GALLACETOPHENONE OXIME AS A REAGENT FOR GRAVIMETRIC DETERMINATION OF COPPER AND ITS SEPARATION FROM OTHER ELEMENTS

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INTRODUCTION

EPHRAIM investigated several ortho-hydroxy aldoximes and ketoximes and came to the conclusion that salicylaldoxime was by far the best for the gravimetric determination of copper. Subsequently, resacetophenone oxime, ortho-hydroxy acetophenone oxime and ortho-vanillin oxime were introduced as gravimetric precipitants for copper and its separation from other elements.

Gallacetophenone oxime which can be readily prepared in a pure crystalline form and is quite soluble in water was not previously investigated as a reagent for copper. In the present investigations it was found that this oxime reacted with several metal ions, viz., Cd\(^{2+}\), Cu\(^{2+}\), Co\(^{2+}\), Hg\(^{2+}\), Ni\(^{2+}\), Pd\(^{2+}\), Pb\(^{2+}\), Zn\(^{2+}\), Al\(^{3+}\), Bi\(^{3+}\), Fe\(^{3+}\), Ga\(^{3+}\), In\(^{3+}\), La\(^{3+}\), Pr\(^{3+}\), Sm\(^{3+}\), Sb\(^{3+}\), Ge\(^{4+}\), Th\(^{4+}\), Ti\(^{4+}\), Zr\(^{4+}\), Nb\(^{5+}\), Ta\(^{5+}\), under different conditions yielding insoluble precipitates and with Fe\(^{3+}\), Ba\(^{2+}\), Ca\(^{2+}\), Sr\(^{2+}\), Uo\(^{2+}\), MoO\(_4^{2-}\), Wo\(_4^{2-}\) giving rise to soluble complexes.

Copper was precipitated quantitatively with this reagent in the pH range 3.5–5.5 whereas below pH 4.5 nickel, cadmium, zinc, selenium and manganese were not precipitated. These are the metals usually associated with copper in its ores. Iron, an associate of copper in its minerals and ores, yielded a blue complex soluble in hot water. This interference, however, could be eliminated by reducing Fe\(^{3+}\) to Fe\(^{2+}\) with ascorbic acid in the cold and copper could be determined in the presence of as much as two to three times its weight of iron.
**EXPERIMENTAL**

*Preparation of Gallacetophenone Oxime*

Gallacetophenone was prepared by condensing pyrogallol with acetic acid in presence of zinc chloride. The ketone (40 g.) was taken in a round-bottomed flask and treated with alcohol (10 ml.) and water (100 ml.) followed by hydroxylamine hydrochloride (40 g.). The mixture was refluxed for about five minutes. The contents were neutralised with a mixture of sodium hydroxide (20 g.) and sodium carbonate (4 g.) (pH 7.0). The product was cooled in ice for six hours, filtered, washed thoroughly with ice-cold water and recrystallised from hot water using animal charcoal. Colourless, needle-shaped crystals, m.p. 162-163° C.

*Reagents*

**Gallacetophenone oxime solution.**—A 2 per-cent solution of gallacetophenone oxime was prepared by dissolving the pure sample in 10 per cent aqueous alcohol.

**Copper sulphate.**—Copper sulphate (ca. 0·1 N) solution was standardised iodometrically.

Solutions of Cd$^{2+}$, Ni$^{2+}$, Zn$^{2+}$, Mn$^{2+}$, SeO$_2^{2-}$, and Fe$^{3+}$ were prepared using A.R. grade salts such that each ml. contained about 8 mg. of the metal.

Solutions of acetic acid (2 N) and sodium acetate (10 per cent) were prepared using A.R. quality substances.

**DETERMINATION OF COPPER**

The authors found that copper could be quantitatively precipitated in the pH range, 3.5 to 5.5. The precipitation was incomplete at pH lower than 3·5 and over pH greater than 5·5 erratic results were obtained. The overall concentration of the alcohol should not exceed 2·5 per cent by volume. Under these conditions copper gave a straw yellow precipitate which could be easily filtered, washed and dried to constant weight at 110-120° C. An acetic acid (2 N) solution of the reagent could as well be used instead of the alcoholic reagent. The probable structure of the copper complex is given below.
It contains 14.86 per cent copper (gravimetric factor 0.1486).

PROCEDURE

Solutions of copper sulphate containing 6.0 to 32.0 mg. of copper were pipetted out into a 400 ml. beaker. 10 ml. acetic acid (2 N) and 10 ml. sodium acetate (10 per cent) were added. The solution was diluted to about 110 ml. with distilled water (the pH of the solution was 4.0), a 2 per cent solution of the reagent added gradually until the precipitation was complete. The contents were heated on a water-bath for 10 minutes, allowed to cool for 10 to 15 minutes, filtered through a sintered glass crucible (Schott-Gen 4) and washed with warm water until free from reagent. (The filtrate should give no colour with ferric chloride.) It was then dried to constant weight at 110–120°C. The results calculated on the basis of 14.86 per cent copper are given in Table I.

TABLE I

Determination of copper

<table>
<thead>
<tr>
<th>Copper (mg.) Taken</th>
<th>Copper (mg.) Found</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.355</td>
<td>6.346</td>
<td>-0.14</td>
</tr>
<tr>
<td>9.536</td>
<td>9.541</td>
<td>+0.05</td>
</tr>
<tr>
<td>12.710</td>
<td>12.730</td>
<td>+0.16</td>
</tr>
<tr>
<td>15.890</td>
<td>15.880</td>
<td>-0.06</td>
</tr>
<tr>
<td>19.070</td>
<td>19.100</td>
<td>+0.16</td>
</tr>
<tr>
<td>22.250</td>
<td>22.260</td>
<td>+0.04</td>
</tr>
<tr>
<td>25.420</td>
<td>25.420</td>
<td>-0.00</td>
</tr>
<tr>
<td>28.600</td>
<td>28.620</td>
<td>+0.07</td>
</tr>
<tr>
<td>31.810</td>
<td>31.780</td>
<td>-0.09</td>
</tr>
</tbody>
</table>
The results show that amounts of copper in the range 6.0 to 32.0 mg. could be determined within ±0.16 per cent error.

**Separation of Copper from Other Metals**

The determination of copper was carried out in presence of varying amounts of Ni\(^{2+}\), Cd\(^{2+}\), SeO\(_3^{2-}\), Mn\(^{2+}\) and Fe\(^{3+}\) maintaining the pH at 3.5 to 4.5. The results are given in Table II.

<table>
<thead>
<tr>
<th>Metal added (mg.)</th>
<th>Copper found (mg.)</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni 16.00</td>
<td>12.70</td>
<td>-0.07</td>
</tr>
<tr>
<td>Ni 24.00</td>
<td>12.73</td>
<td>+0.15</td>
</tr>
<tr>
<td>Ni 32.00</td>
<td>12.75</td>
<td>+0.31</td>
</tr>
<tr>
<td>Cd 16.00</td>
<td>12.70</td>
<td>-0.07</td>
</tr>
<tr>
<td>Cd 32.00</td>
<td>12.70</td>
<td>-0.07</td>
</tr>
<tr>
<td>Cd 40.00</td>
<td>12.73</td>
<td>+0.15</td>
</tr>
<tr>
<td>Zn 16.00</td>
<td>12.73</td>
<td>+0.15</td>
</tr>
<tr>
<td>Zn 32.00</td>
<td>12.70</td>
<td>-0.07</td>
</tr>
<tr>
<td>Zn 40.00</td>
<td>12.73</td>
<td>+0.15</td>
</tr>
<tr>
<td>Se 16.00</td>
<td>12.70</td>
<td>-0.07</td>
</tr>
<tr>
<td>Se 24.00</td>
<td>12.73</td>
<td>+0.15</td>
</tr>
<tr>
<td>Se 40.00</td>
<td>12.70</td>
<td>-0.07</td>
</tr>
<tr>
<td>Mn 8.00</td>
<td>12.70</td>
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</tr>
<tr>
<td>Mn 24.00</td>
<td>12.73</td>
<td>+0.15</td>
</tr>
<tr>
<td>Mn 32.00</td>
<td>12.73</td>
<td>+0.15</td>
</tr>
<tr>
<td>Fe 8.00</td>
<td>12.70</td>
<td>-0.07</td>
</tr>
<tr>
<td>Fe 16.00</td>
<td>12.73</td>
<td>+0.15</td>
</tr>
<tr>
<td>Fe 32.00</td>
<td>12.74</td>
<td>+0.24</td>
</tr>
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</table>

The above results confirm that copper could be gravimetrically determined with gallacetophenone oxime with an error of ±0.31 per cent in
Gallacetophenone Oxime as a Reagent for Gravimetric Determination

presence of nickel, cadmium, zinc, selenium, manganese and iron even when these elements are present in two to three fold excess.

**DETERMINATION OF COPPER IN BRASS**

Brass turnings (ca. 1.2 g.) were dissolved in 50 ml. nitric acid (1:1) by gradual heating. The solution was diluted to 150 ml. with distilled water and boiled to remove oxides of nitrogen. Urea (2 g.) was added and the solution boiled to remove traces of nitrous acid. The solution was cooled, filtered and made up to 250 ml. The copper content in the brass solution was determined by the standard iodometric procedure. One ml. of the solution contained 2.733 mg. of copper.

**Gallacetophenone Oxime Method**

Aliquots of brass solution were pipetted out into a 400 ml. beaker. The solution was neutralised with dilute sodium carbonate (1 N) and acidified with dilute acetic acid (2 N) till the blue precipitate redissolved. 10 ml. of sodium acetate (10 per cent), 20 ml. of acetic acid (2 N) were added and diluted to 110 ml. A 2 per cent solution of the reagent was gradually added until the precipitation was complete. It was heated on hot water-bath for 10 minutes, kept aside for 10-15 minutes, filtered through a sintered glass crucible (Schott-Gen 4) and washed with warm water until the precipitate was free from the reagent. The precipitate was dried at 110-120° C. to constant weight. The results are given in Table III.

**TABLE III**

*Determination of copper in brass*

<table>
<thead>
<tr>
<th>Weight of copper (mg.)</th>
<th>Taken</th>
<th>Found</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.67</td>
<td>13.71</td>
<td>+0.29</td>
<td></td>
</tr>
<tr>
<td>27.33</td>
<td>27.40</td>
<td>+0.26</td>
<td></td>
</tr>
<tr>
<td>41.00</td>
<td>41.11</td>
<td>+0.26</td>
<td></td>
</tr>
<tr>
<td>54.66</td>
<td>54.82</td>
<td>+0.29</td>
<td></td>
</tr>
</tbody>
</table>
The galactophenone oxime method can be successfully employed for the determination of copper in brass with a maximum error ± 0.29 per cent.

CONCLUSION

Gallactophenone oxime is a more useful analytical reagent for the determination of copper in presence of nickel, cadmium, zinc, manganese, selenium and iron than either salicylaldioxime or resacetophenone oxime. It is more soluble in water and its gravimetric factor (0.1486) is more favourable than with either salicylaldioxime (0.1895) or resacetophenone oxime (0.1607).

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