CHAPTER II

...
As described in the general introduction, there is a group of organic reagents which contains an oxime group with a hydroxyl group attached to the α or the β carbon atom as shown below:

Evidently, compounds of such type can act as monobasic acids, the hydrogen of the hydroxyl group being replaceable by a metal, while the metal and the oxime group form a co-ordinate bond.

A number of compounds containing this reactive grouping have been prepared by Feigl and Iondi (loc.cit.) and EPRAIM, (loc.cit.), which resemble one another in their chemical behaviour towards inorganic ions and form with copper a complex salt of the general formula:
Feigl and Bondi (loc.cit.) also showed that the bonding in such oximes is between the metal and oxygen by the fact that no complex is formed if the phenolic hydroxyl is blocked with a methyl group. If the methyl group is introduced into the hydroxyl of the oxime there is no effect on the complex forming ability.

Feigl and Bondi (loc.cit.) also studied the effect of salicylaldoxime \((X = X_1 = X_2 = X_3 = X_4 = H)\) on alkaline or alkaline tartrate solution of copper sulphate and obtained a compound of the formula \(\text{Cu}(C_7H_5O_2N)\) in which the organic reagent behaves as a di-basic acid presumably because the oxime tautomerises to the nitrone form under the influence of the alkali. The product containing one mole each of copper and the reagent is restored back to the usual type of complex by the action of acetic acid.

Ephraim (loc.cit.) and Astin and Rily (J. Chem. Soc., 1933, 34) were the first to show that salicylaldoxime could be used for the detection and determination of copper. Biefield and Howe (Ind. Eng. Chem. Anal. Ed., 1939, 11, 251) used the same reagent for the determination of nickel.

A similar type of study has been made by Th. G. Pearson (Z. anal. Chem. 1938, 112, 179), Flagg and Furman (Ind. Eng. Chem. Anal. 1940, 12, 663) and Simonsen and Christopher (Anal. Chem. 1964, 26, 681) in which they have shown that at lower temperature and with pH less than 8.5, zinc forms
with salicylaldoxime a mixture of mono and di-compounds
of formulae Zn(\(\text{C}_7\text{H}_5\text{O}_2\text{N}\)) and (\(\text{C}_7\text{H}_6\text{O}_2\text{N}\)) but the conversion
from the di- to the mono-acid form is accomplished
merely by heating the weakly alkaline solution.

Besides salicylaldoxime many other compounds of
its type have been studied; they are mentioned below.

Ephraim (Ber., 1931, B. 64, 1210,1215) studied
the reactions of the following oximes:

(i) 2-napthol-1-aldoxime.
(ii) 1-napthol-2-aldoxime.
(iii) orthovanillin oxime, \(X = \text{H}\); \(X_1 = \text{OCH}_3\);
\(X_2 = X_3 = X_4 = \text{H}\).
(iv) 2-hydroxyacetophenone oxime, \(X = \text{CH}_3\);
\(X_1 = X_2 = X_3 = X_4 = \text{H}\) (Podar, loc.cit.).
(v) 2,4-dihydroxyacetophenone oxime, \(X = \text{OH}\);
\(X_1 = X_2 = X_4 = \text{H}\); \(X_2 = \text{OH}\) (Kabadi and
Bhatki, loc.cit.).
(vi) 2-5-dihydroxyacetophenone oxime, \(X = \text{CH}_3\);
\(X_1 = X_2 = X_4 = \text{H}\); \(X_3 = \text{OH}\)
(vii) 2-hydroxy-4-methoxyacetophenone oxime,
\(X = \text{CH}_3\); \(X_1 = X_2 = X_4 = \text{H}\); \(X_2 = \text{OCH}_3\).
(viii) 2-hydroxy-5-methoxyacetophenone oxime,
\(X = \text{OH}\); \(X_1 = X_2 = X_4 = \text{H}\); \(X_2 = \text{OCH}_3\).
(ix) 2,3,4-trihydroxyacetophenone oxime,
\(X_1 = X_2 = \text{OH}\); \(X = \text{CH}_3\); \(X_3 = X_4 = \text{H}\).
(x) 1-aceto-2-napthol oxime.
Felgul and Bondi (Ber., 1931, 2651, 2019) also contributed in the same field by studying the analytical applications of the following oximes:

(i) 2-hydroxybenzophenone oxime, \( X = \text{C}_6\text{H}_5 \);
\[ X_1 = X_2 = X_3 = X_4 = \text{H}. \]

(ii) 1-aceto-2-hydroxynaphthoic acid(3) oxime.

Flagg and Turman (Ind. Eng. Chem. Anal. ed., 1940, 12, 529) studied the reactions of 3-nitro-, 4-methoxy and 3,5 dibromo salicylaldoximes with various metallic ions.

The other similar oximes recently studied are:

(i) salicyldihydroxamic acid, \( X = \text{OH}; X_1 = X_2 = X_3 = X_4 = \text{H} \)
(Shadari and Ray, loc.cit.)

(ii) salicylanalidoxime, \( X = \text{NH}_2; X_1 = X_2 = X_3 = X_4 = \text{H} \)
(Bandyopadhyay and Ray, loc.cit.)

(iii) 3-oximomethylichromic acid, \( X = \text{H}; X_1 = \text{COOH} \);
\[ X_2 = X_3 = X_4 = \text{H} \]
(S. Ray and A. E. Ray, loc.cit.) and

(iv) 2-4-dihydroxypipionicophenone oxime, \( X = \text{C}_6\text{H}_5 \);
\[ X_2 = \text{OH}; X_1 = X_3 = X_4 = \text{H} \]
(Dave and Patel, loc.cit.)

This earlier work shows that all these reagents give similar reactions with certain cations, namely, copper, nickel, cobalt, palladium, ferric, ferric, bismuth, zinc, etc. This can be made use of in the detection of these cations. The cations like copper and nickel can be completely precipitated from their solutions.
The complexes possess a definite composition, are insoluble in water and are stable. Hence these oximes could satisfactorily be used for determination of these cations. Also the pH of incipient precipitation in equimolecular solutions of copper and nickel are different. This can be utilised for estimation of these cations in presence of each other.

In the present case the reactions of 2-hydroxy-5-methylacetophenoneoxime, 2-hydroxy-5-methyl-propio-phenoneoxime and 2-hydroxy-5-methylbensophenoneoxime with various metallic ions have been studied. All these oximes contain the copper specific group. The 2-hydroxy-5-methylacetophenoneoxime may be thus regarded as a derivative of salicylaldoxime obtained by the replacement of an H atom of the benzene nucleus in the 4 position as well as an H atom of the aldoxime by methyl groups. The propio and the benzophenoneoxime are obtained by the replacement of an H atom of the aldoxime by the ethyl and benzoyl groups respectively.

\[
\text{R} = \text{CH}_3, \text{C}_2\text{H}_5 \text{ or } \text{C}_6\text{H}_5.
\]

It might therefore be of interest to find the influence of such substitution as methyl in the benzene ring and heavier groups like \(\text{CH}_3\), \(\text{C}_2\text{H}_5\) and \(\text{C}_6\text{H}_5\) in the aldoxime part on the general characteristics of this specific grouping.
Theoretical

In this section is described the present study on the reactions of 2-hydroxy-3-methylacetophenoneoxime, 2-hydroxy-5-methylpropiophenoneoxime and 2-hydroxy-3-methylbenzophenoneoximes in the same sequence with various metallic ions, namely, copper, nickel, cobalt, palladium, ferrous, ferric, chromium, cadmium, manganese, zinc, aluminium, beryllium, bismuth, lead and mercury. With each oxime, first, it has been shown how the reactions with some of these cations could be utilized for their detections, either individually or severally and in presence of other cations. Then this has been further developed for the determination of copper, nickel and cobalt individually in presence of one another.

2-hydroxy-3-methylacetophenoneoxime

The reagent

2-Hydroxy-3-methylacetophenoneoxime was prepared as described in the experimental. A 1% solution in 75% ethanol was used for all the tests.

Detection of

Copper: A decinolar copper sulphate solution was prepared and standardized as described in the experimental.

It was observed that on a dropwise addition of the reagent to the copper ion solution, a faintly olive green precipitate of the copper complex obtained. The precipitation could be carried out between pH 3.0 to 3.5.
It was also observed that this reagent could detect Cu^{++} up to a dilution of 1.2 \( \mu \text{g} \) and an opalescence could be observed up to a dilution of 0.84 \( \mu \text{g} \).

The complex dissolves in benzene, toluene, xylene, chloroform, and carbon tetrachloride giving an olive green solution which can be kept for weeks without decomposition. The complex is soluble in hot strong alkalis and liquor ammonia and reprecipitates on dilution with water. The complex is decomposed by mineral acids as well as glacial acetic acid.

Nickel: A decimolar solution of nickel sulphate was prepared and standardised as described in the experimental. It was observed that no precipitate was formed on treatment of this solution with the reagent. However, a green precipitate could be obtained if ammonium hydroxide solution or sodium acetate solution was added and the pH raised to 5.0. It could be precipitated in pH range 5.0 to 8.5.

The sensitivity of this reagent for the detection of Mg^{++} ion was found to be as good as copper viz. about 1.2 \( \mu \text{g} \) and the opalescence was observed in the solution containing 0.78 \( \mu \text{g} \) of nickel.

The complex dissolves in chloroform, benzene, toluene, xylene and carbon tetrachloride to give a stable green solution. Strong alkalis and liquor ammonia dissolve the
complex on warming which reprecipitates on dilution. The complex gets decomposed when treated with mineral acids and glacial acetic acid.

**Cobalt:** A decimolar solution of cobalt chloride was prepared and standardized as described in the experimental. No precipitate was obtained on addition of the above reagent directly to the solution. It was observed however, that a yellowish brown precipitate is formed on addition of a dilute solution of ammonium hydroxide or sodium acetate and raising the pH to 6.5 to 6.0. The reagent could be used to detect Co²⁺ ion upto 0.05 ppm.

The cobalt complex dissolves in nonpolar solvents like chloroform, benzene, toluene, xylene and carbon tetrachloride giving a faintly reddish brown solution which can be preserved for a long period. The complex is sparingly soluble in ethanol, ether and petroleum also. Liquor ammonia and strong alkalis dissolve the complex on warming but it reprecipitates on dilution. The cobalt complex is decomposed when treated with mineral acids as well as glacial acetic acid.

**Palladium:** A 0.1% solution of palladium chloride was prepared as described in the experimental. The palladium complex was precipitated even in a dilute hydrochloric acid medium. The precipitation could be carried out between pH 1.0 to 3.5.
The complex dissolved in chloroform, benzene, toluene, xylene and carbon tetrachloride to give a greenish yellow stable solution. The complex is soluble in hot strong alkalis and liquor ammonia from which it reprecipitated on dilution. The complex is decomposed if it is treated with very strong mineral acids.

**Ferrous:** A decimolar solution of ferrous ammonium sulphate was prepared as described in the experimental. A violet solution was obtained on a dropwise addition of the reagent to the ferrous ion solution at about pH 4.0; and on raising the pH to about 5.5 to 7.0, a reddish precipitate was formed which was soluble in chloroform, benzene, toluene, xylene and carbon tetrachloride giving a red solution.

**Ferric:** A decimolar solution of ferric chloride was prepared as described in the experimental. A reddish brown solution was obtained between pH 4.0 to 5.5; but on raising the pH to 6.0 and above a reddish precipitate of ferric hydroxide (with ammonium hydroxide) and basic ferric acetate (with sodium acetate) was obtained.

**Chromium, Cadmium, Manganese, Zinc, Aluminium, Beryllium, Bismuth, Lead and Mercury:**

The solutions of the above mentioned cations were prepared as described in the experimental. No precipitate was obtained on addition of the reagent directly to the solution containing any of the above mentioned cations, however, on raising the pH (by the addition of dilute ammonium hydroxide solution) the respective hydroxides precipitated.
Copper and nickel in presence of each other: It was observed that copper and nickel can be detected in presence of each other using 2-hydroxy-5-methylacetophenone oxime taking advantage of the different range of pH for the precipitation of their complexes. Copper gets precipitated at pH 3.0 and nickel above pH 5.0. It was also observed that in this mixture, below a pH of 6.5, copper complex preferentially precipitated before nickel, but above this pH copper and nickel co-precipitated.

To a solution containing copper and nickel ions an excess of the reagent was added, when copper complex precipitated first. After the precipitation was complete the complex was removed by filtration and the filtrate treated with dilute ammonia or sodium acetate solution to raise the pH to 5.0 when the nickel complex precipitated.

Copper and cobalt in presence of each other: Copper and cobalt were also detected in presence of each other by controlling the pH. The procedure adopted was almost the same as that for a copper-nickel mixture. Copper complex precipitated above pH 3.0 and that of cobalt above pH 5.5. It was observed that in this mixture, copper could be preferentially precipitated up to pH 8.0.

Nickel and cobalt in presence of each other: The different ranges of pH required for the precipitation of nickel and cobalt complexes were similarly utilised to detect them in presence of each other. The nickel complex
precipitated near pH 5.0 and the cobalt complex above pH 6.5. It was observed that in a mixture of these two cations, nickel could be preferentially precipitated up to pH 8.0.

Copper, nickel and cobalt in presence of one another:
The control of pH was also profitably employed for the detection of copper, nickel and cobalt in presence of one another.

To a solution containing copper, nickel and cobalt was added an excess of the reagent. The precipitated copper complex was removed and the pH of the filtrate raised to 5.5, when the nickel complex precipitated. Removal of the precipitate and subsequent raising of pH to above 5.5 gave the precipitate of the cobalt complex.

Copper in the Fehling's solution: When the reagent was added to the Fehling's solution (A + B) a precipitate was observed, the solution turning green in colour. On dilution, further precipitation occurred showing that high alkalinity of the Fehling's solution kept the copper complex formed in solution and which was precipitated on dilution.

Copper in presence of other cations (chromium, cadmium, zinc, aluminium, manganese, beryllium and iron): Copper, in presence of any of the above cations except iron, was detected keeping the pH 3.0 to 3.5. It appeared advisable to keep pH low to avoid complication of precipitation of the hydroxides of the various cations.
The procedure adopted was almost the same as that for copper alone.

The iron complex was found to precipitate along with that of copper. Hence, the precipitation of iron was prevented by the addition of potassium citrate or Rochelle salt, thus converting it into a soluble complex.

A solution containing both copper and iron was treated with ammonium hydroxide solution followed by acetic acid to remove the mineral acidity, and then a sufficient amount of potassium citrate or Rochelle salt was added. The green solution was then warmed and treated with the reagent, when the copper complex separated.

Nickel in presence of other cations: Nickel in presence of any of the above cations except iron was detected by a control of pH near 5.5 and using almost the same procedure as that for nickel alone. The iron complex was also found to precipitate along with nickel, which was prevented by the addition of potassium citrate or Rochelle salt.

A solution containing both nickel and iron was treated with Rochelle salt or potassium citrate till the solution turned faintly green. The solution was then warmed and treated with the reagent which was followed by a dilute ammonium hydroxide or sodium acetate solution to raise the pH to about 5.5, when the nickel complex separated.
All the results are summed up in the Table I given below:

**TABLE I**

Reactions of 2-hydroxy-5-methylacetophenonoxime with 0.1M solutions of metallic ions.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>Faintly olive green ppt.</td>
<td>2.0</td>
<td>Soluble in strong alkalis and ammonia. Decomposed by mineral acids and acetic acid on boiling. Not affected by boiling water. Precipitation complete between pH 3.0 to 5.0.</td>
</tr>
<tr>
<td>(CuSO&lt;sub&gt;4&lt;/sub&gt;, 5H&lt;sub&gt;2&lt;/sub&gt;O)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na&lt;sup&gt;+&lt;/sup&gt;</td>
<td>Green ppt.</td>
<td>5.0</td>
<td>Soluble in ammonia and caustic alkalis. Decomposed by mineral acids and acetic acid on boiling. Not affected by boiling water. Precipitation complete between pH 5.0 to 6.5.</td>
</tr>
<tr>
<td>(Na&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;, 7H&lt;sub&gt;2&lt;/sub&gt;O)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>Deep yellow-brown ppt.</td>
<td>6.5</td>
<td>Soluble in strong alkalis and ammonia. Not affected by boiling water. Decomposed by mineral acids and acetic acid on boiling. Precipitation complete between pH 5.0 to 6.5.</td>
</tr>
<tr>
<td>(CoCl&lt;sub&gt;2&lt;/sub&gt;, 6H&lt;sub&gt;2&lt;/sub&gt;O)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>Yellow ppt.</td>
<td>Acidic medium.</td>
<td>Soluble in strong alkalis and ammonia. Decomposed by mineral acids and acetic acid on boiling.</td>
</tr>
<tr>
<td>(FeCl&lt;sub&gt;2&lt;/sub&gt;)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>pH 2.5-4, violet colour;</td>
<td></td>
<td>Ppt. Decomposed by strong acids. Extractable with chloroform, etc.</td>
</tr>
<tr>
<td>(FeCl&lt;sub&gt;3&lt;/sub&gt;)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>pH 4-5, reddish brown colour; pH above 6, red ppt.</td>
<td></td>
<td>The red ppt. is of basic ferric acetate on ferric hydroxide.</td>
</tr>
</tbody>
</table>
### Determination of:

**Copper**: In the first place, copper was estimated using 2-hydroxy-5-methylacetophenoneoxime under exactly the same conditions as those with salicylaldoxime.

A definite amount of copper sulphate solution was treated with ammonium hydroxide solution followed by acetic acid (pH 3.0 to 4.0) to remove the mineral acidity. The solution was then warmed to 70°C and treated with the reagent, when the complex separated.

The results are given in Table II.

<table>
<thead>
<tr>
<th>Ion</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu³+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Be³⁺</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Bi³⁺</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>UO²⁺</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
</tbody>
</table>
Estimation of Cu⁺⁺ using 2-hydroxy-5-methylacetophenone-
oxime:

<table>
<thead>
<tr>
<th>Copper present (g)</th>
<th>Cu.ppt (g)</th>
<th>Cu.found (g)</th>
<th>Error (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05247</td>
<td>0.3060</td>
<td>0.05266</td>
<td>± 0.00019</td>
</tr>
<tr>
<td>0.05247</td>
<td>0.3858</td>
<td>0.05263</td>
<td>± 0.00012</td>
</tr>
<tr>
<td>0.05247</td>
<td>0.3650</td>
<td>0.05266</td>
<td>± 0.00015</td>
</tr>
<tr>
<td>0.05247</td>
<td>0.3864</td>
<td>0.05273</td>
<td>± 0.00020</td>
</tr>
<tr>
<td>0.03124</td>
<td>0.1924</td>
<td>0.03123</td>
<td>± 0.00011</td>
</tr>
<tr>
<td>0.03124</td>
<td>0.1926</td>
<td>0.03126</td>
<td>± 0.00002</td>
</tr>
</tbody>
</table>

The results were quite in agreement with the calculated values and the error obtained was ± 0.45%.

The same procedure was then repeated, except that the neutralisation of the mineral acid with ammonium hydroxide and subsequent acidification with acetic acid was not carried out. It was observed that quite satisfactory results are obtained, the error observed being ± 0.23%.

The determination was then repeated in presence of (i) free hydrochloric acid and (ii) free acetic acid, when it was observed that those acids prevented a complete precipitation of copper. The error observed was:

(i) -3.0% with hydrochloric acid.
(ii) -9.5% with acetic acid.
Copper in presence of nickel: The procedure was the same as that used for the determination of copper alone, the pH being about 3.0 to 3.5. It was found that only copper was precipitated quantitatively while nickel remained in solution.

The error observed was +0.36%.

Copper in presence of cobalt: The estimation was carried out as that for copper alone, when only copper complex was quantitatively precipitated with pH at 3.0 to 3.5 leaving cobalt in solution.

The error observed was +0.25%.

Copper in presence of iron: A solution containing both copper and iron (cuss or ic) was treated with a dilute ammonium hydroxide solution followed by acetic acid to remove mineral acidity, and then sufficient amount of potassium citrate or Rochelle salt was added. The green solution was then warmed to 70° and treated with the reagent, when the copper complex separated.

The results were quite in agreement with the calculated values and the error obtained was ± 0.11%.

The results are given in Table III-A and III-B.
### TABLE III-A

**Estimation of Cu**⁺⁺ in presence of Fe**⁺⁺** using 2-hydroxy-5-methylacetophenonoxime.

\[ \text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \text{FeSO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O} \]

<table>
<thead>
<tr>
<th>Substance added</th>
<th>Amount taken</th>
<th>Amount of copper found</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium citrate</td>
<td>3.0 g</td>
<td>0.06247 g</td>
<td>0.06252 g + 0.00005 g</td>
</tr>
<tr>
<td></td>
<td>2.0 g</td>
<td>0.06247 g</td>
<td>0.06240 g - 0.00007 g</td>
</tr>
<tr>
<td>Rochelle salt</td>
<td>3.0 g</td>
<td>0.06247 g</td>
<td>0.06252 g + 0.00005 g</td>
</tr>
<tr>
<td></td>
<td>1.5 g</td>
<td>0.03124 g</td>
<td>0.03126 g + 0.00002 g</td>
</tr>
</tbody>
</table>

Drying temp. = 120°.

### TABLE III-B

**Estimation of Cu**⁺⁺ in presence of Fe**⁺⁺** using 2-hydroxy-5-methylacetophenonoxime.

\[ \text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 24\text{H}_2\text{O} + \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \]

<table>
<thead>
<tr>
<th>Substance added</th>
<th>Amount taken</th>
<th>Amount of copper found</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium citrate</td>
<td>3.0 g</td>
<td>0.06247 g</td>
<td>0.06250 g + 0.00003 g</td>
</tr>
<tr>
<td></td>
<td>2.0 g</td>
<td>0.06247 g</td>
<td>0.06242 g - 0.00005 g</td>
</tr>
<tr>
<td>Rochelle salt</td>
<td>3.0 g</td>
<td>0.06247 g</td>
<td>0.06242 g - 0.00005 g</td>
</tr>
<tr>
<td></td>
<td>1.5 g</td>
<td>0.03124 g</td>
<td>0.03123 g + 0.00004 g</td>
</tr>
</tbody>
</table>

Drying temp. = 120°.
Copper in the Fehling's solution: The Fehling's mixture (A + B) diluted to 6 times its volume and heated to 70° was treated with the reagent and the precipitate of the complex was collected. The results obtained were quite in agreement with those obtained by standard methods, the error being ± 0.35% (without removal of mineral acidity) and ± 0.1% (after removing mineral acidity).

If the Fehling's mixture was diluted to only twice its volume, the results were not satisfactory, the error being - 11.4%.

Copper in presence of other cations: The estimation of copper in presence of other cations (see Table IV) mentioned in the table below was carried out by the usual procedure of precipitating at pH of about 3.0 to 3.5. The presence of these cations did not interfere in any way with the precipitation and the results were quite in agreement with the calculated values, the error observed being within ± 0.5% range.

<table>
<thead>
<tr>
<th>Copper present</th>
<th>Cation added</th>
<th>Cu.ppt.</th>
<th>Cu. found</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.06247 g</td>
<td>Chromium</td>
<td>0.0260 g</td>
<td>0.5858 g</td>
</tr>
<tr>
<td>0.06247 g</td>
<td>Cadmium</td>
<td>0.0281 g</td>
<td>0.5960 g</td>
</tr>
<tr>
<td>0.06247 g</td>
<td>Zinc</td>
<td>0.0277 g</td>
<td>0.5922 g</td>
</tr>
<tr>
<td>0.06247 g</td>
<td>Aluminium</td>
<td>0.0271 g</td>
<td>0.3952 g</td>
</tr>
<tr>
<td>0.06247 g</td>
<td>Manganese</td>
<td>0.0274 g</td>
<td>0.3260 g</td>
</tr>
<tr>
<td>0.06247 g</td>
<td>Beryllium</td>
<td>0.0090 g</td>
<td>0.3662 g</td>
</tr>
</tbody>
</table>
**Nickel:** A definite amount of the standard nickel sulphate solution was heated to 70° and treated with a slight excess of the reagent followed by ammonium hydroxide to raise the pH to 5.5, when the nickel 2-hydroxy-5-methylacetophenone oxime complex separated. As the Table V shows, the results were in agreement with those obtained by the standard method, the error being ± 0.32%.

**TABLE V**

**Estimation of Ni**⁺⁺ using 2-Hydroxy-5-methylacetophenone oxime.

<table>
<thead>
<tr>
<th>Ni₂O₄·7H₂O.</th>
<th>Burying temp. = 120°</th>
<th>Log. Factor = 1.1.1.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni precipitate</td>
<td>Ni found.</td>
<td>Error.</td>
</tr>
<tr>
<td>0.06154 g</td>
<td>0.06140 g</td>
<td>± 0.00014 g</td>
</tr>
<tr>
<td>0.06154 g</td>
<td>0.06134 g</td>
<td>± 0.00012 g</td>
</tr>
<tr>
<td>0.06154 g</td>
<td>0.06147 g</td>
<td>± 0.00007 g</td>
</tr>
<tr>
<td>0.06154 g</td>
<td>0.06144 g</td>
<td>± 0.00011 g</td>
</tr>
<tr>
<td>0.03077 g</td>
<td>0.03076 g</td>
<td>± 0.00001 g</td>
</tr>
<tr>
<td>0.03077 g</td>
<td>0.0303 g</td>
<td>± 0.00004 g</td>
</tr>
</tbody>
</table>

The same procedure was then repeated except that sodium acetate solution was used instead of dilute ammonium hydroxide to raise the pH of the solution. The results were quite satisfactory, the error being ± 0.7%.  

**Nickel in presence of copper:** To a solution containing copper and nickel and heated to 70° was added excess of the reagent sufficient to precipitate both the ions, when copper
not precipitated at this low pH (5.0 to 5.5). It was filtered off and to the filtrate containing nickel in solution was added dilute ammonium hydroxide solution to raise the pH to 5.5, when the nickel complex separated. The value was obtained was quite in agreement with the calculated value, the error observed being - 0.22%.

**Nickel in presence of cobalt:** The procedure was the same as that for the estimation of nickel alone. It was found that when the pH was about 5.5 nickel complex was completely precipitated while the cobalt ion remained in solution. The error observed was - 0.16%.

**Nickel in presence of iron:** A solution containing both nickel and iron (nuc or ic) was treated with Rochelle salt or potassium citrate till the solution turned faintly green. The solution was then warmed to 70° and treated with the reagent followed by dilute ammonium hydroxide or sodium acetate solution to raise the pH of the solution to about 5.5, when the nickel complex separated. The results were quite in agreement with the calculated values and the error obtained was ± 0.097% (see Table VI-A and VI-B).
TABLE VI-A

Estimation of $\text{Mg}^{++}$ in presence of $\text{Fe}^{++}$ using 2-Hydroxy-5-methylacetophenoneoxime.

$$\text{MgSO}_4 \cdot 7\text{H}_2\text{O} + \text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$$

Substance added | Amount of nickel taken | Amount of nickel found | Error
---|---|---|---
Potassium citrate | 3.0 g | 0.06154 g | 0.06152 g | 0.00002 g
 | 3.0 g | 0.06154 g | 0.06154 g | 0.00000 g
 | 2.0 g | 0.03077 g | 0.03078 g | 0.00001 g
Roche salt | 3.0 g | 0.06154 g | 0.06156 g | 0.00002 g
 | 3.0 g | 0.06154 g | 0.06148 g | 0.00006 g
 | 1.5 g | 0.03077 g | 0.03076 g | 0.00001 g

TABLE VI-B

Estimation of $\text{Mg}^{++}$ in presence of $\text{Fe}^{+++}$ using 2-Hydroxy-5-methylacetophenoneoxime.

$$\text{MgSO}_4 \cdot 7\text{H}_2\text{O} + \text{Fe}_2(\text{NO}_3)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$$

Substance added | Amount of nickel taken | Amount of nickel found | Error
---|---|---|---
Potassium citrate | 3.0 g | 0.06154 g | 0.06156 g | 0.00002 g
 | 3.0 g | 0.06154 g | 0.06156 g | 0.00002 g
 | 2.0 g | 0.03077 g | 0.0309 g | 0.00003 g
Roche salt | 3.0 g | 0.06154 g | 0.06152 g | 0.00002 g
 | 3.0 g | 0.06154 g | 0.06148 g | 0.00006 g
 | 1.5 g | 0.03077 g | 0.03078 g | 0.00001 g
Nickel in presence of other cations: For the estimation of nickel in presence of other cations (see Table VII), the normal procedure was adopted, the pH of 5.5 being raised by sodium acetate solution, when precipitation occurred. The presence of these ions did not interfere during the precipitation and the results obtained were in agreement with the calculated values. The error observed was within the range of ± 0.22%.

<table>
<thead>
<tr>
<th>Nickel present</th>
<th>Cation added</th>
<th>%1 ppt.</th>
<th>%1 found</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0615 g Chromium</td>
<td>0.036 g</td>
<td>0.046 g</td>
<td>0.06140 g</td>
<td>- 0.00014 g</td>
</tr>
<tr>
<td>0.0615 g Cadmium</td>
<td>0.0281 g</td>
<td>0.052 g</td>
<td>0.06150 g</td>
<td>- 0.0000 g</td>
</tr>
<tr>
<td>0.0615 g Zinc</td>
<td>0.0327 g</td>
<td>0.050 g</td>
<td>0.06147 g</td>
<td>- 0.00007 g</td>
</tr>
<tr>
<td>0.0615 g Aluminium</td>
<td>0.0271 g</td>
<td>0.046 g</td>
<td>0.06140 g</td>
<td>- 0.00014 g</td>
</tr>
<tr>
<td>0.0615 g Manganese</td>
<td>0.0274 g</td>
<td>0.048 g</td>
<td>0.06144 g</td>
<td>- 0.00011 g</td>
</tr>
<tr>
<td>0.0615 g Beryllium</td>
<td>0.0090 g</td>
<td>0.0050 g</td>
<td>0.06147 g</td>
<td>- 0.00007 g</td>
</tr>
</tbody>
</table>

Copper and nickel in presence of each other: Solutions containing copper and nickel ions in different proportions (viz. Cu : Ni :: 1 : 1, 10 : 1, 1 : 10) were estimated for each of the cations separately. The procedure was the same as those for the individual estimation of copper and nickel in presence of the other, described earlier.

To a solution containing copper and nickel ions heated
to 70°, excess of the reagent was added, copper complex precipitated at a pH of about 3.0 to 3.5, which was collected and the filtrate was treated with dilute ammonium hydroxide to raise the pH to 3.5, when nickel precipitated. The error obtained was: \( \text{Cu}^{++} \pm 0.3\% \) and \( \text{Ni}^{++} \pm 0.22\% \) (see Table VIII).

**TABLE VIII**

Estimation of \( \text{Cu}^{++} \) and \( \text{Ni}^{++} \) in presence of each other using 2-Hydroxy-5-methylacetophenoneoxime.

| Serial No.1 | \( \text{Cu}^{++} : \text{Ni}^{++} \) : 1:1 |
| Serial No.2 | \( \text{Cu}^{++} : \text{Ni}^{++} \) : 10:1 |
| Serial No.3 | \( \text{Cu}^{++} : \text{Ni}^{++} \) : 1:10 |

\[
\begin{align*}
\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \\
\text{NiSO}_4 \cdot 7\text{H}_2\text{O}, \quad \text{Drying temp.} = 120^\circ \text{C}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Copper</th>
<th>Nickel</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 0.06247</td>
<td>0.386</td>
<td>0.06256</td>
</tr>
<tr>
<td>2. 0.06247</td>
<td>0.3858</td>
<td>0.06263</td>
</tr>
<tr>
<td>3. 0.06247</td>
<td>0.3860</td>
<td>0.06266</td>
</tr>
</tbody>
</table>

**Copper and nickel in an alloy:** The solution of the alloy was prepared as described in the experimental. From this solution copper and nickel were estimated using this reagent as described above. The results obtained by this method were excellently tallying with the results obtained by the standard methods.

<table>
<thead>
<tr>
<th>Metal</th>
<th>By the oxime</th>
<th>By standard method</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>74.43%</td>
<td>74.63%</td>
<td>-0.225</td>
</tr>
<tr>
<td>Nickel</td>
<td>25.12%</td>
<td>25.12%</td>
<td>0.0%</td>
</tr>
</tbody>
</table>
Cobalt: A definite amount of standard solution of cobalt chloride was warmed to 70° and treated with the reagent followed by dilute ammonium hydroxide to raise the pH to 7.0, when the cobalt 2-hydroxy-5-methylacetophenoneoxime separated. As will be seen from the Table IX, the values were quite in agreement with the calculated values, the error being ± 0.22%.

**TABLE IX**

Estimation of Co⁺⁺ using 2-Hydroxy-5-methylacetophenone oxime.

<table>
<thead>
<tr>
<th>CoCl₂·6H₂O</th>
<th>Drying temp. = 120°</th>
<th>Log factor = 1.123</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt present</td>
<td>Co ppt.</td>
<td>Co found</td>
</tr>
<tr>
<td>0.05842 g</td>
<td>0.05844 g</td>
<td>0.05855 g</td>
</tr>
<tr>
<td>0.05842 g</td>
<td>0.05839 g</td>
<td>0.05832 g</td>
</tr>
<tr>
<td>0.05842 g</td>
<td>0.05840 g</td>
<td>0.05849 g</td>
</tr>
<tr>
<td>0.05842 g</td>
<td>0.05832 g</td>
<td>0.05837 g</td>
</tr>
<tr>
<td>0.02921 g</td>
<td>0.02922 g</td>
<td>0.02928 g</td>
</tr>
<tr>
<td>0.02921 g</td>
<td>0.02920 g</td>
<td>0.02925 g</td>
</tr>
</tbody>
</table>

The above procedure was repeated except that sodium acetate solution was used instead of dilute ammonium hydroxide to raise the pH of the solution, the error being ± 0.17%.

**Cobalt in presence of copper:** To a solution containing both cobalt and copper ions heated to 70° was added the reagent sufficient to precipitate both, when copper precipitated at the pH 3.0 to 3.5. It was filtered off and to the filtrate containing the cobalt ion dilute ammonium hydroxide solution was added.
to raise the pH to 7.0, the cobalt then precipitated. The results were in agreement with the calculated values, the error being ± 0.11%.

**Cobalt in presence of nickel:** In a solution containing nickel and cobalt ions heated to 70°, the reagent sufficient to precipitate both was added followed by dilute ammonium hydroxide to raise the pH to 5.5. Nickel 2-hydroxy-5-methylacetophenoneoxime precipitated which was removed and the filtrate further treated with dilute ammonium hydroxide to get pH 7.0, when the cobalt complex precipitated. The results were quite in agreement with the theoretical values, the error being ± 0.11%.

**Cobalt and copper in presence of each other:** The procedure was the same as that followed for the individual determination of copper and cobalt in presence of the other, which has been discussed earlier.

A solution containing both the cobalt and copper ions was heated to 70° and treated with the reagent sufficient to precipitate both. The copper 2-hydroxy-5-methylacetophenone oxime quantitatively precipitated at this pH (3.0 to 3.5). While the cobalt remained in solution. The precipitate was collected and the pH of the filtrate raised to about 7.0 by the addition of dilute ammonium hydroxide, when the cobalt complex separated. The results were quite in agreement with the theoretical value, the error being: Cu⁺⁺ ± 0.3% and Co⁺⁺ ± 0.03%.
Cobalt and nickel in presence of each other: The procedure was the same as that described for the determination of cobalt and nickel in presence of the other. A solution of both cobalt and nickel ions was treated with the reagent at 70° and the pH raised to 5.5. The precipitate of the nickel complex was collected. The filtrate on further raising the pH to 7.0 gave the precipitate of cobalt complex. The results were quite in agreement with the theoretical values, the error being: Ni\(^{2+}\) = 0.23% and Co\(^{2+}\) = 0.17%.

Copper, nickel and cobalt in presence of one another:

A solution containing copper, nickel and cobalt ions at 70°, was treated with an excess of the reagent. The precipitate of the copper 2-hydroxy-5-methylacetophenoneoxime was collected and the pH of the filtrate was raised to 2.5, when the nickel complex separated. The precipitate was filtered and the filtrate on further raising the pH to 7.0 gave the precipitate of the cobalt complex. The results were quite in agreement with the theoretical values, the error being: Cu\(^{2+}\) = 0.27%, Ni\(^{2+}\) = 0.16% and Co\(^{2+}\) = 0.17%.

(A 2% solution in 95% ethanol was used for all quantitative determinations)
2-Hydroxy-5-methylpropiofenone Oxime

The reagent: 2-Hydroxy-5-methylpropiofenone oxime was prepared as described in the experimental. A 1% solution in 95% ethanol was used for all qualitative tests and a 1% solution for all gravimetric analyses.

Detection of:

Copper: It was observed that on dropwise addition of the 2-hydroxy-5-methylpropiofenone oxime to the copper ion solution, a faintly olive green precipitate of the copper complex was obtained (pH 3.0 to 3.5). This reagent could detect Cu up to a dilution of 1.2% and an opalescence could be observed up to a dilution of 0.48%.

The copper 2-hydroxy-5-methylpropiofenone oxime behaved exactly in the same manner as the corresponding acetophenone oxime so far as its solubility in nonpolar solvents and alkalis is concerned. The complex was decomposed by mineral acids and glacial acetic acid.

Nickel: It was observed that nickel could be detected using this reagent exactly in the same manner as using the acetophenone oxime. The other characteristics of the nickel complex, viz, the pH for precipitation, the sensitivity, the solubility in nonpolar solvents and alkalis and the effect of acids were found to be the same as those of the nickel 2-hydroxy-5-methylacetophenone oxime.
Cobalt: The procedure adopted for the detection of cobalt using this reagent was the same as that followed for its detection with 2-hydroxy-5-methylacetophenone oxime. A faintly reddish brown precipitate was obtained at pH 6.5. The complex behaved in the same manner as the oxime described, as far as the pH for precipitation, the sensitivity, the effects of organic solvents, alkalis and acids are concerned.

Palladium: Palladium was detected using this reagent in the same way as using the corresponding acetophenone oxime. The complex behaved in the same manner as the palladium 2-hydroxy-5-methylacetophenone oxime as far as the pH, solubility in nonpolar solvents and in alkalis, and the effects of acids are concerned.

Ferrous: Ferrous ion was detected in the way similar to that followed for its detection with 2-hydroxy-5-methylacetophenone oxime. The other properties of the ferrous 2-hydroxy-5-methylacetophenone oxime, are similar to those of the ferrous 2-hydroxy-5-methylacetophenone oxime.

Ferric: A reddish brown solution was obtained on dropwise addition of this reagent to a solution of a ferric ion, at pH 4.0 to 5.0, but on raising the pH to 6.0 and above, a reddish precipitate of ferric hydroxide (with ammonium hydroxide) or basic ferric acetate (with sodium acetate) was obtained.

Chromium, cadmium, manganese, zinc, aluminium, beryllium, bismuth, lead and mercury: No precipitate was obtained on addition of the reagent to the solution containing any of the
above cations, however on raising the pH, by the addition of a dilute ammonium hydroxide solution, the respective hydroxides precipitated.

**Copper and nickel in presence of each other:** Copper and nickel in presence of each other were detected with this reagent in exactly the same manner as with the aceto-phenone oxime by a control of pH. Copper precipitated near pH 3.0 and nickel above pH 5.0. It was observed that in this mixture copper could be preferentially precipitated up to pH 6.5, but above this pH copper and nickel co-precipitated.

**Copper and cobalt in presence of each other:** Copper and cobalt were also detected in presence of each other by controlling the pH. The procedure adopted was the same as that for copper-cobalt mixture using 2-hydroxy-5-methyl-acetophenone oxime. The copper complex precipitated near pH 3.0 while that of cobalt above pH 6.5. It was observed that in this mixture copper could be preferentially precipitated up to pH 8.0.

**Nickel and cobalt in presence of each other:** Nickel and cobalt were detected in presence of each other by a control of pH. The nickel complex precipitated near pH 5.0 and the cobalt complex above pH 6.5. It was observed that in this mixture nickel could be preferentially precipitated up to pH 8.0.
Copper, nickel and cobalt in presence of one another:

Detection of copper, nickel and cobalt in presence of one another was carried out by controlling the pH of the solution, the procedure being the same as that with 2-hydroxy-5-methylacetophenone oxime.

Copper in presence of other cations: (chromium, cadmium, zinc, aluminium, manganese, beryllium): Copper in presence of the above cations was detected by following the same procedure as that was followed for its detection using 2-hydroxy-5-methylacetophenone oxime.

 Nickel in presence of other cations: Nickel in presence of any of the above cations was detected by a control of pH. The procedure adopted was almost the same as that for nickel alone using 2-hydroxy-5-methylpropiophenone oxime.

Determinations of:

Copper: Copper was estimated using 2-hydroxy-5-methylpropiophenone oxime exactly in the same way as that with 2-hydroxy-5-methylacetophenone oxime. The results were quite in agreement with the calculated values and the error obtained was ± 0.54% (see Table X)

<table>
<thead>
<tr>
<th>Copper present.</th>
<th>Cu precipitate.</th>
<th>Cu found.</th>
<th>Error.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.06247 g</td>
<td>0.4138 g</td>
<td>0.05269 g</td>
<td>+ 0.00022 g</td>
</tr>
<tr>
<td>0.06247 g</td>
<td>0.4130 g</td>
<td>0.05257 g</td>
<td>+ 0.00012 g</td>
</tr>
<tr>
<td>0.06247 g</td>
<td>0.4128 g</td>
<td>0.05250 g</td>
<td>+ 0.00005 g</td>
</tr>
<tr>
<td>0.06247 g</td>
<td>0.4126 g</td>
<td>0.05242 g</td>
<td>- 0.00009 g</td>
</tr>
<tr>
<td>0.05124 g</td>
<td>0.2064 g</td>
<td>0.03126 g</td>
<td>+ 0.00002 g</td>
</tr>
<tr>
<td>0.05124 g</td>
<td>0.2060 g</td>
<td>0.03121 g</td>
<td>- 0.00003 g</td>
</tr>
</tbody>
</table>
The determination was then repeated in presence of (i) free hydrochloric acid and (ii) free acetic acid when it was observed that these acids prevented a complete precipitation of copper. The error observed was:

(i) -0.03% with hydrochloric acid and (ii) -10.3% with acetic acid.

**Copper in presence of nickel:** The same procedure was followed as that for the determination of copper alone keeping the pH between 3.0 to 3.5. Only copper was precipitated quantitatively and nickel remained in solution. The error observed was ± 0.10%.

**Copper in presence of cobalt:** The estimation was carried out following the same procedure as that for copper alone with the pH between 3.0 to 3.5. It was found that only copper quantitatively precipitated and cobalt remained in solution. The error observed was ± 0.10%.

**Copper in presence of other cations:** The estimation of copper in presence of other cations (see Table 1) was carried out by the usual procedure of precipitating it at the pH of about 3.0 to 3.5. The results were quite in agreement with the calculated values, the error observed being 2.0%. 


### TABLE XI

Estimation of Cu** in presence of other cations.

<table>
<thead>
<tr>
<th>Copper present</th>
<th>Cation added</th>
<th>Cu precip.</th>
<th>Cu found</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>present</td>
<td>Chromium</td>
<td>0.0120 g</td>
<td>0.0320 g</td>
<td>+0.0002 g</td>
</tr>
<tr>
<td></td>
<td>Cobalt</td>
<td>0.0120 g</td>
<td>0.0320 g</td>
<td>+0.0002 g</td>
</tr>
<tr>
<td></td>
<td>Manganese</td>
<td>0.0120 g</td>
<td>0.0320 g</td>
<td>+0.0002 g</td>
</tr>
<tr>
<td></td>
<td>Molybdenum</td>
<td>0.0120 g</td>
<td>0.0320 g</td>
<td>+0.0002 g</td>
</tr>
</tbody>
</table>

**Nickel**: Nickel was estimated using this reagent exactly under the same conditions as those with 2-hydroxy-3-methylisocynophene oxime. The results given in Table XI, were quite in agreement with those obtained by the standard method, the error being ±0.32%.

### TABLE XII

Estimation of Ni** using 2-Hydroxy-3-methylisocynophene oxime.

<table>
<thead>
<tr>
<th>Nickel present</th>
<th>Ni precipitate</th>
<th>Ni found</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>present</td>
<td>0.0315 g</td>
<td>0.0317 g</td>
<td>-0.0002 g</td>
</tr>
<tr>
<td></td>
<td>0.0315 g</td>
<td>0.0317 g</td>
<td>-0.0002 g</td>
</tr>
<tr>
<td></td>
<td>0.0315 g</td>
<td>0.0317 g</td>
<td>-0.0002 g</td>
</tr>
<tr>
<td></td>
<td>0.0315 g</td>
<td>0.0317 g</td>
<td>-0.0002 g</td>
</tr>
<tr>
<td></td>
<td>0.0315 g</td>
<td>0.0317 g</td>
<td>-0.0002 g</td>
</tr>
<tr>
<td></td>
<td>0.0315 g</td>
<td>0.0317 g</td>
<td>-0.0002 g</td>
</tr>
<tr>
<td></td>
<td>0.0315 g</td>
<td>0.0317 g</td>
<td>-0.0002 g</td>
</tr>
<tr>
<td></td>
<td>0.0315 g</td>
<td>0.0317 g</td>
<td>-0.0002 g</td>
</tr>
</tbody>
</table>
The same procedure was then repeated except that sodium acetate solution was used to raise the pH of the solution. The results were quite satisfactory, the error being ± 2.9%.

**Nickel in presence of copper:** The estimation of nickel in presence of copper was carried out exactly in the same way as that using 5-hydroxy-5-methylisourea oxime. The value thus obtained was quite in agreement with the theoretical value, the error observed being ± 4.3%.

**Nickel in presence of cobalt:** The procedure was the same as that followed for the estimation of nickel alone with the pH at about 3.5. It was found that at pH 3 only nickel completely precipitated while cobalt remained in solution. The error observed was ± 3.1%.

**Nickel in presence of other cations:** For the estimation of nickel in presence of other cations (see Table III), the usual procedure was adopted. The pH of 3.5 being raised by addition of sodium acetate solution when precipitation occurred.

### Table III

**Estimation of Ni** in presence of other cations. 

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0156</td>
<td>Ni</td>
<td>0.0156</td>
<td>0.0156</td>
<td>0.0156</td>
</tr>
<tr>
<td>0.0156</td>
<td>Ni</td>
<td>0.0156</td>
<td>0.0156</td>
<td>0.0156</td>
</tr>
<tr>
<td>0.0156</td>
<td>Ni</td>
<td>0.0156</td>
<td>0.0156</td>
<td>0.0156</td>
</tr>
<tr>
<td>0.0156</td>
<td>Ni</td>
<td>0.0156</td>
<td>0.0156</td>
<td>0.0156</td>
</tr>
<tr>
<td>0.0156</td>
<td>Ni</td>
<td>0.0156</td>
<td>0.0156</td>
<td>0.0156</td>
</tr>
<tr>
<td>0.0156</td>
<td>Ni</td>
<td>0.0156</td>
<td>0.0156</td>
<td>0.0156</td>
</tr>
</tbody>
</table>
The results obtained were in agreement with the calculated values, the error being - 0.06%.

(Copper and nickel in presence of each other) Solution containing copper and nickel ions in different proportions (Cu: Ni = 1:1; 1:6; 10:1) was estimated with this reagent. The procedure was the same as for the individual estimation of copper and nickel in presence of the other using 1-hydroxy-2-methylpropophenone oxime (see Table XIV). The error obtained was: Cu**: 0.13% and Ni**: 0.06%.

Table XIV

Estimation of Cu** and Ni** in presence of each other using 1-hydroxy-2-methylpropophenone oxime.

<table>
<thead>
<tr>
<th>Serial No.</th>
<th>Cu** : Ni**</th>
<th>1:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Serial No.</td>
<td>Cu** : Ni**</td>
<td>1:6</td>
</tr>
<tr>
<td>Serial No.</td>
<td>Cu** : Ni**</td>
<td>1:0</td>
</tr>
</tbody>
</table>

Cu**Cl₂

C₂O₂

Drying temp. 100°C

Co factor for Cu** 1:1.1 0.8

Co factor for Ni** 1:1.1.10

<table>
<thead>
<tr>
<th>F</th>
<th>Copper</th>
<th>Nickel</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00397</td>
<td>0.943</td>
</tr>
<tr>
<td>2</td>
<td>0.00902</td>
<td>0.943</td>
</tr>
<tr>
<td>3</td>
<td>0.00397</td>
<td>0.943</td>
</tr>
</tbody>
</table>

Cobalt: Cobalt was estimated with this reagent according to the same conditions as those with 1-hydroxy-2-methylpropophenone oxime. The results, given in the Table XV, were in agreement with the calculated values, the error being - 0.4.
Table 3

Estimation of Co⁺⁺ using 2-hydroxy-2-methylpropionicophenone oxime.

<table>
<thead>
<tr>
<th>Cobalt₂⁺ (g)</th>
<th>Lying temp. (°C)</th>
<th>Log. factor = 1.43</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2042</td>
<td>0.0102 g</td>
<td>0.0025 g</td>
<td>-0.0015</td>
</tr>
<tr>
<td>0.2042</td>
<td>0.0100 g</td>
<td>0.0025 g</td>
<td>-0.0015</td>
</tr>
<tr>
<td>0.2042</td>
<td>0.0110 g</td>
<td>0.0035 g</td>
<td>-0.0028</td>
</tr>
<tr>
<td>0.2050</td>
<td>0.0110 g</td>
<td>0.0035 g</td>
<td>-0.0028</td>
</tr>
<tr>
<td>0.2050</td>
<td>0.0105 g</td>
<td>0.0031 g</td>
<td>-0.0029</td>
</tr>
<tr>
<td>0.2050</td>
<td>0.0105 g</td>
<td>0.0027 g</td>
<td>-0.0030</td>
</tr>
</tbody>
</table>

The above procedure was repeated except that sodium acetate solution was used to raise the pH. The error was -0.05.

Cobalt in presence of copper: The estimation was carried out exactly in the same way as with 2-hydroxy-2-methylacetophenone oxime described earlier. The results were in agreement with the calculated values, the error being -0.05%.

Cobalt in presence of nickel: The procedure was the same as that followed for the individual determination of cobalt in presence of the other using 2-hydroxy-2-methylacetophenone oxime which has been described earlier. The results were quite in agreement with the theoretical value, the error being -0.10%.
Cobalt and copper in presence of each other: The same procedure as that followed for the individual determination of copper and cobalt in presence of the other, discussed earlier, was adopted. The results obtained were quite in agreement with the theoretical value. The error being: \( Cu^{2+} = 0.005 \) and \( Co^{2+} = 0.015 \).

Cobalt and nickel in presence of each other: The procedure adopted was the same as that described for the determination of cobalt and nickel in presence of the other using \( 3 \)-hydroxy-1-methylacetophenone oxine. The results obtained were quite in agreement with the theoretical value. The error was: \( Ni^{2+} = 0.005 \) and \( Co^{2+} = 0.005 \).

Copper, nickel and cobalt in presence of each other: The same procedure was adopted as that described for the determination of the above three ions in presence of one another using \( 3 \)-hydroxy-1-methylacetophenone oxine. The results were quite in agreement with the theoretical value. The error being: \( Cu^{2+} + Ni^{2+} \):

\( \text{Cu}^{2+} = 0.003 \) and
\( \text{Ni}^{2+} = 0.015 \).
A.-hydroxy-3-methylbenzophenone oxime.

The reagent: A.-hydroxy-3-methylbenzophenone oxime was prepared as described in the experimental. A 0.3% solution in 95% ethanol was used for all qualitative tests, while a 0.03% solution was used during quantitative determinations.

Detection of:

Copper: On dropping addition of the reagent to the copper ion solution at a pH 5.0 to 6.5, a faintly olive green precipitate of the copper complex was obtained. This reagent could detect Cu++ up to a dilution of 1.0 %, and opalescence could be observed up to a dilution of 0.05 %.

The copper A.-hydroxy-3-methylbenzophenone oxime possessed properties similar to the copper A.-hydroxy-2-methylacetophenone oxime as regards its solubility in non-polar solvents and aikalis and its reaction with mineral acids and lactic acetic acid.

Nickel: Nickel was detected using the A.-hydroxy-3-methylbenzophenone oxime following the procedure adopted for its detection using the other oximes. The other properties of the complex, viz., the pH for precipitation, constancy, solubility in non-polar solvents and aikalis as also the effect of acids, were the same as those of nickel A.-hydroxy-2-methylacetophenone oxime.

Cobalt: The procedure used for the detection of cobalt
using 2-hydroxy-5-methylbenzophenone oxime was the same as that with other oximes. A dark reddish brown mass was obtained at pH 6.5. The complex behaved in the same manner as the other cobalt complexes so far as its sensitivity, solubility in non-polar solvents, and alkaline, and the effect of acids are concerned.

**Palladium** Palladium was detected using 2-hydroxy-5-methylbenzophenone oxime as with other oximes described. The pH for precipitation, solubility in non-polar solvents and alkaline, and the effects of acids on the palladium complexes resembled those of the other palladium complexes.

**Iron** Iron was detected in the same manner as it was detected using 2-hydroxy-5-methylbenzophenone oxime. The other properties of the iron 2-hydroxy-5-methylbenzophenone oxime are the same as those of iron 3-hydroxy-5-methylbenzophenone oxime.

**Copper** A reddish brown solution was obtained on dropping a solution of the reagent to a copper ion solution at pH 4.0 to 5.0; but on raising the pH with ammonium hydroxide to above 6.0 a reddish precipitate of copper hydroxide was obtained.

Cadmium, calcium, copper, zinc, aluminium, silver, nickel, lead and mercury; to precipitated was obtained on addition of the reagent to a solution containing any of the above cations; however, on raising the pH by adding a dilute ammonium hydroxide solution the respective
Hydrates precipitated.

Copper and nickel in presence of each other: Copper and nickel in presence of each other were detected adopting the same procedure as with other oximes and by controlling the pH.

Copper and cobalt in presence of each other: The procedure adopted was the same as that for a copper-cobalt mixture with 2-hydroxy-3-methylacetophenone oxime.

Nickel and cobalt in presence of each other: Nickel and cobalt were detected in presence of each other by a control of pH. The procedure was the same as that for nickel-cobalt mixture using other oximes.

Copper, nickel and cobalt in presence of one another: The detection of copper, nickel and cobalt in presence of one another was carried out following the same procedure as that followed with 2-hydroxy-3-methylacetophenone oxime.

Copper in presence of other oximes: (chromium, cadmium, zinc, aluminium, manganese, beryllium) Copper in presence of these oximes, was detected, by using a procedure similar to that followed for its detection with other oximes.

Nickel in presence of other oxides: Nickel in presence of any of the above mentioned oxides was detected by a control of pH, the procedure being the same as that for nickel alone.
**Sorption of Cu**

Copper was estimated using 2-hydroxy-2-methylbenzophenone oxime adopting the procedure earlier described for other oximes. The results (see Table 7.3) were quite in agreement with the calculated values, and the error obtained was +0.7%.  

**Table 7.3**

**Estimation of Cu** using 2-hydroxy-2-methylbenzophenone oxime.

<table>
<thead>
<tr>
<th>Copper present.</th>
<th>Cu precipitate.</th>
<th>Cu found.</th>
<th>Error.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0159 g</td>
<td>0.0186 g</td>
<td>0.0156 g</td>
<td>+ 0.003%</td>
</tr>
<tr>
<td>0.0589 g</td>
<td>0.0829 g</td>
<td>0.0587 g</td>
<td>+ 0.003%</td>
</tr>
<tr>
<td>0.0938 g</td>
<td>0.1119 g</td>
<td>0.0938 g</td>
<td>+ 0.003%</td>
</tr>
<tr>
<td>0.1637 g</td>
<td>0.1833 g</td>
<td>0.1632 g</td>
<td>+ 0.003%</td>
</tr>
<tr>
<td>0.0318 g</td>
<td>0.2952 g</td>
<td>0.3147 g</td>
<td>+ 0.003%</td>
</tr>
<tr>
<td>0.0318 g</td>
<td>0.2950 g</td>
<td>0.3149 g</td>
<td>+ 0.003%</td>
</tr>
</tbody>
</table>

The determination was then repeated in presence of
(i) free hydrochloric acid and (ii) free acetic acid when it was found that these acids prevented a complete precipitation of copper. The error observed was:

(i) +0.0% with hydrochloric acid

(ii) +0.0% with acetic acid.

**Copper in presence of Nickel:** The procedure followed was the same as that for copper alone and keeping the pH between 2.0 to 3.5. The error observed was 4.6%.  

```
Copper in presence of cobalt: The estimation was carried out following the same procedure as that for copper alone, keeping the pH between 3.0 to 3.5; the error observed being ±0.72%.

Copper in presence of other cations: The estimation of copper in presence of other cations (see Table VIII) mentioned in the table was carried out by the usual procedure of precipitating it at a pH of about 3.0 to 3.5. The results were quite in agreement with the calculated values, the error being ±0.72%.

**Table VIII.**

Estimation of Cu++ in presence of other cations.

<table>
<thead>
<tr>
<th>Cu₂O₂₅Ag₆</th>
<th>Drying temp. 100°C</th>
<th>Zn factor±T, ml.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>Cation added</td>
<td>Cu ppt.</td>
</tr>
<tr>
<td>present</td>
<td>base</td>
<td>amount</td>
</tr>
<tr>
<td>0.062450 g Chromium</td>
<td>0.0600</td>
<td>0.0098 g</td>
</tr>
<tr>
<td>0.06250 g Cadmium</td>
<td>0.0600</td>
<td>0.0100 g</td>
</tr>
<tr>
<td>0.06250 g Zinc</td>
<td>0.0625</td>
<td>0.0100 g</td>
</tr>
<tr>
<td>0.06250 g Aluminium</td>
<td>0.0671</td>
<td>0.0100 g</td>
</tr>
<tr>
<td>0.06250 g Manganese</td>
<td>0.0675</td>
<td>0.0100 g</td>
</tr>
<tr>
<td>0.06250 g Beryllium</td>
<td>0.0660</td>
<td>0.0100 g</td>
</tr>
</tbody>
</table>

Nickel: Nickel was estimated using this reagent exactly in the same manner as with other oximes. The results were quite in agreement with the calculated values, the error being ±0.32% (see Table VIII).
Table 4

Estimation of Si⁺⁺⁺ using 1-(Hydroxy)-carbolylic acetic oxime.

<table>
<thead>
<tr>
<th>Nickel present (g)</th>
<th>Si precipitate (g)</th>
<th>Si found (g)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.06154</td>
<td>0.5000</td>
<td>0.00189</td>
<td>+ 0.00535</td>
</tr>
<tr>
<td>0.06154</td>
<td>0.5070</td>
<td>0.00179</td>
<td>+ 0.00295</td>
</tr>
<tr>
<td>0.06154</td>
<td>0.5570</td>
<td>0.00190</td>
<td>+ 0.00305</td>
</tr>
<tr>
<td>0.06154</td>
<td>0.5560</td>
<td>0.00209</td>
<td>+ 0.00339</td>
</tr>
<tr>
<td>0.00773</td>
<td>0.2000</td>
<td>0.00089</td>
<td>+ 0.00014</td>
</tr>
<tr>
<td>0.00773</td>
<td>0.2500</td>
<td>0.00099</td>
<td>+ 0.00019</td>
</tr>
</tbody>
</table>

The same procedure was then repeated except that sodium acetate solution was used to raise the pH of the solution. The results were quite satisfactory, the error being ±0.4%. 

Nickel in presence of copper: The estimation was carried out adopting the same procedure as that with other oximes. The value thus obtained is quite in agreement with the theoretical value, the error being ±0.42%.

Nickel in presence of cobalt: The procedure followed was the same as that for nickel alone with the pH at about 9.5 when cobalt remained in solution. The error observed was ±0.49%.

The replacement of iron by calcium oxalate gives a good agreement with the theoretical value, the error being ±0.46%.
Nickel in presence of other cations: The estimation of nickel, in presence of various cations mentioned in the table IX, was carried out by the usual procedure of precipitating it at a pH of about 5.9. The results were quite in agreement with the calculated values, the error being ±0.5%.

**Table IX**

Estimation of Ni\(^{++}\) in presence of other cations.

\[\text{HClO}_{4} \cdot \text{O}_{2}\text{H}_{2}\] Drying temp. 100° Log factor = 1.03.

<table>
<thead>
<tr>
<th>Nickel present</th>
<th>Cation added</th>
<th>Ni ppt.</th>
<th>% found</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0001 g</td>
<td>Chromium</td>
<td>0.0003 g</td>
<td>0.0008 g</td>
<td>±0.0006 g</td>
</tr>
<tr>
<td>0.0001 g</td>
<td>Manganese</td>
<td>0.0003 g</td>
<td>0.0009 g</td>
<td>±0.0001 g</td>
</tr>
<tr>
<td>0.0001 g</td>
<td>Zine</td>
<td>0.0003 g</td>
<td>0.0009 g</td>
<td>±0.0001 g</td>
</tr>
<tr>
<td>0.0001 g</td>
<td>Magnesium</td>
<td>0.0003 g</td>
<td>0.0009 g</td>
<td>±0.0001 g</td>
</tr>
<tr>
<td>0.0001 g</td>
<td>Nickel</td>
<td>0.0003 g</td>
<td>0.0009 g</td>
<td>±0.0001 g</td>
</tr>
</tbody>
</table>

Copper and nickel in presence of each other: The solution containing copper and nickel ions in various proportions (Cu:Ni = 1:1, 1:2, 1:3) was estimated for these cations adopting the procedure described with other oximes. (see Table IX). The error obtained was:

\[\text{Cu}^{++} \pm 0.025\% \text{ and } \text{Ni}^{++} \pm 0.03\%\]
### TABLE XX

**Titration of Cu²⁺ and Ba²⁺ in presence of each other using 2-Hydroxy-3-methylbenzophenone oxime.**

<table>
<thead>
<tr>
<th>Serial No.</th>
<th>Cu²⁺: Ba²⁺</th>
<th>Molar Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1:1</td>
<td>1:1</td>
</tr>
<tr>
<td>2</td>
<td>1:10</td>
<td>1:10</td>
</tr>
<tr>
<td>3</td>
<td>1:10</td>
<td>1:10</td>
</tr>
</tbody>
</table>

- CuCl₂·5H₂O
- BaCl₂·7H₂O
- Drying temp. = 120°C
- Log factor for Cu = 1.5370
- Log factor for Ba = 1.2929

<table>
<thead>
<tr>
<th>Sr.</th>
<th>Copper Complex Found</th>
<th>Error</th>
<th>Nickel Complex Found</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Copper Solution (C)</td>
<td></td>
<td>Nickel Solution (C)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.00287</td>
<td>0.0110</td>
<td>+0.00059</td>
<td>0.00124</td>
</tr>
<tr>
<td>2</td>
<td>0.00347</td>
<td>0.0159</td>
<td>+0.00022</td>
<td>0.000154</td>
</tr>
<tr>
<td>3</td>
<td>0.003247</td>
<td>0.0101</td>
<td>+0.00041</td>
<td>0.00154</td>
</tr>
</tbody>
</table>

**Notes:** Copper was estimated using this reagent under the same conditions as those with other oximes. The results were quite in agreement with the calculated values, the error being +0.40%.

### TABLE XXI

**Titration of Cu²⁺ using 2-Hydroxy-3-methylbenzophenone oxime.**

<table>
<thead>
<tr>
<th>CuCl₂·5H₂O</th>
<th>Drying temp. = 120°C</th>
<th>Log factor = 1.5370</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Obtained</td>
<td>Co precipitate.</td>
<td>Co found.</td>
</tr>
<tr>
<td></td>
<td>CoCl₂·H₂O.</td>
<td></td>
</tr>
<tr>
<td>0.05098 g</td>
<td>0.0509 g</td>
<td>0.0509 g</td>
</tr>
<tr>
<td>0.05098 g</td>
<td>0.0509 g</td>
<td>0.0509 g</td>
</tr>
<tr>
<td>0.05098 g</td>
<td>0.0509 g</td>
<td>0.0509 g</td>
</tr>
<tr>
<td>0.05098 g</td>
<td>0.0509 g</td>
<td>0.0509 g</td>
</tr>
<tr>
<td>0.05098 g</td>
<td>0.0509 g</td>
<td>0.0509 g</td>
</tr>
</tbody>
</table>
The above procedure was repeated using sodium acetate solution for raising the pH of the solution; the error observed was ±0.5%. 

**Cobalt in presence of copper**: The estimation was carried out in the same way as with other oximes described earlier. The results were in agreement with the calculated values, the error being ±0.5%. 

**Cobalt in presence of nickel**: The same procedure as that for the individual estimation of cobalt and nickel with other oximes described, was adopted. The results were quite in agreement with the theoretical value, the error being ±0.5%. 

**Cobalt and copper in presence of each other**: The procedure followed was the same as that for the individual determination of copper and cobalt in presence of the other already discussed. The results were quite in agreement with the theoretical value. The error was: Cu2+ ±0.3% and Co2+ ±0.5%. 

**Cobalt and nickel in presence of each other**: Of cobalt and nickel in presence of the other were individually estimated adopting the same procedure described with other oximes. The results were in agreement with the calculated values, the error being: Ni2+ ±0.3% and Co2+ ±0.5%. 


Copper, nickel and cobalt in presence of one another; the procedure used was the same as that already described for the determination of these ions in presence of one another with other ions. The results were quite satisfactory, the error being: \( \text{Cu}^{++} \pm 0.002, \text{Ni}^{++} \pm 0.003 \) and \( \text{Co}^{++} \pm 0.1 \).
Preparation of solutions:

Copper sulphate (CuSO₄·(H₂O)₂·3H₂O):

Copper sulphate of extra pure quality was crystallised as a blue pentahydrate, dried and 0.6 g. of it was dissolved in distilled water and made to two litres to get a decimolar solution.

Standardisation:

Volumetrically:


10 ml. of the copper sulphate solution pipetted out in a conical flask was treated with sodium bicarbonate to remove mineral acidity followed by 2 ml. of dilute nitric acid and 10 ml. 10% potassium iodide solution. 0.1N sodium thiosulphate solution from a burette was added dropwise till a pale yellow tint developed, 2 ml. starch solution was added and titration continued till a distinct violet colour developed.

10 ml. of copper sulphate = 0.3 ml. 0.1N Sodium thiosulphate.

= 0.9413 g. Cu²⁺

= 0.2463 g. Cu₂S₂O₃ (m.p.)

(1 ml. of 0.1N Na₂S₂O₃ = 0.00527 g. Cu²⁺).

Spectrophotometrically (as oxide):

To 10 ml. of the copper sulphate solution diluted to about 100 ml. was added gradually about 25 cc. sodium hydroxide solution till all the copper precipitated as copper hydroxide. The precipitate was digested on a water-bath for about half an hour, filtered through the Whatman filter paper No. 4 and washed off sodium hydroxide completely with distilled water. It was then dried and ignited to convert into copper oxide.

10 ml. of CuSO₄ solution = 0.0082 g. of Cu₂O₄
= 0.0087 g. of Cu⁺⁺
= 0.0173 g. of Cu₂O₂

Approximately (with salicylaldoxime):


To 10 ml. of the copper sulphate solution diluted to about 100 ml. 25 cc. sodium hydroxide was added to produce a precipitate which was then brought into solution by the addition of acetic acid. A 25 solution of salicylaldoxime in 95 per cent. ethanol was dropped added at room temperature till the precipitation was complete. The precipitate was filtered through a previously weighed sintered glass crucible and washed with cold water till free from the reagent. It was dried to a constant weight at 100° to 105°.

10 ml. of copper sulphate = 0.0080 g. Copper salicylaldoxime.
= 0.0085 g. of Cu⁺⁺
= 0.0170 g. of Cu₂O₂.
Nickel sulphate (0.1%, NiO, 7H₂O):

Nickel sulphate of extra pure quality was crystallized as a green heptahydrate, dried, and 50.0 g. of it was dissolved in distilled water and made to two litres to get a decimolar solution.

Standardization:

Ref: Visc. quixie, p. 20-23.

To 10 ml. of the nickel sulphate solution diluted to about 50 ml. was warmed and doppedwise added a 2% solution of dimethyl glyoxime in ethanol 95%, sufficient to completely precipitate nickel, then a dilute ammonium hydroxide solution was added doppedwise till there was a persistent white. The red precipitate was digested for about half an hour, filtered through a stationary glass crucible, washed with hot water, dried at 180° for an hour and weighed.

10 ml. of nickel sulphate solution = 0.200 g. of nickel dimethyl glyoxime.

= 0.0195 g. of Ni²⁺.

= 0.0044 g. of Ni-C₂O₄. 7H₂O.

Cobalt chloride (0.1%, CoCl₂, 6H₂O):

Cobalt chloride of extra pure quality was crystallized as a pink hemihydrate and dried, 57.5 g. of the above crystals were dissolved in distilled water and the solution was made to two litres so as to get a decimolar solution.

Standardization:

Ref: Visc. quixie, p. 20-23.
9 ml. of the above solution diluted to 1 ml. containing 10 drops of 100 volume hydrogen peroxide was treated with 20 cmole sodium hydroxide to precipitate cobalt as cobaltic hydroxide. 10 ml. of glacial acetic acid was added to dissolve the precipitate and diluted to 25 ml. with boiling water and treated with a freshly prepared solution of \( \text{N-nitroso-}\beta\text{-napthol} \) till the precipitation was complete. It was heated to boiling with vigorous stirring till the precipitate settled, filtered through a sintered glass crucible, washed with 20 cmole acetic acid and finally with boiling water, dried at 120° and recrystallized as cobalt \( \text{N-nitroso-}\beta\text{-napthol} \).

5 ml. of cobalt chloride solution = 0.001 gm. of \( \text{N-nitroso-}\beta\text{-napthol} \).

i.e. 10 ml. of cobalt chloride solution = 0.002 gm. of \( \text{N-nitroso-}\beta\text{-napthol} \).

The following solutions of strength indicated were prepared for qualitative tests causing appropriate amount of the substances, adding mineral acid if required, and diluting it to 250 ml. with distilled water.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Amount</th>
<th>Strong. Acid if added</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCl₃</td>
<td>0.25 g</td>
<td>3.15 hydrochloric acid</td>
</tr>
<tr>
<td>FeCl₂·6H₂O</td>
<td>0.56 g</td>
<td>3.15 nitric acid</td>
</tr>
<tr>
<td>FeCl₂·3H₂O</td>
<td>0.75 g</td>
<td>3.15</td>
</tr>
<tr>
<td>Substance</td>
<td>Amount</td>
<td>strength</td>
</tr>
<tr>
<td>---------------------------</td>
<td>---------</td>
<td>----------</td>
</tr>
<tr>
<td>Fe₂(CO₃)₃·9H₂O</td>
<td>0.05 g</td>
<td>0.0225</td>
</tr>
<tr>
<td>Co₂(CO₃)₃·3H₂O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCl₂·2H₂O</td>
<td>0.66 g</td>
<td>0.15</td>
</tr>
<tr>
<td>BaCl₂·2H₂O</td>
<td>3.61 g</td>
<td>0.05</td>
</tr>
<tr>
<td>Ba(NO₃)₂·4H₂O</td>
<td>5.90 g</td>
<td>0.15</td>
</tr>
<tr>
<td>MnO₂·Y₂H₂O</td>
<td>7.10 g</td>
<td>0.15</td>
</tr>
<tr>
<td>Al₄(OH)₃·15H₂O</td>
<td>8.53 g</td>
<td>0.09</td>
</tr>
<tr>
<td>ZnCO₃·2H₂O</td>
<td>4.42 g</td>
<td>0.10</td>
</tr>
<tr>
<td>Bi(NO₃)₃·5H₂O</td>
<td>6.06 g</td>
<td>0.05</td>
</tr>
<tr>
<td>Pb(NO₃)₂</td>
<td>0.25 g</td>
<td>0.10</td>
</tr>
<tr>
<td>LiCl₂</td>
<td>0.79 g</td>
<td>0.15</td>
</tr>
</tbody>
</table>
2-Acetoxymethylacetophenone oxime.

Preparation of 2-Acetoxymethylacetophenone oxime:

acetate

Cold 2M hydrochloric acid, then added slowly with stirring to a solution of 2-Acetoxymethylacetophenone in methanol. The precipitate formed was filtered, washed with cold methanol, and dried. The acetate obtained was colorless in thin-layer chromatography, Rf 0.8. The acetate was then treated with 2M hydrochloric acid, filtered, and dried. The precipitate formed was filtered, washed with cold methanol, and dried. The oxime obtained was colorless in thin-layer chromatography, Rf 0.8.

Hydroxylamine hydrochloride method:

6.95 g of 2-Acetoxymethylacetophenone oxime were dissolved in a minimum amount of distilled water. The solution was cooled to 0°C and treated with a solution of 2M hydrochloric acid. The precipitate formed was filtered, washed with cold methanol, and dried. The oxime obtained was colorless in thin-layer chromatography, Rf 0.8.
The oxime is sparingly soluble in cold water, easily in hot; it is also easily soluble in ethanol, chloroform, benzene, toluene, xylene, carbon tetrachloride, ether and petroleum ether.

Preparation of the stock-solution of 2-hydroxy-1-methylcinnophenone oxime:

1 g of recrystallized oxime was dissolved in 200 ml of 95% ethanol to get a 1% solution for qualitative tests. A 2% solution was similarly prepared for gravimetric determinations.

Effect of the solvent on different cations:

Copper:

1% 2-hydroxy-1-methylcinnophenone oxime solution was drop by drop added to 1 ml of a warm decinolar copper sulphate solution when a faintly olive green precipitate was obtained. The tests were performed with different pH. The precipitate was obtained at pH as low as 2.0 and as high as 11.0, and even in Beiling's solution. At lower pH however, it was found that mineral acid and glacial acetic acid decomposed the complex, as the oxime could be recovered from the solution. At higher pH, in strong alkali, the complex was found to go in solution, which could be reprecipitated on dilution. For complete precipitation the pH range 3.0 to 2.5 is suitable.

The copper complex was found to be easily soluble in
chloroform, carbon tetrachloride, benzene, toluene and xylene with the development of an olive green colour. The solution was stable and could be kept for weeks without any decomposition. It was insoluble in ether, petroleum ether and ethanol.

**Sensitivity**

1 ml. of 0.25 solution of copper sulphate (H₂SO₄ : 2 copper) was progressively diluted and treated with drops of 1% of 2-hydroxy-2-methylpropiophenone oxime solution. The results are tabulated below:

<table>
<thead>
<tr>
<th>Dilution</th>
<th>V/ml.</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 : 1</td>
<td>10</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>5000</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>7500</td>
<td>1.04</td>
</tr>
</tbody>
</table>

**Nickel**

To 1 ml. of the above 0.25 molar solution of nickel sulphate was added 1% 2-hydroxy-2-methylpropiophenone oxime solution; no precipitate was obtained but on addition of dilute ammonia or sodium acetate (i.e., by raising the pH) a green precipitate was obtained. The precipitate could be obtained between pH 5.0 to 12.0; for complete
precipitation the pH range was 2.5 to 6.9. The complex decomposed when treated with mineral acids and glacial acetic acid with the separation of the azine and dissolved in strong alkaline and ammonia on boiling, from which it reprecipitated on dilution.

The nickel complex was found to be easily soluble in chloroform, carbon tetrachloride, benzene, toluene and xylene giving a green stable solution, which could be kept for weeks without any decomposition. It was insoluble in ether, petrolæum ether, and ethanol.

**Sensitivity:**

1 ml. of 0.1M solution of nickel sulphate \( \frac{1}{2}\)\( \text{M} \) (nickel) was progressively diluted and treated with 2 drops of 1% 2-hydroxy-5-methylanthranilic acid solution followed by 2 drops of very dilute ammonium hydroxide solution. The results are tabulated below:

<table>
<thead>
<tr>
<th>Dilution</th>
<th>( \text{V/ML} )</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 : 10</td>
<td>500</td>
<td>Precipitate.</td>
</tr>
<tr>
<td>20</td>
<td>295</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>99.6</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>39.5</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>14.66</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>11.72</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>5.86</td>
<td></td>
</tr>
<tr>
<td>5000</td>
<td>1.17</td>
<td>Turbidity on boiling, and</td>
</tr>
<tr>
<td>7,000</td>
<td>0.78</td>
<td>keeping azide.</td>
</tr>
</tbody>
</table>
Cobalt

13 2-hydroxy-2-methylacetoephone oxime solution was drop by drop added to 1 ml. of the warm 0.1M solution of cobalt chloride, when no precipitate was obtained; however, on raising the pH by adding dilute ammonium hydroxide or sodium acetate solution drop by drop, all the cobalt was precipitated as a deep yellow-brown mass. The precipitate of the cobalt complex could be obtained between pH 7 to 10.0, for complete precipitation, the pH range was 7.5 to 9.0. Dilute or concentrated mineral acids and also glacial acetic acid decomposed the complex and the oxime separated out. The complex was soluble in caustic alkalis and ammonium hydroxide on boiling but it reprecipitated on dilution.

The cobalt complex was found to be easily soluble in chloroform, carbon tetra-chloride, benzene, toluene and xylene giving a faintly reddish brown solution which was fairly stable and could be kept for weeks without decomposition.

Sensitivity

1 ml. of 0.1M solution of cobalt chloride ( = 0.00299 g. cobalt) was progressively diluted and coated with 2 drops of 13 2-hydroxy-2-methylacetoephone oxime solution followed by a very dilute solution of ammonium hydroxide.
The results are tabulated below:

<table>
<thead>
<tr>
<th>Dilution</th>
<th>Vol.</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 : 1</td>
<td>10</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>1.23</td>
</tr>
<tr>
<td></td>
<td>7500</td>
<td>0.0006</td>
</tr>
</tbody>
</table>

**Palladium**

15 L-β-hydroxy-β-methylcetophenone ozone was drop by drop added to 1 ml. of the warm 0.1N solution of palladium chloride, when a yellow precipitate was obtained (pH 1.0-1.2). The complex decomposed if treated with strong hot mineral acids and glacial acetic acid and ozone separated. Straw, caustic alkalis and ammonia also dissolved the complex which reprecipitated on diluting with water.

The palladium complex dissolved in chloroform, carbon tetrachloride, benzene, toluene and xylene giving a reaction yellow solution. It was insoluble in ether, petrol ether and ethanol.

**COMMENT**

15 L-β-hydroxy-β-methylcetophenone ozone a solution was drop by drop added to 1 ml. of the warm decinolar solution
of ferric ammonium sulphate when a violet colored solution was obtained between pH 4.0 to 5.0. On raising the pH to 5.5 to 7.0 a reddish precipitate was formed. The complex was decomposed by acids.

The complex is soluble in chloroform, carbon, tetra-chloride, benzene, toluene and xylene giving a red solution. It is insoluble in ether, petroleum ether and ethanol.

**Experiment**

15 2-hydroxy-5-methylacetoacetone oxime solution was drop by drop added to 1 ml. of the warm acetic acid solution of ferric chloride; when a reddish brown colored solution was obtained between pH 4.0 to 5.0, on raising the pH above 6.0 a precipitate of ferric hydroxide (with ammonium hydroxide) and basic ferric acetate (with sodium acetate) was obtained.

Chromium, cadmium, manganese, zinc, aluminium, beryllium, Eisen, lead, mercury.

To 1 ml. of each of the above warm salt solution was added 15 2-hydroxy-5-methylacetoacetone oxime solution. No precipitate of the complex was obtained even on boiling or by raising the pH with dilute ammonium hydroxide, however, their respective hydroxides precipitated.

**Detection of copper and nickel in presence of each other:**

1 ml. each of 0.01 m solutions of copper sulphate and nickel sulphate were mixed, warmed and an excess of 15

2-hydroxy-5-methylacetoacetone oxime solution was drop by
drop added when a faintly olive green precipitate of copper 2-hydroxy-2-methylacetoephone oxime was obtained at \( \text{pH} \) 7.5 which was filtered off.

To the warmed filtrate was added a few drops of dilute aqueous ammonium hydroxide or sodium acetate solution when a green precipitate of nickel 2-hydroxy-2-methylacetoephone oxime was obtained at pH 9.0 to 9.5.

It was observed that in a mixture of these two solutions, copper got preferentially precipitated up to pH 7.5 and above that pH nickel co-precipitated.

**Detection of copper and cobalt in presence of nickel oxime**

1 ml. each of 0.1M solutions of copper acetate and cobalt chloride were mixed, warmed and an excess of a 2-hydroxy-2-methylacetoephone oxime solution was kept in drop and a drop added when a faintly olive green precipitate of copper 2-hydroxy-2-methylacetoephone oxime was obtained at pH 7.5 which was filtered off.

To the warm filtrate was added a few drops of dilute aqueous ammonium hydroxide or sodium acetate solution a brownish precipitate of cobalt 2-hydroxy-2-methylacetoephone oxime was obtained at pH 9.0 to 9.5.

It was observed that in a mixture of these two solutions, copper got preferentially precipitated up to pH 7.5.
Detection of nickel and cobalt in presence of each other.

1 ml. each of 0.1M solutions of nickel sulphate and cobalt chloride were mixed, warmed and an excess of 1-
2-hydroxy-5-methylacetophenone oxime was added followed by a dilute solution of sodium acetate, when a green precipitate of nickel 2-hydroxy-5-methylacetophenone oxime was obtained at pH 6.5 which was filtered off.

To the warmed filtrate was added a few drops of dilute aqueous ammonium hydroxide, when a brownish precipitate of cobalt 2-hydroxy-5-methylacetophenone oxime was obtained at pH 8.5 to 9.0.

It was observed that in a mixture of these two oximes, nickel got preferentially precipitated up to pH 11.

Detection of copper, nickel and cobalt in presence of another using 2-hydroxy-5-methylacetophenone oxime:

If 2-hydroxy-5-methylacetophenone oxime solution was drop by drop added in excess to the warm solution containing copper sulphate, nickel sulphate and cobalt chloride (0.1M; 1 ml. each), when a faintly olive green precipitate of copper 2-hydroxy-5-methylacetophenone oxime was obtained (pH = 7.0) which was filtered off, to the warmed filtrate was added a few drops of sodium acetate solution, when precipitate of nickel 2-hydroxy-5-methylacetophenone oxime was obtained (pH = 6.5) which was filtered. In 2H1 more a warmed and a little dilute ammonium hydroxide was added to
raise the pH to about 4.0. Cobalt precipitated as a brownish mass.

**Copper in the Feinin's solution:**

To a mixture of 1 ml. each of the Feinin's solutions (A) and (B) a 1% solution of 3-hydroxy-1-methylacetophenone oxime solution was added dropwise. Very little precipitate was obtained which was soluble in chloroform. The above solution gave further precipitate on dilution which was also soluble in chloroform.

Copper in presence of other cations: (chromium chloride, cadmium sulphate, zinc sulphate, aluminium sulphate, copper sulphate, and barium sulphate)

1 ml. of 0.1M copper sulphate solution was mixed with 1 ml. of 0.1M solution of the desired cation, aqueous 3-hydroxy-1-methylacetophenone oxime was added dropwise when a faintly olive green precipitate of copper 3-hydroxy-1-methylacetophenone oxime was obtained keeping the other in solution (pH 3.0 to 3.5).

Copper in presence of iron(II) ammonium sulphate, iron(II) ammonium sulphate;

1 ml. of 0.1M copper sulphate solution was mixed with 1 ml. of solution containing iron(II) ammonium sulphate, and was treated with ammonium hydroxide solution followed by acetic acid solution, sufficient amount of pale yellow citrate or Rochelle salt was then added. The green solution was warmed and treated with the 1% reagent, green copper complex precipitated keeping iron in solution.
Nickel in presence of other cations (chromium chloride, calcium sulphate, zinc sulphate, aluminium sulphate, beryllium sulphate, and magnesium sulphate):

1 ml. of 0.1 M nickel sulphate solution was mixed with 1 ml. of 0.1 M solution of the desired cation, warmed and 1 ml. of 3-hydroxy-5-methylacetoephone oxime was drop by drop added followed by sodium acetate solution to adjust the pH to about 5.5. The nickel complex precipitated keeping the other in solution.

Nickel in presence of iron (ferrous ammonium sulphate and ferric ammonium sulphate):

1 ml. of 0.1 M nickel sulphate solution and 1 ml. of solution containing iron (ferrous or ferric) were mixed and treated with dilute ammonium hydroxide solution followed by acetic acid solution, a sufficient amount of Rochelle salt or potassium citrate was then added, the green solution was warmed and treated with the 10% reagent followed by sodium acetate solution when nickel complex precipitated at pH 5.5 and iron remained in solution.

Quantitative estimations using 3-hydroxy-5-methylacetoephone oxime:

Estimation of copper:

To a definite amount (10 ml.) of the standard solution of copper sulphate was added a dilute solution of ammonium hydroxide or sodium hydroxide dropwise till a permanent sky blue precipitate developed. Dilute acetic acid was added to dissolve the precipitate adjusting the pH of the solution between 5.0 to 5.5; the volume was adjusted to
about 100 ml. The solution was warmed in a bath at about 70° to 80° and a 25% solution of \( \beta \)-hydroxy-\( \beta \)-methylacetoephone oxime was added dropwise till the precipitation was complete. The faintly olive green precipitate was then dried on a water-bath for about half an hour when all the precipitate settled down and a clear supernatent solution was observed. The precipitate was filtered hot through a sintered glass crucible and washed five to six times with hot water (to remove the oxime which is fairly soluble in hot water) followed by two to three washings by hot ethanol (95%) to remove the last traces of the oxime. The precipitate was dried at about 40° for an hour and weighed as copper \( \beta \)-hydroxy-\( \beta \)-methylacetoephone oxime.

**Results**

**Found:**

<table>
<thead>
<tr>
<th>10 ml. of copper sulphate</th>
<th>0.586</th>
<th>( \text{Cu}^{++} )</th>
<th>( \text{Cu}^{++} )</th>
</tr>
</thead>
</table>

**Caled:**

<table>
<thead>
<tr>
<th>10 ml. of copper sulphate</th>
<th>0.063297</th>
<th>( \text{Cu}^{++} )</th>
<th>( \text{Cu}^{++} )</th>
</tr>
</thead>
</table>

*All the results are given in table 6 as such.*

The estimation was also carried out with some variations in the procedure as under:

1. **10 ml. of the standard solution of copper sulphate** was warmed and directly treated with a 25% solution of \( \beta \)-hydroxy-\( \beta \)-methylacetoephone oxime without addition of ammonium hydroxide to remove the mineral acidity.
Result:

Found:

10 ml. of the copper sulphate = 0.0650 g. Copper(II) hydroxy
2-hydroxy-3-methylisoctophenone oxime.

= 0.0650 g. Cu²⁺

Calcd.:

10 ml. of the copper sulphate = 0.0650 g. Cu²⁺

\[ \text{error} = \frac{0.0650 - 0.0650}{0.0650} \]

= 0%

(ii) 10 ml. of the standard solution of copper sulphate
was treated with 5 ml. of concentrated hydrochloric acid,
warmed and a 25 solution of 2-hydroxy-3-methylisoctophenone
oxime was added as above till the precipitation was complete.
All the results are given in Table II on page 6.

Result:

Found:

10 ml. of the copper sulphate = 0.0695 g. Copper(II) hydroxy
2-hydroxy-3-methylisoctophenone oxime.

= 0.0695 g. Cu²⁺

Calcd.:

10 ml. of copper sulphate = 0.0695 g. Cu²⁺

\[ \text{error} = \frac{0.0695 - 0.0695}{0.0695} \]

= 0%

(iii) 10 ml. of the standard solution of copper sulphate
was treated with 10 ml. of glacial acetic acid except that a
25% solution of 2-hydroxy-3-methylisoctophenone oxime was added
as above till the precipitation was complete.
Results

Found:

10 ml. of the copper sulphate \( \equiv 0.5008 \text{ g. copper 2-hydroxy-5-methyleinocetophene oxime} \)

\( = 0.0508 \text{ g. Cu}^{++} \)

Calc:

10 ml. of the copper sulphate \( \equiv 0.0508 \text{ g. Cu}^{++} \)

\[ \therefore \text{Error} = 0.0000 \text{ g.} \]

= -0.2%

In the Fehling's solution:

A mixture of 10 ml. of the Fehling's solution (A) and 10 ml. of the Fehling's solution (B) was diluted exactly to 40 ml.

(i) Took 10 ml. from the above solution and estimated copper volumetrically as previously done.

Results:

10 ml. of the Fehling's solution \( \equiv 2.0 \text{ ml. CuSO}_4 \text{ -sulphate} \)

\( = 0.00035 \text{ g. Cu}^{++} \)

(ii) To 10 ml. of the diluted warm solution was added a 23 solution of 2-hydroxy-5-methyleinocetophene oxime drop-wise till the precipitation was complete. The colour of the supernatent solution was green. The precipitate was digested for half an hour, filtered through a sintered glass crucible, washed ten to fifteen times with hot water to remove the alkali and the oxime, dried at 100\(^\circ\) and subjected as copper 2-hydroxy-5-methyleinocetophene oxime.
Results

Found:
10 ml. of the Fehling's solution = 0.0562 g. copper 2-hydroxy-5-acetylacetophenone oxime.

= 0.05925 g. Cu^{++}

Calcd:
10 ml. of the Fehling's solution = 0.05025 g. Cu^{++}

:. Error = +0.0097 g.

= +1.95%

(iii) 10 ml. of the diluted solution was further diluted to 50 ml. warmed and a 25 solution of 2-hydroxy-5-acetylacetophenone oxime was added drop by drop till the precipitation was complete. The precipitate of copper 2-hydroxy-5-acetylacetophenone oxime was digested, filtered, washed, dried and weighed as usual.

Remita

Found:
10 ml. of the Fehling's solution = 0.015 g. copper 2-hydroxy-5-acetylacetophenone oxime.

= 0.01145 g. Cu^{++}

Calcd:
10 ml. of the Fehling's solution = 0.00925 g. Cu^{++}

:. Error = +0.0023 g.

= +0.25%

(iv) 10 ml. of the diluted solution was acidified with acetic acid, warmed and a 25 solution of 2-hydroxy-5-acetylacetophenone oxime was added drop by drop till the precipitation was complete. The precipitate of copper 2-hydroxy-5-acetylacetophenone oxime was digested, filtered, washed, dried and weighed as usual.
10 ml. of the kobali's solution = \( \text{Cu}^+\) + \( \text{O}_2 \) + \( \text{H}_2\text{O} \) + \( \text{H}^+ \)

0.0436 g

10 ml. of the kobali's solution = \( \text{Cu}^+\) + \( \text{O}_2 \) + \( \text{H}_2\text{O} \) + \( \text{H}^+ \)

0.0424 g

Sodium in presence of nickel:

10 ml. each of the standard solutions of sodium nitrate and nickel sulphate were mixed and treated with dilute ammonia hydroxide solution to make it a basic solution. Sodium acetate was then added to make the solution basic. Nickel was precipitated as nickel hydroxide and nickel remained in solution. The solution was then diluted to about 25 ml. and evaporated to 10 ml. of a 25% solution of sodium hydroxide code, and chlorine was evolved. The mixture was heated and the mixture was filtered. The filtrate was treated with nitric acid and the precipitate was filtered and washed with nitric acid. The precipitate was washed with dilute ammonia, washed with distilled water and dried at 100°C and weighed to a constant weight.

Equation:

10 ml. of copper sulphate = \( \text{Cu}^+\) + \( \text{O}_2 \) + \( \text{H}_2\text{O} \) + \( \text{H}^+ \)

0.0436 g

10 ml. of copper sulphate = \( \text{Cu}^+\) + \( \text{O}_2 \) + \( \text{H}_2\text{O} \) + \( \text{H}^+ \)

0.0424 g
Copper in presence of cobalt

10 ml. each of the standard solutions of copper sulphate and cobalt chloride were mixed. The procedure was followed as exactly as above.

Result:
Found:
10 ml. of copper sulphate = 0.3059 g. copper 3-hydroxy-5-methylacetophenone oxime.
= 0.06435 g. Cu**

Calcd:
10 ml. of copper sulphate = 0.05347 g. Cu**
• Error = +0.00035 g.
= +0.3555 g.

Copper in presence of iron

10 ml. of the standard solution of copper sulphate was mixed with 5 ml. of 0.10 solution of ferrous ammonium sulphate. The mixture was treated with a dilute solution of ammonium hydroxide till alkaline, when a reddish green precipitate developed. Dilute acetic acid was then added till the solution became acidic and the precipitate of the hydroxide dissolved with the development of a red colour. 2-3 g. of potassium nitrate were added to the above solution, the colour of the solution turned bluish green due to the formation of the complex of iron with the salt. The solution was then diluted to about 100 ml. and warmed to 70° 25 ml. of a 25 solution of 3-hydroxy-5-methylacetophenone oxime was then added dropwise, when the copper complex precipitated and iron remained in solution. The precipitate was digested for about half an hour,
when the bluish green colour of the solution gradually disappeared, it was filtered hot through a sintered glass crucible, washed with hot water, dried at 110° and solubilized to a constant weight.

Results

Found:

10 ml. of copper sulphate = 0.0384 g. copper (hexacyano-
triacetylacetone) oxide

= 0.03820 g. Cu^{++}

Calcd:

10 ml. of copper sulphate = 0.03824 g. Cu^{++}

Error = +0.00027 g.

(ii) the same estimation was repeated, however, gelatin
salts was used instead of potassium citrate.

Results

Found:

10 ml. of copper sulphate = 0.0382 g. copper (hexacyano-
triacetylacetone) oxide

= 0.03820 g. Cu^{++}

Calcd:

10 ml. of copper sulphate = 0.03824 g. Cu^{++}

Error = +0.0002 g.

(iii) 10 ml. of the standard solution of copper sulphate
was mixed with 5 ml. of 0.025N solution of ferric ammonium
sulphate. The above procedure was repeated using both potassium
citrate and gelatin salt.
**Results (potassium citrate)**

**Found:**

10 ml. of copper sulphate = 0.0627 g. copper (II) hydroxy-2-methylacetophenone chelate

= 0.00040 g. cu
t**

**Calcd.:**

10 ml. of copper sulphate = 0.0624 g. Cu
t

- Error = 0.0003 g.

= 0.03%.

**Results (cobalt salt)**

**Found:**

10 ml. of copper sulphate = 0.063% g. copper (II) hydroxy-2-methylacetophenone chelate

= 0.00057 g. cu
t**

**Calcd.:**

10 ml. of copper sulphate = 0.0624 g. Cu
t

- Error = 0.0001 g.

= 0.01%.

All the results are given in Tables III-IV (tol.) on page 34.

**Copper in presence of other cations:**

The solutions of chromium chloride, calcium nitrate, zinc sulphate, aluminium sulphate, manganese sulphate and beryllium sulphate prepared as described earlier, were used. 10 ml. of the standard solution of copper sulphate and 10 ml. of a standard solution containing the desired cation were mixed and the pH was adjusted to about 12.0 to 12.5. It was diluted to about 50 ml. and warmed to about 80°C. The solution of 2-hydroxy-2-methylacetophenone chelate (e.g. 50 ml.) was
then added when copper 2-hydroxy-3-methylacetophenone oxime precipitated. It was digested for about half an hour and filtered hot. It was washed with hot water followed by ethanol, dried at 130° and weighed to a constant weight.

All results are given in Table IV on page 2.

Determination of nickel

10 ml. of the standard solution of nickel sulfate, diluted to 50 ml. and heated to 50° to 60° was treated with the solution of 2-hydroxy-3-methylacetophenone oxime (25 ml. 10 ml.) no precipitate was obtained. A dilute solution of ammonium hydroxide was then added dropwise to raise the pH to 3.5, when a green precipitate of nickel 2-hydroxy-3-methylacetophenone oxime was obtained. The precipitate was then digested for about half an hour on a water-bath till it settled down. It was then filtered hot through a screened glass crucible, washed with hot water followed by ethanol, dried at about 120° for an hour and weighed to a constant weight.

Results

Found:
10 ml. of nickel sulfate = 0.0215 g. nickel 2-hydroxy-3-methylacetophenone oxime

= 0.006380 g. Ni

Calculated:
10 ml. of nickel sulfate = 0.0215 g. 14%

Error = -0.0001 g.

= -0.006380 g.

All the results are given in Table V on page 3.
The above estimation was repeated except that a solution of sodium acetate was used instead of a dilute solution of ammonium hydroxide to raise the pH to 3.5.

**Results**

**Found:**

10 ml. of nickel sulphate = 0.045 g.

\[ \text{nickel} \cdot \text{hydroxy} \cdot \text{methylacetophenone} \]

\[ = 0.041 \text{ g. Ni}^+ \]

**Found:**

10 ml. of nickel sulphate = 0.0015 g.

\[ \text{error} \quad = 0.0002 \text{ g.} \]

\[ = 0.325. \]

**Nickel in presence of copper:**

10 ml. each of the standard solutions of nickel sulphate and copper sulphate were mixed and treated with a dilute solution of ammonium hydroxide to make it just alkaline followed by 1 ml. of acetic acid to bring the pH to about 3.5 to 3.8. It was then diluted to about 500 to 700 ml. and warmed to 30°C. A excess of a 2% solution of 1-hydroxy-1-methylacetophenone oxime sufficient to precipitate both the ions was then added. When all the copper precipitated as copper 1-hydroxy-1-methylacetophenone oxime and nickel remained in solution, it was digested, filtered hot, washed with hot water and ethanol as usual.

The filtrate along with the washing was washed and treated with a dilute solution of ammonium hydroxide to raise the pH to 3.5 when nickel 1-hydroxy-1-methylacetophenone oxime
precipitated. It was digested, filtered, washed, dried and weighed as usual.

Result:

Found:

10 ml. of nickel sulphate = 0.0086 g. nickel = 0.0086 g. nickel sulphate, obtained crude.

= 0.0039 g. Ni**

Calcd.:

10 ml. of nickel sulphate = 0.0084 g. Ni**

= 0.0039 g.

Error = 0.0001 g.

Ni** in presence of cobalt:

A mixture of 10 ml. each of the standard solution of nickel sulphate and cobalt chloride diluted to about 60 ml. was boiled to 80°. 10 ml. of a 2% solution of the reagent was added followed by sodium acetate solution so as to make the pH to 4.5, when the nickel complex precipitated and cobalt remained in solution. It was digested, filtered, washed, dried and weighed as usual.

Results:

Found:

10 ml. of nickel sulphate = 0.0086 g. nickel = 0.0086 g. nickel sulphate, obtained crude.

= 0.0039 g. Ni**

Calcd.:

10 ml. of nickel sulphate = 0.0084 g. Ni**

= 0.0039 g.

Error = 0.0001 g.

Ni** in absence of iron:

10 ml. of the standard solution of nickel sulphate and 1 ml. of 15% solution of ferric ammonium sulphate were mixed and treated with 2-3 g. of Rochelle salt, when the colour of the solution turned faintly bluish green. The solution was then diluted to about 100 ml. and warmed to 70. 20 ml. of a 2% solution of 3-bromophenylacetophenone oxime was then added followed by a dilute solution of ammonium hydroxide or sodium acetate to raise the pH to about 9.5, when the nickel complex
separated and iron removed in solution. The precipitate was digested for about half an hour, filtered hot, washed, dried and weighed as unguar.

**Result:**

**Found:**

10 ml. of nickel sulphate = 0.463 g. nickel 2-hydroxy-2-
ethyipheheated cousins

= 0.0333 g. Ni++

**Calcd.**

10 ml. of nickel sulphate = 0.0315 g. Ni++

\[ \text{Error} = \frac{0.0333 - 0.0315}{0.0315} \times 100\% = +0.06\% \]

The sample estimation was repeated. However, potassium citrate was used instead of stoechiolic salt.

**Result:**

**Found:**

10 ml. of nickel sulphate = 0.0333 g. nickel 1-hydroxy-2-
ethyipheheated cousins

= 0.0333 g. Ni++

**Calcd.**

10 ml. of nickel sulphate = 0.0315 g. Ni++

\[ \text{Error} = \frac{0.0333 - 0.0315}{0.0315} \times 100\% = +0.06\% \]

10 ml. of the standard solution of nickel sulphate was mixed with 5 ml. of 0.02N solution of ferric ammonium sulphate. The above procedure was repeated using both potassium citrate and stoechiolic salt.
Results (Cadmium citrate):  
Found:  
10 ml. of nickel sulphate = 0.4896 g. nickel 1-hydroxy-3-methylacetophenone oxime  
= 0.4896 g. 91%  
Calcd.:  
10 ml. of nickel sulphate = 0.4923 g. 91%  
Error = +0.0027 g.  
= +0.0027%  

Results (Fuchsine salt):  
Found:  
10 ml. of nickel sulphate = 0.4865 g. nickel 1-hydroxy-3-methylacetophenone oxime  
= 0.4865 g. 93%  
Calcd.:  
10 ml. of nickel sulphate = 0.4854 g. 93%  
Error = -0.0011 g.  
= -0.0011%  

All the results are given in Table Vb and Vc on page 98.

Nickel in presence of other cations  
The solutions of ferrous chloride, cadmium citrate, zinc sulphate, aluminium sulphate, manganese sulphate and beryllium sulphate described earlier, were used.

A mixture of 10 ml. each of the standard solutions of nickel sulphate and the desired cation was diluted to about 50 ml. and heated to about 60°. 10 ml. of a 2% solution of 1-hydroxy-3-methylacetophenone oxime was added followed by
a dilute solution of sodium acetate to raise the pH to 3.5, when nickel precipitated as nickel 2-hydroxy-5-methyl acetone oxime. It was digested, filtered, washed, dried and weighed as usual.

All the results are given in Table VII on page 57.

Copper and nickel in presence of each other:

Copper-Nickel...III.

10 ml. each of the standard solutions of copper sulphate and nickel sulphate were mixed and treated with a dilute solution of ammonium hydroxide to raise the pH to 12, followed by 5 ml. acetic acid so as to bring the pH to about 3.5. The solution was diluted to about 50 ml. and cooled to 30°C. A 25 solution of 2-hydroxy-5-methyl acetone oxime (40 ml.) was then added, when copper 2-hydroxy-5-methyl acetone oxime precipitated. It was digested, filtered, washed, dried and weighed as usual.

The filtrate and washings were mixed together, filtered and treated with a dilute solution of ammonium hydroxide to raise the pH to about 5.5, when nickel 2-hydroxy-5-methyl acetone oxime precipitated. It was digested, filtered, washed, dried and weighed as usual.

Results:

<table>
<thead>
<tr>
<th>10 ml. of copper sulphate</th>
<th>0.505 g. copper 2-hydroxy-5-methyl acetone oxime acid.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5055 g. Cu++</td>
</tr>
<tr>
<td>10 ml. of copper sulphate</td>
<td>0.0527 g. Cu++</td>
</tr>
<tr>
<td>Error</td>
<td>0.0009 g. Cu++</td>
</tr>
<tr>
<td></td>
<td>+0.09%</td>
</tr>
</tbody>
</table>
Results:

Coulometry:

10 ml. of nickel sulphate = 3.386 g. nickel - by eq., -
 ex. Pt. electrode, hydrogen artery.

\[ \text{Cu}^{2+} + \text{Ni}^{2+} \rightarrow \text{Ni}^{2+} + \text{Cu}^{2+} \]

= 3.3864 g. \( \text{Cu}^{2+} \)

Calcd:

10 ml. of nickel sulphate = 3.15 g. \( \text{Cu}^{2+} \)

\( \text{Error} = \frac{3.3864 - 3.15}{3.15} \approx 7.4\% \)

Copper I Nickel II 10.1:

10 ml. of the standard solution of copper sulphate and 1 ml. of the standard solution of nickel sulphate were mixed, warmed and the estimation was carried out as above.

Results:

Coulometry:

10 ml. of copper sulphate = 0.5067 g. copper - by eq., -
 ex. Pt. electrode, hydrogen artery.

= 0.5069 g. \( \text{Cu}^{2+} \)

Calcd:

10 ml. of copper sulphate = 0.5267 g. \( \text{Cu}^{2+} \)

\( \text{Error} = \frac{0.5069 - 0.5267}{0.5267} \approx 3.8\% \)

Coulometry:

1 ml. of nickel sulphate = 0.065 g. nickel - by eq., -
 ex. Pt. electrode, hydrogen artery.

= 0.05132 g. \( \text{Ni}^{2+} \)

Calcd:

1 ml. of nickel sulphate = 0.06414 g. \( \text{Ni}^{2+} \)

\( \text{Error} = \frac{0.05132 - 0.06414}{0.06414} \approx 20.8\% \)
Copper : Nickel :: 1:10

1 ml. of the standard solution of copper sulphate and
10 ml. of the standard solution of nickel sulphate were mixed,
treated and the estimation was carried out as described earlier.

Results

Found

1 ml. of copper sulphate = 0.05260 g. copper (II-hydroxy-β-

= 0.00056 g. Cu^{++}

Caled.

1 ml. of copper sulphate = 0.05257 g. Cu^{++}

Error = +0.0003 g.

= +0.03%

Found:

10 ml. of nickel sulphate = 0.0635 g. nickel (II-hydroxy-β-

= 0.0014 g. Ni^{++}

Caled.

10 ml. of nickel sulphate = 0.0635 g. Ni^{++}

Error = -0.0001 g.

= -0.06%

In 25 ml.

0.7122 g. of the alloy was dissolved in a 50% v/v in an

in an evaporating dish and the solution was evaporated to
drystness. The residue was dissolved in hydrochloric acid and
diluted to 250 ml.

To 25 ml. of the original solution was added dilute
ammonia hydroxide till a sky blue precipitate was formed. Dilute acetic acid was added to dissolve the precipitate adjusting the pH between 5.5 to 6.0. The solution was diluted to about 60 ml., warmed to 80°C and treated with a 25% solution of 2-hydroxy-5-methylesterophenone oxime sufficient to precipitate both the copper and nickel. Only the copper complex precipitated which was digested for half an hour, filtered hot, washed, dried and weighed as usual.

The filtrate and the washings were mixed and warmed and to it was added a dilute solution of ammonia hydroxide till a green precipitate of nickel 2-hydroxy-5-methylesterophenone oxime was obtained (pH 5.5). The precipitate was digested for half an hour, filtered, washed, dried and weighed as usual.

**Result:**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu^2+</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 ml. of the solution</td>
<td>0.3448 g. copper 2-hydroxy-5-methylesterophenone oxime</td>
<td>0.2258 g.</td>
</tr>
<tr>
<td>250 ml. of the solution</td>
<td>0.3376 g. Cu^2+</td>
<td>0.2258 g.</td>
</tr>
<tr>
<td>0.7722 g. of the alloy</td>
<td>0.5706 g. Cu^2+</td>
<td>0.2258 g.</td>
</tr>
<tr>
<td>160 g. of the alloy</td>
<td>78.47% Cu^2+</td>
<td>0.2258 g.</td>
</tr>
<tr>
<td>by standard method (given below)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Error</td>
<td>0.2258 g.</td>
<td></td>
</tr>
</tbody>
</table>

**Result:**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ni^2+</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 ml. of the solution</td>
<td>0.1273 g. nickel 2-hydroxy-5-methylesterophenone oxime</td>
<td>0.3130 g.</td>
</tr>
<tr>
<td>250 ml. of the solution</td>
<td>0.106 g. Ni^2+</td>
<td>0.3130 g.</td>
</tr>
<tr>
<td>0.7722 g. of the alloy</td>
<td>0.198 g. Ni^2+</td>
<td>0.3130 g.</td>
</tr>
<tr>
<td>160 g. of the alloy</td>
<td>39.12% Ni^2+</td>
<td>0.3130 g.</td>
</tr>
<tr>
<td>by standard method (given below)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Error</td>
<td>0.3130 g.</td>
<td></td>
</tr>
</tbody>
</table>

**Result:**
**Copper in the alloy using acetylacetone**

To 30 ml. of the original solution was added 1 ml. of hydrochloric acid. The solution was warmed to 65° and hydrogen sulphide was passed. The copper sulphide which precipitated was dissolved in nitric acid and the solution was diluted to 100 ml.

From this 50 ml. of the solution was taken to estimate copper as copper acetylacetone as described previously.

**Analysis**

Found:

<table>
<thead>
<tr>
<th>Volume of solution</th>
<th>Cu % as Copper acetylacetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 ml. of solution</td>
<td>0.560 g. Copper acetylacetone</td>
</tr>
</tbody>
</table>
| 100 ml. of solution | 0.285 g. Cu**
| 250 ml. of original solution | 0.1151 g. Cu**
| 500 ml. of original solution | 0.5755 g. Cu**

**Nickel in the alloy using dimethylglyoxime**

The filtrate and the precipitate after the removal of copper as copper sulphide were mixed and boiled to cook off all the sulphide. A 1% solution of dimethylglyoxime sufficient to completely precipitate nickel was added followed by a dilute solution of sodium hydroxide till there was a persistent smell. The red precipitate of nickel dimethylglyoxime was digested, filtered, washed, dried and weighed as described earlier.
Results:

Found:

50 ml. of the solution = 0.1034 g. nickel dimethylglyoxime.

\[ \text{mol. of Ni} = \frac{0.1034}{58.69} = 0.0174 \text{ mol.} \]

\. 250 ml. of the solution = 0.0333 g. Ni**;

\. i.e. 0.7752 g. of the alloy = 0.1652 g. Ni**;

\. 100 g. of the alloy = 33.12 Ni**

Intention of method:

10 ml. of the standard solution of cobalt chloride
diluted to 40 ml. was warmed to 70° and treated very gradually
with 30 ml. of a 2M solution of 3-hydroxy-3-methylisoacetonaphene
amine followed by a dilute solution of ammonium hydroxide to
raise the pH to about 7.3. The very yellow brown precipitate
formed was then digested for about half an hour till it settled
down leaving a very faintly yellow supernatant liquid. It was
filtered hot through a slotted glass crucible, washed with
hot water only, and dried at 120° for an hour and weighed as
cobalt 3-hydroxy-3-methylisoacetonaphene amine.

Results:

Found:

10 ml. of cobalt chloride = 0.1564 g. cobalt 3-hydroxy-3-
methylisoacetonaphene amine.

\[ \text{mol. of Co} = \frac{0.1564}{58.93} = 0.0026 \text{ mol.} \]

\[ \text{mol. of Ni} = \frac{0.0333}{58.69} = 0.00057 \text{ mol.} \]

Colloidal:

10 ml. of cobalt chloride = 0.0562 g. Co++;

\. Error = +0.0002 g. = +0.22%.

All the results are given in Table II on page 31.
The above estimation was repeated except that a solution of sodium acetate was used instead of that of ammonium hydroxide to raise the pH to 9.0.

Results

Found:

10 ml. of cobalt chloride = 0.0532 g. cobalt (2-hydroxy-3-methylacetophenone azine) = 0.0532 g. Co^{2+}

Calcd.:

10 ml. of cobalt chloride = 0.05342 g. Co^{2+}

Error = -0.0032 g. = -0.16%

Cobalt in presence of copper:

10 ml. each of the standard solutions of cobalt chloride and copper sulphate were mixed and treated with dilute ammonium hydroxide solution to make it just alkaline followed by 5 ml. acetic acid so as to bring the pH to about 8.0. It was then diluted to about 70 ml. and warmed, from which copper was precipitated as copper 2-hydroxy-3-methylacetophenone azine as usual by adding an excess of the reagent. The filtrate and the washings were mixed and warmed; and a dilute solution of ammonium hydroxide was added to raise the pH to about 7.0, when cobalt 2-hydroxy-3-methylacetophenone azine precipitated. It was digested, filtered hot, washed, dried and weighed as usual.

Results

Found:

10 ml. of cobalt chloride = 0.0540 g. cobalt (2-hydroxy-3-methylacetophenone azine) = 0.0540 g. Co^{2+}

Calcd.:

10 ml. of cobalt chloride = 0.05342 g. Co^{2+}

Error = +0.0037 g. = +0.69%
Cobalt in presence of nickel

10 ml. each of the standard solution of cobalt chloride and nickel sulphate were mixed, warmed and treated with 80 ml. of 2-hydroxy-2-methylacetophenone oxime followed by a dilute sodium acetate solution to precipitate cobalt and nickel 2-hydroxy-2-methylacetophenone oxime as usual at pH 5.5. The filtrate and washings were mixed, warmed to 100°C, a dilute solution of ammonium hydroxide was added to raise the pH to 8.0 when the cobalt complex precipitated. It was digested, filtered, washed, dried and weighed as cobalt.

Results:

Found:

10 ml. of cobalt chloride = 0.0580 g. cobalt (g. of cobalt chloride)

= 0.00008 g. Co

Calcd.: 

10 ml. of cobalt chloride = 0.05525 g. Co

: Error = +0.00075 g.

= +1.125.

Cobalt and copper in presence of each other:

A mixture of 10 ml. each of the standard solution of copper sulphate and cobalt chloride was diluted to 100 ml, warmed and treated with a dilute solution of ammonium hydroxide till just alkaline. This was then treated with 5 ml. of nitric acid and a 15 solution of 2-hydroxy-2-methylacetophenone oxime sufficient to precipitate both the ions. The precipitate was
copper 3-hydroxy-2-methylacetophenone oxime was digested for half an hour, filtered, washed, dried and weighed as such.

The filtrate and washings from the above were all added and warmed, and treated with a dilute solution of sodium hydroxide so as to raise the pH to about 8.5, then cobalt 3-hydroxy-2-methylacetophenone oxime precipitated. It was digested, filtered, washed, dried and weighed as such.

**Results**

<table>
<thead>
<tr>
<th>Test</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 ml of copper sulphate</td>
<td>0.355 g copper (II) or 35.5 cobalt(II) acetophenone oxime.</td>
</tr>
<tr>
<td></td>
<td>Calculated</td>
</tr>
<tr>
<td></td>
<td>Difference</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Test</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 ml of cobalt chloride</td>
<td>0.5715 g cobalt (II) or 57.15 cobalt(II) acetophenone oxime.</td>
</tr>
<tr>
<td></td>
<td>Calculated</td>
</tr>
<tr>
<td></td>
<td>Difference</td>
</tr>
</tbody>
</table>

**Calculations**

A mixture of 10 ml each of the standard solutions of nickel sulphate and cobalt chloride was diluted to 20 ml.
warmed and treated with an excess of a 5% solution of
3-hydroxy-5-methylacetophenone oxide followed by a dilute
solution of sodium acetate so as to raise the pH to 7.5,
when nickel precipitated as nickel 3-hydroxy-5-methylace-
tophenone oxide. It was digested, filtered, washed, dried
and weighed as usual.

The filtrate and washings from the above were mixed,
warmed to 80° and a dilute solution of ammonium hydroxide
was added so as to raise the pH to about 10, when cobalt
3-hydroxy-5-methylacetophenone oxide precipitated. It was
digested, filtered, washed, dried and weighed as usual.

Found:

10 ml. of nickel sulphate = 0.0046 g. nickel 3-hydroxy-5-
methylacetophenone oxide,
= 0.0034 g. Ni++

Calc.:

10 ml. of nickel sulphate = 0.0045 g. Ni++
• Error = -0.0001 g.
= 0.22%

Found:

10 ml. of the cobalt chloride = 0.3033 g. cobalt 3-hydroxy-5-
methylacetophenone oxide,
= 0.0023 g. Co++

Calc.:

10 ml. of the cobalt chloride = 0.0023 g. Co++
• Error = -0.0001 g.
= 0.22%
A mixture of 10 ml. each of the standard solutions of copper sulphate, nickel sulphate and cobalt chloride was diluted to 20 ml., warmed to 80° and treated with a dilute solution of ammonium hydroxide till just alkaline, this was treated with 5 ml. of acetic acid and a 2% solution of 5-hydroxy-3-methylacetophenone amine sufficient to precipitate all the three cations. Only the copper complex precipitated at pH 5.0 to 5.5. It was digested, filtered, washed, dried and weighed as usual.

The filtrate and washings from the above were mixed, warmed and a dilute solution of sodium acetate was added to raise the pH to 5.5, when the nickel complex precipitated. It was digested, filtered, washed, dried and weighed as usual.

To the warmed filtrate and washings from the above was added a dilute solution of ammonium hydroxide to raise the pH to about 7.0, the cobalt 2-hydroxy-3-methylacetophenone amine precipitated which was digested, filtered, washed, dried and weighed as usual.

Results

Found:
10 ml. of copper sulphate = 0.766 g. copper 2-hydroxy-3-
 methylacetophenone amine
= 0.0766 g. Cu**

Calcd.:
10 ml. of copper sulphate = 0.8237 g. Cu**
:. Error = +0.06019 g.
= +0.06
10 ml. of nickel sulphate $= 0.0120 g. \text{ nickel } \text{II} \text{SO}_4 \text{H}_2 \text{O}
\text{calcd.}

10 ml. of nickel sulphate $= 0.0120 g. \text{ Ni}^{2+}$
\text{error} $= -0.0001 g.$
= -0.076%.

10 ml. of cobalt chloride $= 0.0228 g. \text{ cobalt } \text{II} \text{SO}_4 \text{H}_2 \text{O}
\text{calcd.}

10 ml. of cobalt chloride $= 0.0228 g. \text{ Co}^{2+}$
\text{error} $= -0.0001 g.$
= -0.076%.
-Hydroxymethylpropiophenone oxime

Preparation of 1-hydroxymethylpropiophenone oxime

m. recr. propanoate:

of 10.0 g. (11.42) of 1-hydroxy-4-nitroacetophenone oxime and 4.21 g. (0.03 mol) of sodium bicarbonate were heated on a water-bath for six hours in the presence of 5 to 6 drops of pyridine. It was then poured over 1 l. of hydrochloric acid, separated, washed with aqueous 10% bicarbonate and water and dried. The propanoate obtained was a colourless liquid, b.p. 106° (lit., b.p. 120°-130°).

Solid oxime.

of 10.0 g. (11.42) of sodium chloride added gradually to 11.0 g. (0.03 mol) of 1-hydroxy-4-nitroacetophenone oxime and heated at 110° for four hours, cooled and treated with ice and hydrochloric acid. The oxime was collected on a filter, dried, colourless liquid. b.p. 159° (lit., b.p. 122°-123°).

-Hydroxy-4-methylpropiophenone oxime:

of 10.0 g. (11.42) of sodium methylate, private communication.

1.0 g. (0.011 mol) of hydroxymethylpropiophenone oxime was dissolved in a minimum volume of glacial acetic acid, treated with an alcoholic solution of 1.0 g. (0.011 mol) of 4-hydroxy-3-methylpropiophenone oxime and warmed on a water-bath for six hours and kept overnight. The colourless oxime was recrystallised from ethanol, the crystals were needle shaped. b.p. 120° (lit. 170°).
3-hydroxy-2-methylpropiothonone oxime was found to be sparingly soluble in cold water, easily in hot, also easily in ethanol, chloroform, benzene, toluene, xylene, carbon tetrachloride, ether and petrolæus ether.

Preparation of the stock solution

1.0 g. of the pure re-crystallised oxime was dissolved in 100 ml. of 95% ethanol to get a 1% solution for qualitative tests. A 2% solution was similarly prepared for quantitative determinations. The solution thus prepared could be kept for a long period.

Effect of the presence of different cations

Copper

To 1 ml. of the 0.2% decimal solution of copper sulphate was added a 1% solution of 3-hydroxy-2-methylpropiothonone oxime dropwise when a faintly olive green precipitate was obtained. The pH range for complete precipitation was determined to be 3.0 to 8.5, while incipient precipitation could be observed as a pH as low as 2.0 and as high as 11.0.

The complex decomposed when treated with mineral acids and glacial acetic acid and the oxime separated. It was soluble in strong caustic alkalis and ammonium hydroxide from which it reprecipitated on dilution.

The copper complex was found to be insoluble in ether, petrolæus ether and ethanol but easily soluble in chloroform, carbon tetrachloride, benzene, toluene and xylene giving
stable olive green solution which could be preserved for a long time.

Sensitivity:

1 ml. of 0.1% solution of copper oxinate (cupric oxide • copper) was progressively diluted and treated with 1 ml. of 1% of 2-hydroxy-5-methylpropiophenone oxime solution. The results are tabulated as under:

<table>
<thead>
<tr>
<th>DILUTION</th>
<th>1 ml.</th>
<th>CONC.</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>600</td>
<td>Precipitate.</td>
</tr>
<tr>
<td>20</td>
<td>300</td>
<td>&quot;</td>
</tr>
<tr>
<td>100</td>
<td>67</td>
<td>&quot;</td>
</tr>
<tr>
<td>500</td>
<td>12.6</td>
<td>&quot;</td>
</tr>
<tr>
<td>1000</td>
<td>6.3</td>
<td>&quot;</td>
</tr>
<tr>
<td>5000</td>
<td>1.03</td>
<td>&quot;</td>
</tr>
<tr>
<td>7500</td>
<td>0.35</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

Nickel:

1 ml. solution of the reagent was dropped by drop with 1 ml. of the same decinormal solution of nickel chloride, no precipitate was obtained, but on addition of a dilute solution of ammonium hydroxide a green color was obtained. The precipitate could be obtained between pH 4.5 to 11.0, however, for complete precipitation the pH range was 8.5 to 10.0. On decomposition on treated with mineral acid the nickel chloride acid with the separation of the oxime. It dissolves in an alkaline and ammonium hydroxide on boiling and regains acidity on dilution.
The nickel complex readily lost its iron countercomplex giving a stable green solution.

**Sensitivity**

1 ml. of 0.1M solution of nickel salicylate (4.15 cm. nickel) was progressively diluted and treated with 1 drop of EN (hydroy)-methylpropiononc almine solution followed by 6 drops of very dilute ammonium hydroxide solution.

The results are tabulated below:

<table>
<thead>
<tr>
<th>Dilution</th>
<th>Vol.</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 : 10</td>
<td>500</td>
<td>Precipitate</td>
</tr>
<tr>
<td>100</td>
<td>50.0</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>25.0</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>5000</td>
<td>0.02</td>
<td>Turbidity of well kept keeping aside.</td>
</tr>
<tr>
<td>7500</td>
<td>0.02</td>
<td>Precipitation</td>
</tr>
</tbody>
</table>

**Cobalt**

To 1 ml. of the same decimolar solution of cobalt nitrite was added a 10 solution of the reagent, no precipitate was formed even on heating, but on mixing, the 50 to 100 in a dilute solution of ammonium hydroxide or sodium carbonate, all the cobalt was precipitated as a finely divided brown floc. The precipitate could be obtained between pH 1.0 to 1.5, but for complete precipitation, the pH range was 1.5 to 2.0.

Equimolar acids and glacial acetic acid decomplexed the cobalt and the almine separated out. The complex dissolved in stron
alkaline and ammonium hydroxide on heating, from which it reprecipitated on dilution.

The cobalt complex gives a stable reddish brown solution in the usual solvents.

**Results:**

1 ml. of 0.1M solution of cobalt chloride (0.00051 g. cobalt) was progressively diluted and treated with 2 drops of 15% hydroxy-ethylaminoporphine orine solution followed by a very dilute solution of ammonium hydroxide.

The results are tabulated as under:

<table>
<thead>
<tr>
<th>Dilution</th>
<th>1 ml.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 : x =</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>500</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>1000</td>
<td>0</td>
</tr>
<tr>
<td>5000</td>
<td>1.25</td>
</tr>
<tr>
<td>7500</td>
<td>0.3</td>
</tr>
</tbody>
</table>

**Observation:**

Precipitate.

... 

Reddish brown on heating and boiling with... Sporescence.

**Method:**

To 1 ml. of the same 0.15% solution of gallium chloride a 15% solution of the reagent was drop by drop added when a yellow precipitate was obtained (pH 1.9 to 2.4). The complex decomposed if treated with strong acetic acid and oxalic acid, and the oxide separated. Strong acetic amine and ammonium hydroxide also dissolved the complex which reprecipitated on dilution.
The palladium complex dissolved in the usual non-polar solvents giving a stable greenish yellow solution.

**Experimental**

A 1% solution of the reagent was drop by drop added to 1 ml. of the same decinolar solution of ferric ammonium sulphate when a viable solution was obtained between pH 1.0 to 4.0. On raising the pH above 5.5 to 7.0 a reddish brown precipitate was formed. The complex decomposed by strong acids. The complex was found to be soluble in the non-polar solvents giving a red solution.

**Results**

To 1 ml. of the same decinolar solution of ferric chloride was added a 1% solution of the reagent drop by drop when a reddish brown solution was obtained between pH 1.0 to 5.5. On raising the pH above 6.0 a reddish precipitate was obtained which was of ferric hydroxide (with ammonium hydroxide) or basic ferric acetate (with sodium acetate).

Chemically, calcium, strontium, zinc, aluminium, beryllium, magnesium, lead and copper.

To 1 ml. of each of the above warm salt solution was added a 1% solution of the reagent drop by drop. No precipitate of the complex was obtained even on boiling, or by raising the pH with dilute ammonium hydroxide, however, their respective hydroxides precipitated.
I ml. each of 0.1M solutions of copper II and nickel nitrate were mixed, warmed and an excess of 0.1M ammonia dropwise added when a faintly olive colored solution of copper II-hydroxy-acetylacetoephone oxide was obtained at pH 9.0 which was filtered off.

To the warm filtrate few drops of 0.1M sodium ammonium hydroxide were added; a green precipitate of nickel II-hydroxy-acetylacetoephone oxide was obtained at pH 10.

It was observed that in a mixture of these two solutions copper II got preferentially precipitated while nickel II co-precipitated.

Copper and cobalt in presence of each other

I ml. each of 0.1M solutions of copper II and cobalt chloride were mixed, warmed and an excess of 0.1M ammonia dropwise added when a faintly olive colored solution of copper II-complex was obtained at pH 9.0 which was filtered off.

Few drops of sodium ammonium hydroxide were added to the warm filtrate when a faintly reddish brown solution of cobalt II-hydroxy-acetylacetoephone oxide was obtained at pH 9.5 to 10.

It was observed that in a mixture of these two solutions copper II got preferentially precipitated upto pH 9.
nickel and cobalt in presence of each other:

1 ml. of 0.1M solutions of nickel sulphate and cobalt chloride were mixed, warmed and an excess of solution of the reagent was added followed by a dilute solution of sodium acetate when a green precipitate of nickel 2-hydroxy-5-methylpropylphenone oxime was obtained at pH 5.5 which was filtered off.

To the warm filtrate was added dilute ammonium hydroxide solution when a faintly reddish brown precipitate of cobalt 2-hydroxy-5-acetylpropylphenone oxime was obtained (pH 5.5-7.4)

It was observed that in a mixture of these two cations nickel preferentially precipitated up to pH 8.0.

Copper, nickel and cobalt in presence of one another:

A 1M solution of the reagent (cyanine) was drop by drop added to a warm solution containing copper sulphate, nickel sulphate, and cobalt chloride (0.1M; 1 ml. each), when a faintly olive green precipitate of the copper complex was obtained (pH 3.0) which was filtered off. To the warm filtrate few drops of dilute solution of sodium acetate were added; a green precipitate of the nickel complex was obtained (pH 5.5) which was filtered off; few drops of a dilute solution of ammonium hydroxide were added to the warm filtrate to raise the pH to 7.0. Cobalt complex precipitated as a faintly reddish brown mass.

Copper in presence of other cations (chromium sulphate, cobalt sulphate, zinc sulphate, aluminium sulphate, manganese sulphate, and palladium sulphate).

1 ml. of 0.1M copper sulphate solution was mixed with
1 ml. of 0.1M solution of the desired salt, warmed to 70° C,
of the reagent solution was added dropwise under a faintly olive
green precipitate of the copper complex was obtained keeping
the other in solution. (pH = 3.0 to 3.5).

Nickel in presence of other cations (Chromium chloride, silver,
calciun, zinc sulphate, aluminium chloride, and iron chloride
and beryllium sulphate).

1 ml. of 0.1M nickel sulphate solution was mixed with 2 ml.
of 0.1M solution of the desired salt, warmed and 15 mL acetone
2-methyl-5-ethylphenone azine was dropwise added followed by reac-
tion of acetic acid to bring the pH to 5.0 the nickel complex
precipitated keeping the other in solution.

Quantitative estimations

Titration of:

Copper:

To 10 ml. of the standard copper sulphate solution was
dropped added a dilute solution of ammonia hydroxide or sodium
hydroxide till a permanent sky blue precipitate developed. Acetic
acid was added to dissolve the precipitate adjusting the
pH of the solution between 3.0 to 3.5 and the volume was adjusted
to about 100 ml, the solution was warmed and a 25 solution of
2-hydroxy-5-methylphenone azine was added dropwise till
the precipitation was complete (30 ml). The faintly olive green
precipitate was digested, filtered hot, washed, dried (120° C)
and weighed as described earlier.
Result:

Found:

10 ml. of copper sulphate = 0.0422 g. copper 2-hydroxy-1-naphthylacetophenone

= 0.05209 g. Cu^{++}

Calcd.:

10 ml. of copper sulphate = 0.0324 g. Cu^{++}

Error = +0.0202 g.

= +0.56%.

All the results are given in Table 1 on page 47.

Some variations were made in the above procedure, which are as under:

10 ml. of the standard copper sulphate solution was treated with 5 ml. of concentrated hydrochloric acid, warmed and the reagent was added as above till the precipitation was complete.

Found:

10 ml. of copper sulphate = 0.0362 g. copper 2-hydroxy-1-naphthylacetophenone

= 0.05721 g. Cu^{++}

Calcd.:

10 ml. of copper sulphate = 0.0324 g. Cu^{++}

Error = +0.0081 g.

= +2.6%.

10 ml. of the standard solution of copper sulphate was treated with 10 ml. of glacial acetic acid, warmed and the reagent was added till the precipitation was complete.
**Copper in presence of nickel:**

10 ml. each of the standard solutions of copper sulphate and nickel sulphate were mixed and treated with a dilute solution of ammonium hydroxide to make it just alkaline followed by 0.1 ml. of acetic acid as and when the pH to close 5.5-6, as were diluted to about 75 ml. and warmed. 10 ml. of the warm mix than added to copper 2-hydroxy-7-oxylpyridophenone oxide precipitated. It was digested, filtered, washed, oxidized and weighed as usual.

**Result:**

**Calc.**

10 ml. of copper sulphate = 0.0667 g. Cu^{2+}

: Error = -0.0004 g.

: 0.0663 g.

**Copper in presence of cobalt:**

10 ml. each of the standard solutions of copper sulphate and cobalt chloride were mixed and the same procedure was followed as above.
Copper in presence of other cations

The solution of copper chloride, nitric acid, sodium sulphate, aluminium sulphate, and azetate was used to precipitate copper prepared as described earlier in this.

10 ml. of the standard copper sulphate solution was mixed with 1 ml. of a standard solution containing 1 M sodium acetate and pH was adjusted to above 6.5. The procedure was repeated and the same as earlier described.

All the results are given in Table I as per the

Labetation of nickel

10 ml. of the standard solution of nickel chloride were diluted to about 60 ml. and warmed, 1 M nitric acid was added (1 ml. and ml.) followed by a dilute solution of oxalic acid to raise the pH to 5.6 when a green precipitate of nickel 2-hydroxy-5-methylpyridophenone oxime was obtained. The precipitate was then filtered, washed, washed, dried (1 l.) and weighed as before.
**Results**

10 ml. of nickel sulphate = 0.025 g. nickel (as hydroxide) = 0.00125 g. nickel

Calcd.: 0.00125 g. Ni²⁺

10 ml. of nickel sulphate = 0.025 g. nickel (as hydroxide) = 0.00125 g. nickel

Calcd.: 0.00125 g. Ni²⁺

All the results are given in Table 12 on p. 189.

The above reaction was repeated except that solid sodium acetate was used to raise the pH of the solution.

**Results**

10 ml. of nickel sulphate = 0.025 g. nickel (as hydroxide) = 0.00125 g. nickel

Calcd.: 0.00125 g. Ni²⁺

10 ml. of nickel sulphate = 0.025 g. nickel (as hydroxide) = 0.00125 g. nickel

Calcd.: 0.00125 g. Ni²⁺

**Nickel in presence of copper**

10 ml. each of the standard solutions of nickel and copper sulphate were mixed and treated with dilute sodium hydroxide to make it just alkaline followed by — ml. of nitric acid to bring the pH to about 11. To the solution of about 20 ml. not warmed. In excess of the copper in that in to precipitate both the cations was then added when the solution was jet

...
precipitated. The precipitate was digested, filtered and washed as usual. The filtrate along with the washings was warmed and treated with a dilute solution of ammonium hydroxide to raise the pH to 3.2, when nickel 3-hydroxy-5-methylpropiophenone oxime precipitated. It was digested, filtered, washed, dried and weighed as usual.

**Solution Found:**

10 ml. of nickel sulphate = 0.052 g. nickel 3-hydroxy-5-methylpropiophenone oxime  
= 0.0435 g. Ni⁺⁺

**Calcium**

10 ml. of nickel sulphate = 0.0615 g. Ni⁺⁺

---

**Nickel in presence of cobalt**

A mixture of 10 ml. each of the standard solutions of nickel sulphate and cobalt chloride was diluted to about 50 ml. and warmed. 20 ml. of the reagent was added followed by a dilute solution of sodium acetate to raise the pH to 3.5 when nickel 3-hydroxy-5-methylpropiophenone oxime precipitated. It was digested, filtered, washed, dried and weighed as usual.

**Solution Found:**

10 ml. of nickel sulphate = 0.0542 g. nickel 3-hydroxy-5-methylpropiophenone oxime  
= 0.05167 g. Ni⁺⁺

**Calcium**

10 ml. of nickel sulphate = 0.0615 g. Ni⁺⁺

---

**Iron**

10 ml. of nickel sulphate = 0.0615 g. Ni⁺⁺
Nickel in presence of other cations:

The solution of ammonium chloride, copper chloride, nickel chloride, and iron chloride described earlier were used.

A mixture of 10 ml. of the standard solution of each sulphate and the desired cation was diluted to about 50 ml. and warmed to about 70°C. 20 ml. of this solution were added followed by a dilute solution of sodium acetate to make the pH about 5.5 when nickel complex precipitated. It was diluted, filtered, washed, dried and weighed as usual.

All the results are given in Table 3.

Copper and nickel in presence of each other:

Copper-nickel III.

10 ml. each of the standard solutions of copper and nickel sulphate were mixed and the mixture diluted to make it just alkaline followed by 1 ml. of 0.1 N HCl to adjust the pH to about 5.5. The solution was diluted to about 50 ml. and warmed to about 70°C. The precipitate was filtered, washed, dried and weighed as usual.

The filtrate and the mother liquor were mixed, heated and treated with a dilute solution of ammonium hydroxide to make the pH to about 5.5. When the nickel complex precipitated, it was diluted, filtered, washed, dried and weighed as usual.
Solutions found:

10 ml. of copper sulphate = 0.415 g. copper 2-hydroxy-3 propylpropanedioate oxide.

= 0.0827 g. Cu⁺⁺

Calc.:

10 ml. of copper sulphate = 0.0827 g. Cu⁺⁺

\[ \text{Error} = 0.0008 \text{ g.} \]
\[ = 0.08\% \]

Solutions found:

10 ml. of nickel sulphate = 0.4336 g. nickel 2-hydroxy-3 propylpropanedioate oxide.

= 0.0333 g. Ni⁺⁺

Calc.:

10 ml. of nickel sulphate = 0.0333 g. Ni⁺⁺

\[ \text{Error} = 0.0001 \text{ g.} \]
\[ = 0.03\% \]

Comparative: 1:10:1

10 ml. of the standard solution of copper sulphate and 1 ml. of the standard solution of nickel sulphate were mixed, and each estimated as described above.

Results:

Found:

10 ml. of copper sulphate = 0.415 g. copper 2-hydroxy-3 propylpropanedioate oxide.

Calc.:

10 ml. of copper sulphate = 0.0333 g. Cu⁺⁺

\[ \text{Error} = 0.0002 \text{ g.} \]
\[ = 0.06\% \]
Results:

Found:
1 ml. of nickel sulphate = 0.6884 g. nickel 1-hydroxy-4-
methylpyridophenone oxime.

= 0.00144 M. M.

Calcd:
1 ml. of nickel sulphate = 0.6905 g. M. M.

: Error = -0.0021 g.

: Error = -0.32%.

Copper: Nickel 1:110.

1 ml. of the standard solution of copper sulphate =
10 ml. of the standard solution of nickel sulphate were mixed
and estimations carried out as before.

Results:

Found:
1 ml. of copper sulphate = 0.6112 g. copper 1-hydroxy-4-
methylpyridophenone oxime.

= 0.00282 M. M.

Calcd:
1 ml. of copper sulphate = 0.6122 g. M. M.

: Error = -0.0010 g.

: Error = -0.23%.

Results:

Found:
15 ml. of nickel sulphate = 0.4336 g. nickel 3-hydroxy-5-
methylpyridophenone oxime.

= 0.00155 M. M.

Calcd:
15 ml. of nickel sulphate = 0.4334 g. M. M.

: Error = -0.0016 g.

: Error = -0.37%.


**Separation of Cobalt**

10 ml. of the standard solution of cobalt chloride was diluted to about 20 ml., was warmed to 70° and treated with 30 ml. of a 2% solution of 3-hydroxy-1-methylpropiophenone oxime followed by a dilute solution of ammonium hydroxide to raise the pH to about 7.0. The faintly reddish brown precipitate formed was digested, filtered, washed, dried (110°) and weighed as before.

**Results**

**Found:**

10 ml. of cobalt chloride = 0.0182 g. cobalt 
3-hydroxy-1-methylpropiophenone oxime.

= 0.0091 g. Co²⁺

**Calcd.:**

10 ml. of cobalt chloride = 0.0082 g. Co²⁺

:: Error = ±0.00014 g.

= ±0.24%

All the results are given in Table XV on page 20.

The above estimation was repeated using a sodium acetate solution to raise the pH.

**Results**

**Found:**

10 ml. of cobalt chloride = 0.018 g. cobalt 
3-hydroxy-1-methylpropiophenone oxime.

= 0.00905 g. Co²⁺

**Calcd.:**

10 ml. of cobalt chloride = 0.0082 g. Co²⁺

:: Error = ±0.00017 g.

= ±2.05%
Cobalt in presence of copper:

10 ml. each of the standard solutions of cobalt chloride and copper sulphate were mixed and treated as usual to remove mineral acidity and adjust the pH to about 5.9. It was then diluted to 50 ml, and warmed to 80° from which copper complex was precipitated and removed as usual by adding an excess of the reagent. The filtrate and the washings were mixed, warmed and treated with a dilute solution of ammonium hydroxide to raise the pH to about 7.0; when cobalt 2-hydroxy-2-carboxyphosphonato crino precipitated. It was digested, filtered, washed, dried and weighed as usual.

Found:

10 ml. of cobalt chloride = 0.0210 g. cobalt 2-hydroxy-2-carboxyphosphonato crino = 0.0552 g. Co²⁺

Calcd:

10 ml. of cobalt chloride = 0.03042 g. Co²⁺

:Error = -0.0092 g.

= -0.30%.

Cobalt in presence of nickel:

10 ml. each of the standard solutions of cobalt chloride and nickel sulphate were mixed, warmed and treated with an excess of the reagent followed by a dilute solution of sodium acetate to precipitate and remove the nickel complex as usual at pH 5.9.
The filtrate and washings were mixed and warmed (70°) and pH raised to 7.0 by adding a dilute solution of ammonium hydroxide, when the cobalt complex precipitated. It was digested, filtered, washed, dried and weighed as usual.

**Results**

**Found:**

10 ml. of cobalt chloride = 0.4412 g. cobalt 2-ethylcrotonyl crotonate oxide = 0.3328 g. Co

**Calcd:**

10 ml. of cobalt chloride = 0.3334 g. Co

\[ \text{Error} = 0.0080 \text{ g.} \]

\[ \text{= 0.08}\]

Cobalt and copper in presence of each other:

A mixture of 10 ml. each of the standard solutions of copper sulphate and cobalt chloride was treated for the removal of mineral acidity as usual and brought to pH of 5.0 in excess of the reagent (40 ml.) was added.

The faintly olive green precipitate of the copper complex was digested, filtered, washed, dried and weighed as usual.

The filtrate and washings were mixed, warmed and treated with a dilute solution of ammonium hydroxide to raise the pH to 7.0, when the cobalt complex precipitated. It was digested, filtered, washed, dried and weighed as usual.
Result:
Found:
10 ml. of copper sulphate = 0.4120 g. copper (II) acetate
= 0.035 g. Cu²⁺

Calcd:
10 ml. of copper sulphate = 0.03527 g. Cu²⁺
∴ Error = +0.0003 g.
= +0.85%.

Found:
10 ml. of cobalt chloride = 0.4102 g. cobalt (-II) oxalate
= 0.03689 g. Cu²⁺

Calcd:
10 ml. of cobalt chloride = 0.03942 g. Cu²⁺
∴ Error = -0.0014 g.
= -3.6%.

Cobalt and nickel in presence of each other:

A mixture of 10 ml. each of the standard solutions of nickel sulphate and cobalt chloride diluted to about 70 ml. was added and treated with an excess of the reagent followed by a dilute solution of sodium acetate to raise the pH to 5.5. When the nickel complex precipitated, which was precipitated, filtered, washed, dried and weighed as usual.

The filtrate and washings were mixed, warmed and a dilute solution of ammonium hydroxide was added to raise the pH to 7.0, when the cobalt complex precipitated. It was diluted, filtered, washed, dried and weighed as usual.
Results

Calc.

10 ml. of nickel sulphate = 0.0288 mol. nickel

\[ \text{mol. nickel} = 0.0288 \times 2 \times 10^{-2} \text{ mol. nickel} \]

10 ml. of nickel sulphate = 0.0288 x 2 x 10^{-2} mol. nickel

Calc.

10 ml. of cobalt chloride = 0.0029 mol. cobalt

\[ \text{mol. cobalt} = 0.0029 \times 2 \times 10^{-2} \text{ mol. cobalt} \]

10 ml. of cobalt chloride = 0.0029 x 2 x 10^{-2} mol. cobalt

error = +0.0002 g.

error = +0.0002 g.

Copper, nickel and cobalt in presence of one another:

A mixture of 10 ml. each of the standard solutions of copper sulphate, nickel sulphate and cobalt chloride was usual treated for the removal of mineral acidity and the pH adjusted to 3.0. In excess of the reagent was added to the copper complex precipitated. It was digested, filtered, washed, dried and weighed as usual.

The filtrate and washings were mixed, normal and a solution of sodium acetate was added to make 500 ml. and when the nickel complex precipitated which was digested, filtered, washed, dried and weighed as usual.
In the warmed filtrate and washings was added a dilute ammonium hydroxide solution to raise the pH to about 7.5. The cobalt complex was digested, filtered, washed, dried and weighed as usual.

**Results**

<table>
<thead>
<tr>
<th>Solution</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 ml. of copper sulphate</td>
<td>$0.017$ g. Cu$^{2+}$</td>
</tr>
<tr>
<td>Colloidal:</td>
<td></td>
</tr>
<tr>
<td>10 ml. of copper sulphate</td>
<td>$0.0237$ g. Cu$^{2+}$</td>
</tr>
<tr>
<td>Error</td>
<td>$0.0001$ g.</td>
</tr>
<tr>
<td></td>
<td>$0.003$ g.</td>
</tr>
<tr>
<td>Formula:</td>
<td></td>
</tr>
<tr>
<td>10 ml. of nickel sulphate</td>
<td>$0.0566$ g. Ni$^{2+}$</td>
</tr>
<tr>
<td>Colloidal:</td>
<td></td>
</tr>
<tr>
<td>10 ml. of nickel sulphate</td>
<td>$0.0514$ g. Ni$^{2+}$</td>
</tr>
<tr>
<td>Error</td>
<td>$-0.0002$ g.</td>
</tr>
<tr>
<td></td>
<td>$-0.002$ g.</td>
</tr>
<tr>
<td>Formula:</td>
<td></td>
</tr>
<tr>
<td>10 ml. of cobalt chloride</td>
<td>$0.012$ g. Co$^{2+}$</td>
</tr>
<tr>
<td>Colloidal:</td>
<td></td>
</tr>
<tr>
<td>10 ml. of cobalt chloride</td>
<td>$0.0508$ g. Co$^{2+}$</td>
</tr>
<tr>
<td>Error</td>
<td>$-0.0002$ g.</td>
</tr>
<tr>
<td></td>
<td>$-0.002$ g.</td>
</tr>
</tbody>
</table>
I.O.

Hydroxy-2-naphthalenophenone oxime.

Preparation of 2-hydroxy-2-naphthalenophenone oxime.

-royal hawker;

a few, private communication.

9.0 g. p-cresol b.p. 181° and 33 g. 1-bromo-4 chloride (b.p. 120°) were heated on a water-bath for six hours in the case of 3 drops of pyridine. It was then poured over ice and 15%

chloric acid, separated, washed with aqueous sodium hydride and finally with water and dried. The base so was extracted from ethanol, colourless needle, m.p. 69° (lit., m.p. 69°).

Hydroxy-2-naphthalenophenone:


470 g. of anhydrous aluminium chloride (p. 337) was gradually added to 48.3 g. of pure dry p-cresol benzene. The mixture was cooled at 85° for four hours, cooled and treated with 1N hydrochloric acid. It was crystallised from ethanol, yellow needle, m.p. 69° (lit., m.p. 69°).

Hydroxy-2-naphthalenophenone oxime:

of: Duncans and Cruickshank, m.p. 139°, 140°.

0.05 g. of hydroxy-2-naphthalenophenone hydrochloric (p. 337) sodium acetate (p. 337) dissolved in minimum amount of distilled water was mixed with an alcoholic solution of 4.0 g. of 2-hydroxy-2-naphthalenophenone (p. 337) and warmed on a water-bath for six hours and kept overnight. The oxime precipitated, collected and crystallised from ethanol, colourless needles, m.p. 70° (lit., m.p. 105°).
The oxime was insoluble in cold water, moderately soluble in hot, it was easily soluble in ethanol, chloroform, benzene, toluene, xylene, carbon tetrachloride, ether and petroleum ether.

Preparation of the stock solution:

1.0 g. of the pure recrystallized oxime was dissolved in 100 ml. of 95% ethanol to get a 1% solution for qualitative tests. A 2% solution was prepared in the similar manner for quantitative estimations. The solution thus prepared could be kept for a long period.

Effect of the reagent on different actions:

Results:

To 1 ml. of the warm decimolar solution of copper sulphate was dropwise added a 1% solution of 2-(4-dimethylamino-phenyl)pyrimidine oxime when a faintly olive green precipitate was obtained. The incipient precipitation could be observed at a pH as low as 3.0 and as high as 11.0, but the pH range for complete precipitation was determined to be 5.0 to 8.0. The complex decomposed when treated with mineral acids and glacial acetic acid and the oxime separated. It was soluble in strong acetic alkalies and camena and reprecipitated on dilution.

The copper complex was soluble in non-polar solvents giving an olive green stable solution.

Sensitivity:

1 ml. of 0.01% solution of copper sulphate (0.0035 g. copper) was progressively diluted and treated with 2 drops of the reagent solution.

The results are tabulated as under:


<table>
<thead>
<tr>
<th>Dilution</th>
<th>Vol.</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 + 10</td>
<td>650</td>
<td>Precipitate</td>
</tr>
<tr>
<td>100</td>
<td>65.0</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>6.5</td>
<td></td>
</tr>
<tr>
<td>5000</td>
<td>1.25</td>
<td>Turbidity settled on heating, and soluble acida.</td>
</tr>
<tr>
<td>7500</td>
<td>0.60</td>
<td>Opalescence.</td>
</tr>
</tbody>
</table>

**Nickel**

A 1% solution of the reagent was drop by drop added to 1 ml. of the warm decinormal solution of nickel sal. acetate, no precipitate was obtained but on addition of a dilute solution of ammonium hydroxide or sodium acetate a green filings mass was obtained. The precipitate could be obtained between 2 ml. to 11.0; however, for complete precipitation the volume can be up to 0.5 ml.

The complex was decomposed by addition to well or lactic acetic acid with the separation of the oxime. It dissolved in strong lactic and acetic acid on boiling; but it reprecipitated on dilution.

The nickel complex dissolved in non-polar solvents giving a green stable solution.

**Sensitivity**

1 ml. of 0.1M solution of nickel salophate (Caution: nickel) was progressively diluted and treated with 1 drops of the reagent followed by 2 drops of very dilute ammonium hydroxide solution.
The results are tabulated as under:

<table>
<thead>
<tr>
<th>Solution</th>
<th>%Co</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:2</td>
<td>10</td>
<td>533</td>
</tr>
<tr>
<td>100</td>
<td>500</td>
<td>93.5</td>
</tr>
<tr>
<td>1000</td>
<td>5.86</td>
<td>5</td>
</tr>
<tr>
<td>5000</td>
<td>1.17</td>
<td>Turbidity on boiling and keepin acid.</td>
</tr>
<tr>
<td>7000</td>
<td>0.78</td>
<td>Opalescence.</td>
</tr>
</tbody>
</table>

**Labali**

In 1 ml. of the warm dianoin solution of cobalt chloride was added a 1% solution of the reagent, no precipitate was obtained even on heating. On cooling, the pH by addinf a dilute solution of ammonium hydroxide or sodium carbonate, all the cobalt precipitated as a dark reddish brown mass. The precipitate could be obtained between pH 6.9 to 10.0. But for complete precipitation, the pH range was 6.5 to 6.9.

Linaloc acid as well as glacial acetic acid decomposes the complex and the oxime separated out. The complex dissolved is strongly caustic alkaline and amounts on boiling, from which it reprecipitated on dilution.

The cobalt complex was soluble in the non-polar solvents giving a stable reddish brown solution.

**Sensitivity**

1 ml. of 0.1% solution of cobalt chloride (15 ml. 1:1, cobalt) was progressively diluted and treated with 1 gms. of the reagent followed by a very dilute solution of ammonium hydroxide.
The results are given as under:

<table>
<thead>
<tr>
<th>Dilution</th>
<th>Vol.</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 : 10</td>
<td>600</td>
<td>Precipitate.</td>
</tr>
<tr>
<td>100</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>5000</td>
<td>1.25</td>
<td>Suspended on heating and keeping cold.</td>
</tr>
<tr>
<td>7500</td>
<td>0.5</td>
<td>Opalescence.</td>
</tr>
</tbody>
</table>

Palladium

To 1 ml. of the warm 0.15 solution of palladium chloride was added a 15 solution of the reagent when a yellow precipitate was formed (pH 1.5 to 2.5).

The complex decomposed when treated with hot acetic acid or glacial acetic acid, and the azine separated. Strong acetic alcohol and ammonia dissolved the complex which reprecipitated on dilution.

The palladium complex dissolved in non-polar solvents giving a stable greenish yellow solution.

Iron(II)

A 15 solution of the reagent was drop by drop added to 1 ml. of the warm decimal solution of ferrous ammonium sulphate when a violet solution was obtained between pH 0.5 to 2.5; on raising the pH above 3.5 to 7.0 a reddish brown precipitate was formed. The complex was decomposed by strong acids.

The complex dissolved in non-polar solvents giving
a red solution.

**FERRISI**

To 1 ml. of the warm decimolar solution of ferric chloride was added a 15 solution of the reagent when a reddish brown solution was obtained between pH 4.0 to 5.5, but on raising the pH above 6.0 a reddish precipitate of ferric hydroxide (with ammonium hydroxide) or basic ferric acetate (with sodium acetate) was formed.

Chromium, calcium, copper, zinc, aluminium, beryllium, bismuth, lead and mercury

To 1 ml. of each of the above warm salt solution was added a 15 solution of the reagent, no precipitate of the complex was obtained even on boiling or by raising the pH with dilute ammonium hydroxide, however, the respective hydroxide precipitated.

**Selection of:**

Copper and nickel in presence of each other

1 ml. each of 0.1M solutions of copper sulphate and nickel sulphate were mixed, warmed and an excess of the reagent was drop by drop added when a faintly olive green precipitate of the copper complex was obtained at pH 5.0, which was yellowish.

To the warmed filtrate was added a few drops of dilute aqueous ammonium hydroxide, when a green precipitate of the nickel complex was obtained (pH 9.0 to 9.5).

It was observed that in a mixture of these two solutions, copper preferentially precipitated upto pH 6.5, above that a copper and nickel co-precipitated.
Copper and cobalt in presence of each other:

1 ml. each of 0.1 M solutions of copper sulphate and cobalt chloride were mixed, warmed and an excess of 10 solution of the reagent was added when the copper complex separated as a faintly olive green precipitate at pH 3.5. It was removed and the warmed filtrate was treated with dilute aqueous ammonium hydroxide, when a dark reddish brown precipitate of the cobalt complex was obtained at pH 8.5 to 9.0.

It was observed that in a mixture of these two cations, copper preferentially precipitated up to pH 4.0.

Nickel and cobalt in presence of each other:

1 ml. each of 0.1 M solutions of nickel sulphate and cobalt chloride were mixed, treated with an excess of reagent followed by a dilute solution of sodium acetate, when a green precipitate of nickel 3-hydroxy-5-methylphenanthrene oxide was obtained at pH 5.5. It was filtered and a dilute solution of ammonium hydroxide was added to the warm filtrate. The cobalt complex separated as a dark reddish brown mass between pH 6.5 to 7.0.

It was observed that in a mixture of these two cations nickel preferentially precipitated up to pH 2.5.

Copper, nickel and cobalt in presence of one another:

An excess of the reagent was added to a warm solution containing copper sulphate, nickel sulphate and cobalt chloride (0.1M; 1 ml each) when a faintly olive green precipitate of the copper complex separated (pH = 5.0). It was filtered off.
the filtrate was warmed and treated with a dilute solution of sodium acetate, when a green precipitate of nickel was obtained at pH 5.5, which was filtered off. A dilute solution of ammonium hydroxide was added to the warm filtrate to raise the pH to about 7.0; cuvet precipitated as a dark reddish brown mass.

Copper in presence of other cations (copper chloride, calcium, carbonate, zinc sulphate, aluminium sulphate, magnesium sulphate, potassium sulphate). 1 ml. of 0.1M copper sulphate solution was mixed with 1 ml. of 0.1M solution of the desired cation, warmed and 1 ml. solution of the reagent was added dropwise, when a subtly olive green precipitate of the copper complex was obtained keeping the other in solution (pH = 5.0 to 5.5).

Nickel in presence of other cations (copper chloride, calcium chloride, zinc sulphate, aluminium sulphate, magnesium sulphate, potassium sulphate and barium sulphate). 1 ml. of 0.1M nickel sulphate solution was mixed with 1 ml. of 0.1M solution of the desired cation, warmed and 1 ml. of the reagent solution was added followed by sodium acetate solution to adjust the pH to about 5.5. The nickel complex precipitated keeping the other in solution.

Quantitative estimations

Estimation of copper
10 ml. of the standard copper sulphate solution was treated as usual for the mineral acidity and the pH adjusted to 3.0 to 3.5 and volume 50 ml. It was warmed (30°) and a 25 solution of the reagent was prepared added till the precipitation was complete. The olive green precipitate was filtered,
filtered, washed, dried (120°) and weighed as usual.

**Results:**

**Found:**

10 ml. of copper sulphate = 0.0208 g. copper 3-hydroxy-5-methylbenzophenone oxime.

= 0.02055 g. Cu²⁺

**Calcd.:**

10 ml. of copper sulphate = 0.02057 g. Cu²⁺

=. Error = +0.0002 g.

= +0.002.

All the results are given in Table 571 on page 17.

10 ml. of the standard copper sulphate solution was treated with 5 ml. of concentrated hydrochloric acid heated and the reagent was added as above till the precipitation was complete.

**Results:**

**Found:**

10 ml. of copper sulphate = 0.0214 g. copper 3-hydroxy-5-methylbenzophenone oxime.

= 0.02093 g. Cu²⁺

**Calcd.:**

10 ml. of copper sulphate = 0.02087 g. Cu²⁺

= Error = +0.00012 g.

= +0.0012.

10 ml. of the standard solution of copper sulphate was treated with 10 ml. of glacial acetic acid, heated and the reagent was added till the precipitation was complete.
Results:

Found:

10 ml. of copper sulphate = 0.062 g. copper (2-hydroxy-3-ethylbenzophenone oxime)

= 0.09939 g. Cu++

Calcd:

10 ml. of copper sulphate = 0.06287 g. Cu++

Error = +0.00352 g.

= +0.57%

Copper in presence of nickel:

10 ml. each of the standard solutions of copper sulphate and nickel sulphate were mixed and treated as usual to remove mineral acidity and adjusted the pH to 3.0 or 3.5 and volume to about 65 ml. It was warmed to 60° and 20 ml. of the solution was then added when the copper complex precipitated. It was digested, filtered hot, washed, dried (100°) and weighed as before.

Results:

Found:

10 ml. of copper sulphate = 0.109 g. copper (2-hydroxy-3-ethylbenzophenone oxime)

= 0.30399 g. Cu++

Calcd:

10 ml. of copper sulphate = 0.08287 g. Cu++

Error = +0.02112 g.

= +2.58%

Copper in presence of cobalt:

10 ml. each of the standard solutions of copper sulphate and cobalt chloride were mixed and the same procedure was
followed as above.

Result:

Copper sulphate

10 ml. of copper sulphate = 0.104 g. copper (as)

Sulphuric acid

= 0.36493 g. Cu²⁺

Calc.: 10 ml. of copper sulphate = 0.107 g. Cu²⁺  

Error = 0.00313 g.

Copper in presence of other cations:

The solutions of chromium chloride, calcium chloride, zinc sulphate, aluminium sulphate, manganese sulphate, and beryllium sulphate prepared as described earlier were used.

10 ml. of the standard solution of copper sulphate was mixed with 10 ml. of a standard solution containing the desired cation, adjusted the pH to about 3.0, and the same procedure was adopted as described earlier.

All the results are given in Table A7 on page...

Nickel:

10 ml. of the standard solution of nickel sulphate, diluted to about 50 ml. was treated at 70° with 25 ml. of the reagent. A dilute solution of ammonium hydroxide was then added to raise the pH to 3.0 when a green precipitate of nickel 2-hydroxy-1-methylbenzophenone oxime was obtained. The precipitate was digested, filtered hot, washed, dried at 110°, and weighed as described earlier.
Results

Found:

10 ml. of nickel sulphate = 0.318 g. nickel (-dihydrate)*

= 0.318 g. Ni²⁺

Calcd.:

10 ml. of nickel sulphate = 0.318 g. Ni²⁺

Error = +0.0008 g.

= +0.008 g.

All the results are given in Table XIV on page 27.

The above estimation was repeated using a solution of sodium acetate to raise the pH.

Incl.:  

Found:

10 ml. of nickel sulphate = 0.327 g. nickel (-dihydrate)*

= 0.318 g. Ni²⁺

Calcd.:

10 ml. of nickel sulphate = 0.3185 g. Ni²⁺

Error = +0.0005 g.

= +0.005 g.

Nickel in presence of copper:

10 ml. each of the standard solutions of nickel sulphate and copper sulphate were mixed and treated for the removal of mineral acidity. The pH was adjusted to 5.0 to 5.5, volume to 70 ml. and at 0°C, an excess of the reagent was added. The copper complex precipitated was digested, filtered and washed.
The filtrate along with the washings was warmed and treated with a dilute solution of ammonium hydroxide to raise the pH to 5.5 when the nickel complex separated. It was digested, filtered, washed, dried and weighed as usual.

**Results:**

**Found:**

10 ml. of nickel sulphate = 0.527% \( \text{g. nickel} \cdot \text{hydroxy-5-}
\text{methylisophthalone}
\text{amine} \)

= 0.05184 g. \( \text{Ni}^{2+} \)

**Calcd:**

10 ml. of nickel sulphate = 0.56184 g. \( \text{Ni}^{2+} \)

\[ \text{Error} = +0.00023 \text{g.} \]

= +0.44%

**Nickel in presence of cobalt:**

A mixture of 10 ml. each of the standard solutions of nickel sulphate and cobalt chloride was diluted to about 25 ml. and warmed (90°). 25 ml. of the reagent was added followed by a dilute solution of sodium acetate to raise the pH of the solution to 5.5 when the nickel complex precipitated. It was digested, filtered, washed, dried and weighed as usual.

**Results:**

**Found:**

10 ml. of nickel sulphate = 0.5330 g. \( \text{nickel} \cdot \text{hydroxy-5-}
\text{methylisophthalone}
\text{amine} \)

= 0.05184 g. \( \text{Ni}^{2+} \)

**Calcd:**

10 ml. of nickel sulphate = 0.56184 g. \( \text{Ni}^{2+} \)

\[ \text{Error} = +0.00023 \text{g.} \]

= +0.44%
Nickel in presence of other cations:

The solutions of chromium chloride, cadmium sulphate, copper sulphate, aluminium sulphate, manganese sulphate and beryllium sulphate prepared as described earlier were used.

A mixture of 10 ml. of the standard solution of nickel sulphate and 10 ml. of standard solution of the desired cation, was diluted to about 50 ml. and warmed. 50 ml. of the reagents was added followed by dilute sodium acetate solution to maintain the pH to 5.5 when the nickel complex precipitated. It was digested, filtered, washed, dried and weighed as usual.

All the results are given in Table XII on page 106.

Copper and nickel in presence of each other:

Copper-Nickel (1:1):

10 ml. each of the standard solutions of copper sulphate and nickel sulphate were mixed and the mineral sediment was removed as usual. The solution was adjusted to pH 2.0, diluted to about 70 ml. and warmed. The reagents (45 ml., 15%) were then added when the copper complex precipitated. It was digested, filtered, washed, dried and weighed as usual.

The filtrate and the washings were mixed, warmed to 100° and treated with a dilute solution of ammonium hydroxide to raise the pH to 5.5 when the nickel complex precipitated. It was digested, filtered, washed, dried and weighed as usual.
Results:

Found:

10 ml. of copper sulphate = 0.5093 g. 

\[ \text{copper}^{2+} \text{oxo-3-nitrophenolphthalein} \]

= 0.00366 g. Cu²⁺

Calcd:

10 ml. of copper sulphate = 0.6526 g. Cu²⁺

\[ \text{error} = +0.00366 \text{g.} \]

= +0.56%

Found:

10 ml. of nickel sulphate = 0.5270 g. 

\[ \text{nickel}^{2+} \text{oxo-3-nitrophenolphthalein} \]

= 0.3611 g. Ni²⁺

Calcd:

10 ml. of nickel sulphate = 0.6419 g. Ni²⁺

\[ \text{error} = +0.00366 \text{g.} \]

= +0.44%

Copper:Nickel 1:10.1

10 ml. of the standard solution of copper sulphate and 1 ml. of the standard solution of nickel sulphate were mixed and estimation carried out as above.

Results:

Found:

10 ml. of copper sulphate = 0.5092 g. 

\[ \text{copper}^{2+} \text{oxo-3-nitrophenolphthalein} \]

= 0.00379 g. Cu²⁺

Calcd:

10 ml. of copper sulphate = 0.6524 g. Cu²⁺

\[ \text{error} = +0.00379 \text{g.} \]

= +0.59%
1 ml. of nickel sulphate = $0.0525 \text{ mole} = 0.0525 \text{ moles} = 0.0525 \text{ mole}

\text{Calc:}

1 ml. of nickel sulphate = $0.0525 \text{ mole} = 0.0525 \text{ moles} = 0.0525 \text{ mole}

\text{Copper: Nickel 1:1:10}

1 ml. of the standard solution of copper sulphate at 10 ml. of the standard solution of nickel sulphate at 1:1, and estimated as usual.

\text{Calc:}

1 ml. of the copper sulphate = $0.006247 \text{ mole} = 0.006247 \text{ moles} = 0.006247 \text{ mole}

\text{Error} = +0.00025 \text{ mole}

\text{Calc:}

10 ml. of nickel sulphate = $0.0525 \text{ mole} = 0.0525 \text{ moles} = 0.0525 \text{ mole}

\text{Calc:}

10 ml. of nickel sulphate = $0.0525 \text{ mole} = 0.0525 \text{ moles} = 0.0525 \text{ mole}
Extraction of cobalt

10 ml. of the standard solution of cobalt chloride diluted to about 60 ml. was warmed and treated with 15 ml. of the reagent followed by a dilute solution of ammonium hydroxide to raise the pH to about 7.0. The dark reddish brown precipitate formed was then digested, filtered hot, washed, dried and weighed as before.

**Results**

**Found:**

10 ml. of cobalt chloride = 0.9504 g. cobalt \(\text{Co}^{2+}\), amalgamated, benzene (in the above solution of cobalt acetate to adjust the pH, the above extraction was repeated using a solution of cadmium acetate to adjust the pH.

**Calcd.:**

10 ml. of cobalt chloride = 0.9504 g. cobalt \(\text{Co}^{2+}\), amalgamated, benzene (in the above solution of cobalt acetate to adjust the pH, the above extraction was repeated using a solution of cadmium acetate to adjust the pH.)
Cobalt in presence of copper

10 ml. each of the standard solutions of cobalt chloride and copper sulphate were mixed and warmed for about 15 minutes. The pH was adjusted to 3.5 to 4.5, volume = 5 ml., warmed to about 50° and the complex of cobalt precipitated as usual by adding a sufficient reagent solution. The filtrate and washings were mixed, warmed and treated with dilute solution of ammonium hydroxide to raise the pH to about 11, when the cobalt complex precipitated. It was filtered, washed, dried and weighed as usual.

Results

Found:

10 ml. of cobalt chloride = 0.0044 g. cobalt

Calcd:

10 ml. of cobalt chloride = 0.0043 g. cobalt

Error = +0.008%

Cobalt in presence of nickel

10 ml. each of the standard solutions of cobalt chloride and nickel sulphate were mixed, warmed and treated in an excess of the reagent followed by solution of sodium acetate to precipitate the nickel complex as usual at pH 4.7, the filtrate and washings were mixed, warmed to about 50° for a dilute solution of ammonium hydroxide was added to raise the pH to about 7.5, when the cobalt complex precipitated. It was filtered, washed, dried and weighed as usual.
Cobalt and copper in presence of each other.

A mixture of 10 ml. each of the standard solution of copper sulphate and cobalt chloride was treated for visual acidity as usual, diluted to about 50 ml., warmed (50° C.) until an excess of the reagent was added. The faintly olive-green precipitate of the copper complex was digested, filtered, washed, dried and weighed as usual.

A dilute solution of ammonium hydroxide was added to the warmed mixture of filtrate and washing to make the pH to about 7.0, the cobalt complex precipitated was digested, filtered, washed, dried and weighed as usual.

Cobalt

Found:

10 ml. of cobalt chloride = 0.05388 g. cobalt 

Calcd:

10 ml. of cobalt chloride = 0.05388 g. cobalt 

Error = +0.0006 g. 

= 0.022%.
10 ml. of cobalt chloride = 0.0354 g. cobalt 2-hydroxy-5-
methylibenzophenone

= 0.0354 g. Co**

Calcd:
10 ml. of cobalt chloride = 0.03542 g. Co**

\[ \text{Error} = \pm 0.00029 \text{ g.} \]

\[ \text{Error} = \pm 0.3\% \]

Cobalt and nickel in presence of each other:

A mixture of 10 ml. each of the standard solutions of
nickel sulphate and cobalt chloride was diluted (30 ml.),
warmed and treated with an excess of the reagent followed by
a solution of sodium acetate to raise the pH to 3.5, when the
nickel complex precipitated. It was digested, filtered, washed,
dried and weighed as usual.

The filtrate and the washings were mixed, warmed and
a dilute solution of aqueous hydroxide was added so on to
raise the pH to 7.0, when the cobalt complex precipitated. It
was digested, filtered, washed, dried and weighed as usual.

Result:
found:
10 ml. of nickel sulphate = 0.0579 g. nickel 2-hydroxy-5-
methylibenzophenone

= 0.0579 g. Ni**

Calcd:
10 ml. of nickel sulphate = 0.06154 g. Ni**

\[ \text{Error} = \pm 0.0039 \text{ g.} \]

\[ \text{Error} = \pm 0.6\% \]
10 ml. of cobalt chloride = 0.006 g. cobalt, as Co+.

Sulfonlt.

10 ml. of cobalt chloride = 0.5,702 g. Co++

Solv. = 4.00 g. to 10.

Dissolve nickel and cobalt in presence of ortho-

sulfate.

A mixture of 10 ml. each of the solutions with one of

ammonium hypochlorite, nickel sulfate and cobalt chloride was taken for the mineral acidity as usual. In the solution (pH = 4) an excess of the reagents was added, and a cobalt complex precipitated. It was filtered, washed, dried and weighed as usual.

The filtrate and washings were taken to pH 2 by adding a solution of sodium hydroxide. A nickel complex precipitated was filtered, washed, dried and weighed as usual.

A dilute solution of ammonium hydroxide was added to form a precipitate of cobalt complex. It was filtered, washed, dried and weighed as usual.
<table>
<thead>
<tr>
<th>Compositions</th>
<th>Calculations</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 ml. of copper sulphate</td>
<td>0.0066</td>
<td>0.066 g</td>
</tr>
<tr>
<td>10 ml. of nickel sulphate</td>
<td>0.0112</td>
<td>0.112 g</td>
</tr>
<tr>
<td>10 ml. of cobalt chloride</td>
<td>0.0089</td>
<td>0.089 g</td>
</tr>
</tbody>
</table>
Saliycilaldazine, 2-hydoxyetethylsulphonamide oxime and 2-hydroyetethylbenzothiazolone oxime, which like salicylaldazine contain the copper specific groups: 

\[ \mathcal{O} = \mathcal{O} = \mathcal{O} = \mathcal{O} = \mathcal{O} \]

have been found, as would be expected, similar in their reactions with various actions.

Saliycilaldazine.

The copper complex is precipitated by all the three reagents between the pH 5.0 to 6.0. These oximes like other reagents of the same type, also precipitate copper from an acetic acid medium. The sensitivity of these reagents (in cupferion) (0.01% w/w) is quite comparable with the other reagents. This can be observed from the table given below;

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Sensitivity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saliycilaldazine</td>
<td>0.5</td>
<td>Yosef and Raphael, loc. cit. 121, 125. 126</td>
</tr>
<tr>
<td>Benzoinic acid</td>
<td>0.03</td>
<td>Yosef, loc. cit. 12. 14, 126. 127. 128</td>
</tr>
<tr>
<td>Phosphoasphyric acid</td>
<td>0.3</td>
<td>Yosef and Raphael, loc. cit. 125, 126, 127</td>
</tr>
<tr>
<td>Suberic acid</td>
<td>0.005</td>
<td>Yosef and Raphael, loc. cit. 125, 126, 127</td>
</tr>
<tr>
<td>Saliycilaldazine</td>
<td>0.5</td>
<td>Yosef and Raphael, loc. cit. 121, 125. 126</td>
</tr>
<tr>
<td>Saliycilaldazine (Caprin)</td>
<td>0.50</td>
<td>Yosef, loc. cit. 12. 14, 126. 127. 128</td>
</tr>
<tr>
<td>Alizarin blue</td>
<td>0.004</td>
<td>Yosef and Raphael, loc. cit. 125, 126, 127</td>
</tr>
<tr>
<td>Ammonium mercuric thioselenate</td>
<td>0.1</td>
<td>Yosef and Raphael, loc. cit. 125, 126, 127</td>
</tr>
<tr>
<td>Catalytic effect on the ferric triscuprate acetate reaction</td>
<td>0.02</td>
<td>Yosef and Raphael, loc. cit. 125, 126, 127</td>
</tr>
</tbody>
</table>
The copper complexes of the oximes, as would be expected are soluble in non polar solvents. They dissolve in concentrated nitric acid, probably due to salt formation with HNO₃ as in case of methylidenonin complexes (cf. Aoki and Uda, J. Chem. Soc., 1928, 2389; 1929, 2380). They are reprecipitated on dilution, which may be due to the hydrolysis of the salts on dilution. The complexes are decomposed by hot concentrated acids.

The nickel complex is precipitated by the reagents between the pH 5.0 to 5.5. The sensitivity of these oximes for nickel ion (0.78 v/m) is quite comparable with the oximes examined earlier, the table for which is given below:

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Sensitivity</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylidionine</td>
<td>0.9</td>
<td>I. P. Steege, loc. cit., 395, 396.</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>0.12</td>
<td>W. F. and W. J., loc. cit.</td>
</tr>
<tr>
<td>Methylidionine</td>
<td>0.25</td>
<td>E. C. B. H., loc. cit., 1923, 642.</td>
</tr>
<tr>
<td>L-Ascorbic acid</td>
<td>0.10</td>
<td>B. A. D. B. D., loc. cit., 1923, 662, 663.</td>
</tr>
</tbody>
</table>

The solubility of the nickel complexes in non polar solvents as well as their behavior towards alkalis and acids are similar to those of copper.

The cobalt complex is precipitated by these reagents between the pH 5.0 to 5.5. The sensitivity of these oximes for cobalt ion (0.2 v/m) is comparable with the oximes examined earlier, the table for which is given below:

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Sensitivity</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylidionine</td>
<td>0.9</td>
<td>I. P. Steege, loc. cit., 395, 396.</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>0.12</td>
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</tr>
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<td>Methylidionine</td>
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</tr>
<tr>
<td>L-Ascorbic acid</td>
<td>0.10</td>
<td>B. A. D. B. D., loc. cit., 1923, 662, 663.</td>
</tr>
</tbody>
</table>
The solubility of the cobalt complexes in non-polar solvents is similar to that of copper. The behaviour of the cobalt complexes towards alkaline and acidic in similar to those of copper. 

With ferric ion a yellow complex even in a solution containing dilute hydrochloric acid. The solubility of the palladium complexes in organic solvents as well as their tendency towards alkaline occur and acids are similar to those of copper.

With feroce ion a violet solution not extractable with non-polar solvents is formed with the exclusion between p\text{H} 3.2 and 3.0; but on raising the \text{pH} above \text{pH} 3.5 up to \text{pH} 5.0, a white precipitate is obtained which is extractable with some polar solvents.

With ferrocene the reagent forms a reddish brown solution extractable with non-polar solvents between \text{pH} 4.0 to 5.0 on raising the \text{pH} to about 5.5 a reddish precipitate of ferrocene hydroxide is formed.
cisses; however, at a higher pH the respective hydroxides are precipitated.

The advantage can be taken of the different ranges of pH required by these reagents for the precipitation of copper, nickel, and cobalt ions, for their individual detection in presence of one another - copper precipitating first at a low pH (below 3.0), followed by nickel (3.5 - 6.5) and finally cobalt above 6.5. Further it has been observed that copper always precipitates first in the presence of the other two cations, nickel does not interfere up to pH 3.5, cobalt does not interfere up to pH 6.0 with copper or nickel or both. The interference of iron during the precipitation of copper and nickel can be prevented by suppressing it as a soluble complex by the addition of Rochelle salts or potassium citrate.

The iron salt present in the solution was hydrolyzed once the mineral acid in neutralized and acidified with acetic acid. In order to prevent the hydrolysis of the iron salt one of the above salts is required to be added to the solution. After the suppression of iron, copper and nickel can be precipitated at their required pH. Copper and nickel can be extracted in presence of other cations mentioned before (copper, nickel) by the usual method followed for their individual detection if no cation interferes upto pH 6.5.

**Estimation of copper:**

The determination of copper using any of these reagents can be carried out by almost the same procedure as iron with salicylaldazine or any oxine having a similar specific group.
The results are quite comparable with any of the other reagents used in gravimetric analysis. Even, it can be used to determine copper in Töpler's solution, taking certain precaution. Ordinarily when the reagent is added directly to Töpler's solution, there is no complete precipitation. However, on dilution a complete quantitative precipitation occurs. This, as pointed out earlier may probably be due to salt formation with CuCl in concentrated alkaline solutions but the salt goes hydrolysed on dilution.

The reagents can be easily and successfully used for the estimation of copper in presence of cations like chromium, zinc, zinc, aluminum, beryllium or manganese which ordinarily do not interfere. Even when cations like nickel, cobalt are present; advantage can be taken of the lower pH of 3.4. Under copper gets precipitated as compared to pH 5.0 for nickel and at pH 3.5 for cobalt and copper can be successfully determined. The interference of iron (Fe^{3+} or Fe^{2+}) can be controlled by the addition of Rochelle salt or potassium chloride.

The advantages these reagents have over molybdenum are:

1. Töpler's solution decomposes slowly in a solution and the reagent can not be kept for more than three days (cf. p. 163: A text-book of quantitative Inorganic analysis, Longman, Green S Co., Ltd. 1936, p.163). On the other hand the present reagent can be kept for weeks without decomposition. This is significant, as alizarine are more susceptible to oxidation than alizarine. The same would apply to the corresponding CuCl chelates from alizarine and alizarine, there then the former...
(ii) These reagents can precipitate copper even in a boiling solution and the precipitate can be safely washed with hot water.

(iii) As compared to salicyaldehyde, there is a comparatively wider range of pH for precipitation of copper and nickel which can thus be used for individual determination of one another in a mixture. (Dinelli and Ilcre, Ind. Geol. Chem., vol. 33, 1935, p. 321).

<table>
<thead>
<tr>
<th>pH for complete precipitation of copper</th>
<th>pH for interference (\text{by nickel} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salicyaldehyde</td>
<td>3.5</td>
</tr>
<tr>
<td>Pyrocatechol</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Over and above the reagents of the similar type mentioned earlier, there is a large number of reagents used for the quantitative determination of copper.

The reagents most commonly used are oximines, thiocyanate, benzoquinone, \(-\)-nitroso-\(-\)-naphthol, quinidine, pyridine, cupferren, anthraquinone acid, \(3\)-hydroxy quinoline, and benzoic acid.

The thiocyanate method though accurate and reliable, is not quick as the precipitated copper compound has to be allowed to stand overnight (Vogel, op. cit., p. 312) while the pyridine method though rapid has the disadvantage that cobalt, nickel, manganese, cadmium and molybdenum also form precipitates simultaneously (Vogel, op. cit., p. 312).

The procedure for the quantitative determination
of nickel using these reagents is just similar to that followed for its determination using other oximes of the same group as well as dimethylglyoxime. The results obtained can be compared with any of the other reagents used in spectrometric analyses.

The oximes can be conveniently used for the quantitative determination of nickel in presence of other oximes like chromium, etc., mentioned previously, which generally do not interfere at pH 5.5. The interference of cobalt can be prevented by precipitating the nickel complex at pH 5.5 when cobalt does not interfere. In case of iron, an addition of Rochelle salt or potassium citrate keeps iron in solution and thereby prevents its co-precipitation with the nickel complex.

Dimethylglyoxime is the most commonly used reagent for the quantitative determination of nickel due to its specificity for the same; however, the present reagents have got certain advantages over dimethylglyoxime as shown below:

(i) Dimethylglyoxime does not keep very long and the reagent solution gradually decomposes (Dillion and Macginn, A Treatise of Chemical Analysis, 5th Ed., McGraw-Hill, 1950, p.423), while the present oximes can be kept for weeks without decomposition.

(ii) Dimethylglyoxime is very sparingly soluble even in hot water hence it requires more washings and a controlled addition of the reagent (Goyal, op.cit., p.129). On the other hand, the present oximes are soluble in hot water and hence can be readily washed-off.

(iii) The nickel dimethylglyoxime dissolves in 2.5 volumes of ethanol (Goyal, op.cit., p.129), while the nickel complexes
ure quite insoluble and hence can be very safely shaken with ethanol and thus be more rapidly dried.

(iv) One more advantage of the present amines over dimethylglyoxime is that the former have got larger molecular weights than the latter which thus give a larger weight of precipitate for a given weight of nickel.

<table>
<thead>
<tr>
<th>Dimethylglyoxime</th>
<th>Chloroform</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Hydroxy-2-methylacetophenone oxime</td>
<td>130.0</td>
</tr>
<tr>
<td>2-Hydroxy-3-methylpropionophenone oxime</td>
<td>170.0</td>
</tr>
<tr>
<td>2-Hydroxy-3-methylbenzophenone oxime</td>
<td>177.0</td>
</tr>
</tbody>
</table>

Using these reagents copper and nickel can be quantitatively determined in presence of each other even in the proportion of 1:1 or 1:10; with dimethylglyoxime also the separation gives good results in a copper-nickel ratio of 5:1 (University and and D. Alley, J. Chem. Soc., 1953, 395). The reagents can separate copper and nickel from an alloy. It appears from literature that not much attention has been paid for the quantitative determination of cobalt using the reagents containing this specific grouping, though it has been observed that they form a normal complex with cobalt.

It has now been observed that cobalt can be quantitatively determined in the bistetrazos form using these reagents adjusting the pH of about 7.0 and avoiding an excess of ethanol due to the solubility of the complex in the excess of ethanol. The complex is found to dissolve above pH 7.0 hence it can be in precipitated below that pH.
Nitroso-β-naphthol is commonly used for the quantitative determination of cobalt but it has got certain disadvantages which are mentioned below:

(i) This method is complicated and lengthy (Vogel, op. cit., p. 105).

(ii) In this method cobaltous is to be oxidized to cobaltic state to obtain the formula-gure compound. (Vogel, op. cit., p.106).

(iii) The oxidation with hydrogen peroxide followed by the precipitation of cobaltic hydroxide in a very vigorous reaction and if the precipitation is not done with proper precautions, there are all chances of loss; one of the precipitations due to spiring. (Vogel, op. cit., p.107).

(iv) Another drawback of the reagent is, that the final precipitate of the cobalt complex requires a long period, first with hot acetic acid and then with boiling water.

(v) By this method not more than 25 mg. of cobalt can be determined, since drying of large amount of precipitate requires several hours before a constant weight is reached (M. Prodingar : Organic reagents used in quantitative inorganic analysis; Alvinier Publishing Co. Inc., 1950, p.112).

(vi) Finally −nitroso-β-naphthol is very unstable in the aqueous solution and must be freshly prepared. (Vogel, op. cit., p. 546).

The advantage of the wide scope of pH of precipitation of copper, nickel and cobalt in taken base and all the three cations can easily estimated in presence of one another by simply a control of pH.