions but decomposed by mineral acids. Unlike dimethylglyoxime, it is soluble in water, and this is a highly significant point, for an aqueous solution of the compound can be used as the reagent and there is no danger of the free dioxime precipitating with the nickel compound and affecting the results. The higher molecular weight is also a further advantage over dimethylglyoxime, the nickel compound containing only 17.21 per cent nickel.

It is unfortunate that no satisfactory method for the synthesis of cyclohexanedionedioxime has been devised and that the reagent is not available.

As a qualitative test, cyclohexanedionedioxime is reported by Wallach to give with 1 part of nickel in 2,000,000 parts of a slightly ammoniacal solution a red coloration and after a few hours a red precipitate. The reagent gives with cobalt a brownish yellow coloration which does not interfere with the detection of nickel.

The uses of cyclohexanedionedioxime as a quantitative reagent remain to be investigated, although preliminary experiments indicate that it precipitates nickel completely.

V. ALPHA-FURILDIOXIME



$C_{10}H_8O_4N_2$
Molecular weight = 220.2.

Alpha-furildioxime was proposed by Soule (*114*) as a reagent for the detection and determination of nickel. Like dimethylglyoxime it yields a red insoluble nickel derivative which, being less soluble than nickel dimethylglyoxime is more sensitive as a qualitative test, and being a much larger molecule yields a precipitate having a lower content of nickel, which is more desirable from a quantitative viewpoint. The great advantage of α-furildioxime, however, is its solubility in water, which precludes the possibility of contaminating the precipitate of the nickel derivative with free reagent.

The behavior of the reagent toward palladium and platinum has not been studied.

Synthesis of Alpha-Furildioxime

The synthesis of α-furildioxime involves three steps, the condensation of furfural to furoin by the benzoin condensation, the oxidation of furoin to furil by air, and the oximation of furil to its dioxime. Commercial furfural can be used as the starting material without preliminary purification.

Reflux a mixture of 1.0 mole of furfural, 1.5 mole of methyl alcohol, 6.0 mole of water and 0.12 mole of sodium cyanide for 30 to 40 minutes. Cool, filter and wash the precipitate of furoin which is then used in the next step without further purification. Yield: 25 per cent.

Dissolve the furoin in dilute alcohol containing sufficient sodium hydroxide to effect solution. Cool to 0° and bubble air through the solution. The yield is good.

Reflux a mixture of the crude furil, which should melt above 160°, and hydroxylamine hydrochloride, dissolved in methyl alcohol for 5 to 6 hours. Filter off the light brown crystals. Yield: 85 per cent. Recrystallize the product from water and then from alcohol. The product is a colorless crystalline material which effloresces to a white powder on drying, and which softens and decomposes at 168° (uncorr.).

Preparation of Reagent

A two per cent solution of the reagent in water is used. Such a solution is apparently stable indefinitely.

The Detection of Nickel

As a qualitative test for nickel α-furildioxime is more sensitive than either dimethylglyoxime or α-benzildioxime. As little as 1 part of nickel in 6,000,000 parts of water yields a precipitate which may be distinctly seen after filtering the solution on paper. The sensitivity of this test has been confirmed by Harwood and Theobald (50) who recommend its use in the detection of the small amounts of nickel in silicate rocks.

The concentration of ammonium hydroxide is of importance in this test, there being an upper and a lower limit for maximum precipitation. Too little ammonia does not make the solution sufficiently alkaline, too much exerts a solvent effect. About 2 ml. of dilute ammonia (*1:4*) added to a neutral solution is about the optimum amount.

Silver, copper, and zinc in ammoniacal solution give no color with the reagent. Cobalt in ammoniacal solution gives a dark coloration. Ferric iron, aluminum, and chromium in ammoniacal solutions containing citrate or tartrate give no reaction. Amounts of ferrous iron, less than 1 part in 3,000,000, give a greenish color; increasing amounts, a purple colored solution, and still larger amounts a purple precipitate.

Small amounts of nickel in the presence of large amounts of cobalt are difficult to detect, but oxidation of the cobalt before carrying out the test eliminates this difficulty. In the presence of manganese the test must be carried out in a solution buffered with acetate. This modification also works well in the presence of cobalt and zinc.

The Gravimetric Determination of Nickel

The precipitation of nickel by α-furildioxime is complete from weakly ammoniacal solutions of pure nickel salts and from those containing, in addition to nickel, large amounts of ammonium chloride, ammonium sulfate, ammonium nitrate, ammonium citrate, ammonium tartrate or sodium pyrophosphate. The latter compounds are of interest since they must be added to the solution to prevent the precipitation of ferric hydroxide when the nickel is precipitated in the presence of iron. The separation of nickel from zinc quantitatively is satisfactory, as well as from cobalt when the latter is first oxidized to the trivalent state. The quantitative separation of nickel

from manganese in an acetate buffered solution is not entirely satisfactory.

The separation of nickel from large amounts of iron is satisfactory and the method may be used for the determination of nickel in iron and steel. It is necessary to filter the precipitate off within 30 minutes, however, since ferric iron is reduced by the tartrate or citrate which must be added to prevent the precipitation of ferric iron; ferrous iron forms a green precipitate which contaminates the nickel precipitate.

The nickel in the precipitate may be determined either by weighing the precipitate itself after drying, by ignition to the oxide, or by the cyanide titration method.

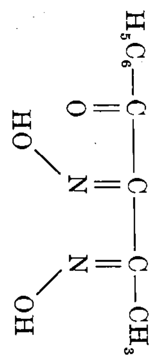
The method was checked by the analysis of pure nickel salts to which the various metals and salts were added. The results were uniformly good, the average error being about 0.1 mg. of nickel. Bureau of Standards Samples No. 33 and 33a, nickel steels were analyzed by the method; the greatest deviation from the probable values was 0.04 per cent. Separation as nickel furildioxime followed by the cyanide titration gave the most consistent results, the error being less than 0.01 per cent on four analyses.

Procedure for the determination of nickel in steel. Dissolve about 0.7 g. of steel in 50 ml. of dilute nitric acid (1 : 2) and 5 ml. of concentrated hydrochloric acid. Dilute the solution to 200 ml. and heat almost to the boiling point. Add 6 g. of citric acid and 34 ml. of concentrated ammonia, bringing the volume to about 300 ml. Add a 2 per cent solution of α-furildioxime in water in slight excess. Digest for 15 minutes and filter.

If the nickel is to be determined as nickel furildioxime, filter on a Gooch crucible using mild suction and wash by decantation. Wash well with water, dry at 120 to 130° and weigh as nickel furildioxime, $(C_{10}H_7O_2N_2)_2Ni$, containing 11.81 per cent nickel.

If the nickel is to be determined as the oxide, filter on paper and wash well with water. Wrap the filter in a second sheet of paper and place in a covered porcelain crucible. Place the crucible in a muffle at about 300° to char the paper and decompose the compound. If the ignition is carried out in the open, the compound decomposes suddenly at about 250° ejecting some of the material. Remove the cover and ignite in contact with air. Cool and weigh.

VI. BENZOYLMETHYLGLYOXIME



$$H_5C_6{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{N-OH}{\|}}{C}{-}\underset{\underset{N-OH}{\|}}{C}{-}CH_3$$

$C_{10}H_{10}O_3N_2$ Molecular weight: 206.2.

Benzoylmethylglyoxime was proposed by Hanus, Jilek, and Lukas (*116*) as a reagent for the detection and gravimetric determination of palladium. The palladium derivative is a yellow compound, insoluble in dilute mineral acids, definite in composition, and stable toward drying so that the precipitate may be weighed. The precipitate is soluble in ammonia.

The reagent is specific for palladium in acid solution, giving no reaction with platinum, iridium, rhodium, osmium, and ruthenium. The statement that the reagent will separate palladium from gold has been disputed by Holzer (*117*) who claims that gold is partially precipitated. Nor do the common metals—copper, bismuth, cadmium, mercury, arsenic, antimony, tin, molybdenum, tungsten, vanadium, iron, nickel, cobalt, zinc, chromium, manganese, and uranium—interfere if the precipitation is made in acid solution.

The method was tested on known amounts of palladium alone and in the presence of the various ions. Amounts of palladium less than 10 mg. were used usually and the results were fairly satisfactory.

Benzoylmethylglyoxime may be synthesized by the method of Ceresol (*115*); it is a white crystalline solid, melting at 179° with decomposition. The reagent used is a 2 per cent solution of the compound in alcohol.

Procedure for the gravimetric determination of palladium. Dilute the solution to a volume of 200 ml. and adjust the acidity to about 6 per cent by volume of concentrated hydrochloric acid. If antimony is present add tartaric acid; and if molybdenum, tungsten or vanadium is present add potassium dihydrogen phosphate. Heat to boiling and precipitate the palladium by the addition of a 2 per cent solution of benzoylmethylglyoxime in alcohol adding an excess of 40 per cent. Boil a few minutes and allow to stand 12 to 24 hours. Filter on a Gooch or porcelain filtering crucible, wash with 200 ml. of water containing 6 ml. of hydrochloric acid, and then with water until free from chloride. Dry at 100 to 105° and weigh as palladium benzoylmethygloxime, $(C_{10}H_9O_3N_2)_2Pd$, containing 20.64 per cent palladium.

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