A Comparative Study on the Chemical and Instrumental Methods for Quantitative Determination of Copper in Malachite

By

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Date of Examination 10.07.2010
Dedication

I want to dedicate

TO My Mother

To My Father

To All who believe on the oneness of ALLAH

And to the soul of my dear sisters

Heba & Hadeel

To my sisters

Molok, Zeniub & Zehour

To my brother

Ahmed

&

Step mother
Acknowledgement

First and above all thankful to ALLAH whom under his will, assistance and kindness this research has reached its final stage.

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Thanks to the Corporation of Geological Center for providing analytic sample Particularly Dr. Eltaher Mosalam & ostaza Gada Elhindy.

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Great thanks to my sisters Zehour & Molok Saeed & my brother in low Mr. Mohayad Sideg for their financial contributions.

Finally I find myself grateful to all who have participated in the printing revising or production of this thesis.
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Master of Science in Chemistry, July 2010
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Abstract

The major ore of the metal copper pyrite (CuFeS\textsubscript{2}) which is estimate to account for about 5\% of all copper ores. Malachite is also an important ore of copper, (basic carbonate).

This study is about different methods of analysis of malachite copper ore which has molecular formula CuCO\textsubscript{3}.Cu (OH)\textsubscript{2}. The samples are collected by Geological research center from Red sea hills, Eastern Sudan, Obear area. The analysis is made by classical iodometric methods, and Spectroscopic methods.

The results by both methods show copper percentages in range 4-5 \% copper. Comparing these results with previous study by Corporation of Geological Center, it is approximately identical.

The iodometric method was found to be simpler, of lower cost and time saving.
دراسة مقارنة الطرق الكيميائية و الصناعية
لتحليل النحاس كمياً في خام الملكايت

مريم محمد سعيد محمد

ماجستير العلوم في الكيمياء، يوليو 2010
قسم الكيمياء التطبيقية و تكنولوجيا
كلية الهندسة و التكنولوجيا
جامعة الجزيرة

الملخص

أهم خامات النحاس هو البيرايت (C₄FeS₂) والذي يمثل 5% من جملة خامات النحاس، هو خام مهم من خامات النحاس. هذه الدراسة شملت تحليل النحاس كمياً بعدة طرق و مقارنتها لعينه من خام الملكايت (كربونات النحاس القاعدية) (CuCO₃(OH)₂) (C₄FeS₂) (CuCO₃(OH)₂). العينات جمعت بواسطة هيئة الأبحاث الجيولوجية من شرق السودان مناطق جبال البحر الأحمر من منطقة أوهير. التحليل شمل تحليل النحاس بالطرق الأيونومترية والوزنية وطرق التحليل الطيفي. وجدت نسبة النحاس في المدى 5-4%. بمقارنة هذه النتائج بالنتائج السابقة من هيئة الأبحاث الجيولوجية وجد أنها متطابقة تقريباً. وجد أن طريقة التحليل الأيونومترية هي الطريقة الأفضل للطرق لأنها البسيطة والغير معقدة والأقل تكلفة ولا تستهلك زمن.
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Introduction:

1- Copper: History and Occurrence

Copper appears to have been known from prehistoric times the Neolithic Age long before histories of the ancient peoples were engraved on Stone Pillars or inscribed on Papyri. The "Copper Age" followed the "Stone Age". At the time of Ramses (about 1300 B.C), copper was costly that it was stored among the treasures of Egyptian temples.

Copper was appear to have been used for making utensils and instrument for war before iron. This is probably due to the fact that copper occurs native in a form requiring no metallurgical treatment. The ancient used the term χαλός (chalcos) and aes for copper, brass, and bronze. In fact, the terms for copper, brass, and bronze are much confused by the old writers, showing that they did not understand the difference- e.g. Piliny.

Copper was afterwards called aes cyprium (i.e, Cyprian brass), since the Romans first obtained it form the isle of Cyprus; the term aes cyprium was soon abbreviated to cyprum, hence, the modern symbol "Cu".

Copper is known for at least in thirty two localities in the Sudan ( table 1 ), but only one of these Hofrat en Nahas, has been proved and attracted commercial interests.

Table (1)
List of Copper Localities, Sudan

<table>
<thead>
<tr>
<th>Name</th>
<th>Coordinates</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Southern Darfur und</strong></td>
<td></td>
<td></td>
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<tr>
<td>Western Bahre el Ghazal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>77. Hofrat en Nahas</td>
<td>09° 45' N</td>
<td>Hofrat en Nahas</td>
</tr>
<tr>
<td></td>
<td>24° 18' E</td>
<td>65-I</td>
</tr>
<tr>
<td>78. J. Jangi</td>
<td>09° 16' N</td>
<td>Hofrat en Nahas</td>
</tr>
<tr>
<td></td>
<td>24° 22' E</td>
<td>65-I</td>
</tr>
<tr>
<td>79. J. Terezol</td>
<td>09° 01' N</td>
<td>Hofrat en Nahas</td>
</tr>
<tr>
<td></td>
<td>24° 18' E</td>
<td>65-I</td>
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<tr>
<td>80. J. Zanad</td>
<td>09° 27' N</td>
<td>Hofrat en Nahas</td>
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<td></td>
<td>24° 15' E</td>
<td>65-I</td>
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<tr>
<td>81. J. Nebi</td>
<td>?</td>
<td>Hofrat en Nahas</td>
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<td>65-I</td>
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<tr>
<td>82. Khor Sirri</td>
<td>09° 14' N</td>
<td>Hofrat en Nahas</td>
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<td></td>
<td>24° 07' E</td>
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<td>83. J. Bishara</td>
<td>09° 31' N</td>
<td>Hofrat en Nahas</td>
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<td>23° 37' E</td>
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<td>84. J. Yirongo</td>
<td>09° 28' N</td>
<td>Hofrat en Nahas</td>
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<td>24° 05' E</td>
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<td>85. J. Warranga</td>
<td>09° 22' N</td>
<td>Hofrat en Nahas</td>
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<td>24° 02' E</td>
<td>65-I</td>
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<tr>
<td>86. J. Sirri</td>
<td>09° 16' N</td>
<td>Bir Khadra</td>
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<td></td>
<td>23° 59' E</td>
<td>65-L</td>
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<tr>
<td>87. J. Kairia</td>
<td>09° 28' N</td>
<td>Bir Khadra</td>
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<td></td>
<td>23° 53' E</td>
<td>65-L</td>
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<tr>
<td>88. K. between Ndongo-K. Kairia</td>
<td>09° 07' N</td>
<td></td>
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<td></td>
<td>23° 52' E</td>
<td></td>
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<tr>
<td>89. J. Patapan</td>
<td>09° 25' N</td>
<td>Hofrat en Nahas</td>
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<td>24° 08' E</td>
<td>65-1</td>
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<td><strong>Northern Jubal el Bahre el Ahmer</strong></td>
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<td>90. Mohammed Qol</td>
<td>?</td>
<td>Mohd. Qol</td>
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<td>Two localities details uncertain</td>
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<td></td>
<td></td>
<td>36-M</td>
</tr>
<tr>
<td>91. Halaib area</td>
<td>?</td>
<td>Halaib</td>
</tr>
<tr>
<td></td>
<td></td>
<td>One locality</td>
</tr>
<tr>
<td>92. Sufaya or Safaia</td>
<td>21° 17' N</td>
<td>Dungunab</td>
</tr>
<tr>
<td></td>
<td>36° 14' E</td>
<td>36-1</td>
</tr>
<tr>
<td>93. Shishiteib or Shashitaib Mine</td>
<td>21° 59' N</td>
<td>Halaib</td>
</tr>
<tr>
<td></td>
<td>36° 03' E</td>
<td>Traces of copper carbonate</td>
</tr>
<tr>
<td>94. Ferokit Well</td>
<td>21° 30' N</td>
<td>Gungunab</td>
</tr>
<tr>
<td></td>
<td>36° 39' E</td>
<td>Traces of copper carbonate</td>
</tr>
<tr>
<td><strong>Southern Jubal el Bahre el Ahmer Tokar Prospecting Syndicate</strong></td>
<td></td>
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</tr>
<tr>
<td>95. Karora area</td>
<td>?</td>
<td>Karora</td>
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<td></td>
<td>46-J</td>
</tr>
</tbody>
</table>

Copper silver and gold, collectively\(^{(3)}\) known as the coinage metals, because of their former usage. These elements were
almost certainly the first three metals known to man. All of them occur in the elemental or native.

Estimates of the earliest use of copper vary, but 5000BC is not reasonable, by about 3500 BC, it was being obtained in the middle east by charcoal reduction, of it is ores, and by 3000 BC the advantages of addition Tin in order to produce the harder Bronze was appreciate in India, Mesopotamia and Greece. This established the Bronze age, so Copper has obtained to be one of man's most important metal.

Metallic copper is found in many localities; e.g. considerable masses have been found in Michigan, on the shores of lake superior; and small quantities, in many other places-Cornwall, Seberia, Ural, Australia and Chile, compounds of copper are distributed in nature as oxide in cuprite, copper also occur in many places as basic carbonate, Malachite \( \text{Cu} \text{CO}_3 \cdot \text{Cu(OH)}_2 \). Copper silicate, arsenate, phosphate, etc are also known to occur native. Copper has also been found in the feather of some birds.

Copper mineralization occurs in many parts of the Sudan. Normally in closed association with the green stone (ophiolite belts). Most of the record occurred, have only been examined superficially and only two areas have been investigated specifically for their copper potential. These two areas are Hofrat en Nahas in Southern Dar Fur (approximately 10 million Tons at 2.7%) and the Ariab basin in Southern red sea hills.
where several massive sulphide deposits have recently been located which cumulatively total about 70 million ton containing low value of copper, lead, zinc, gold and silver. The close association of copper mineralization with the green stone ophiolite belts suggests by analogy with similar geological environments in Canada and Western Australia that two types of copper deposit exist in Sudan.

1.2 Ores:

Copper is found mainly as the sulfide, oxide, or carbonate. It's major ores being copper pyrite (chalcopyrite \(\text{CuFeS}_2\)), which is estimate to account for about 5% of all copper glance (chalcopyrite) \(\text{Cu}_2\text{S}\), cuprite \(\text{Cu}_2\text{O}\) and malachite \(\text{Cu}_2\text{CO}_3(\text{OH})_2\). Large deposits are found in various parts of North and South America, and in Africa and the former Soviet Union. The natural copper found near Lakes Superior is extremely pure but the vast majority of current supplies of copper are obtained from low grade areas containing only about 1% copper.

\textit{a - Malachite} is a carbonate mineral known as copper carbonate with the formula \(\text{Cu}_2\text{CO}_3(\text{OH})_2\), the mineral was given this name because due to its resemblance to the leaves of the Mallow plant. Malachite was used as a mineral pigment in green paints from antiquity until about 1800. The pigment is moderately lightfast, very sensitive to acids and varying in color. The natural form was being replace by its synthetic form.
Malachite often results from weathering of copper ore and is often found together with azurite \((\text{Cu}_3\text{CO}_3\text{)}_2(\text{OH})_2\), goethite, and calcite. Except for its green color, the properties of malachite are similar to those of azurite and aggregates of the two minerals occur frequently together. Malachite is more common than azurite and is typically associated with copper deposits around limestone, the source of carbonate. Large quantities of malachite have been mined in Urals, Russia. It is found worldwide including in the Democratic Republic of Congo; Zambia; Namibia; Mexico\(^{(5)}\) . . .

It's a copper-bearing mineral, with as much\(^{(6)}\) as 58% copper content. The distinctive bright-green hydrous CARBONATE MINERAL malachite is a common but minor ore of copper. It is usually found in copper deposits associated with LIMESTONE, occurring with AZURITE as the weathering product of other copper ore minerals. Hardness is 3 1/2 to 4; streak is pale green, specific gravity is 3.9 to 4.1, and luster is a damantine to silky. Malachite forms needle-like prismatic crystals (monoclinic system) that are rarely distinct; it is usually found in granular, earthy, or fibrous masses and rounded, banded crusts. Malachite is used as a decorative stone when cut and polished, a semiprecious gem, and a green pigment.

Half of the world's copper deposits are in the form of chalcopyrite ore. All important copper-bearing ores fall into two main classes: oxidized ores and sulfide ores.
Sulfide ores more important commercially. Ores are removed either by open-pit or by underground mining. Ores containing as little as 0.4% copper can be mined profitably in open-pit mining, but underground mining is profitable only if an ore contains 0.7% - 6% copper. The oxidized ores, such as cuprites and tenorite, can be reduced directly to metallic copper by heating with carbon in a furnace, but the sulfide ores, such as chalcopryite and chalcocite, require a more complex treatment in which low-grade ores have to be enriched before smelting begins. This involves the ore-flotation process, in which the ore is crushed and powdered before it is agitated with water containing a foaming agent and an agent to make the copper-bearing particles water-repellent. These particles accumulate in the froth on the surface of the flotation tank, and this froth is the water as well as antimony, arsenic, and sulfur, which are also present.

1.3 Importance of the elements:

Metal and their alloys play important\textsuperscript{7} role in civilization. Without metal no railway, airplanes, motor car, electric motor or interplanetary space vehicle could operate weapon coin…etc.

The mining of metals from deposit, ore has been a human activity since time immemorial. Civilization has grown with this art. It is safe to say that the production of metal and their various alloys is the genesis and sustenance of modern aspects of
modern technology in the Arab World. This part of the world is very virgin and very rich in its mineral deposit.

Mankind emerged from the Stone Age upon discovery of copper in its native form. With dawn of the Bronze Age, in 8000 BC, it was discovered that copper-tin alloy could be easily shaped into implement to weapons.

Copper deposits in Cyprus were worked as early as 3000 BC by the Egyptian and these deposits become the chief source of the metal for the Roman Empire.

1.4 Abundance:-
Copper is moderately abundant and is the twenty\(^{8}\) – fifth most abundant element in the earth's crust. It occurs to the extent of 6888 by weight. Silver and gold are quite rare.

1.5 Properties of Copper:
(i) Physical properties:

Copper has a characteristic reddish-brown\(^{1}\) color when a clean surface is seen by reflected light; but in transmitted light thin layers are green. It can obtain in octahedral crystals (cubic system).

Copper melt at 1083°C if heated in atmosphere of carbon monoxide; in air melting point is some 20°C lower owing to the formation of cuprous oxide which dissolve in the molten metal. It is fairly conductor of heat and electricity. The molten metal mixes readily with many other metals forming alloys.

(ii) Chemical properties:
Copper does not burn in air\(^1\), but gradually converted into cuprous (\(\text{Cu}_2\text{O}\)) and cupric oxide (\(\text{CuO}\)) on its surface when heated to redness. It does not react with steam at any temperature below white heat. Copper is below hydrogen in electro-chemical series and hence, does not react with acids unless they are also oxidizing agents, or form a complex ion with copper. It is however, also slowly attached by some acids in presence of air, due to the slow oxidizing action of the air.

Although affected by dry air at the ordinary temperature, exposure to most air causes the formation of a beautiful green coating or patina. This was for long said to be a basic copper carbonate, but Morgan has recently shown that it is in inland places, a basic sulphate \(\text{CuSO}_4.3\text{Cu(OH)}_2\).

Copper reacting with nitric acid, oxides of nitrogen being formed with the dilute acid, nitric oxide (a long with a little nitrogen peroxide) is formed; while with the concentrated acid nitrogen peroxide predominate:

\[
\begin{align*}
3\text{Cu} + 8\text{HNO}_3 & \rightarrow 3\text{Cu(NO}_3\text{)}_2 + 2\text{NO} + 4\text{H}_2\text{O} \\
\text{Cu} + 4\text{HNO}_3 & \rightarrow \text{Cu(NO}_3\text{)}_2 + 2\text{N}_2\text{O}_2 + 2\text{H}_2\text{O}
\end{align*}
\]

Copper is only attacked by dilute sulphuric acid if air is present, and then only slowly: in that case copper sulphate results:

\[
\begin{align*}
2\text{Cu} + 2\text{H}_2\text{SO}_4 + \text{O}_2 & \rightarrow 2\text{CuSO}_4 + 2\text{H}_2\text{O}
\end{align*}
\]

Hot strong acid, Sulphuric acid readily reacts with copper sulphur dioxide being evolved.
Caustic solutions are without action on copper. At it is so low in the electro-chemical series, copper is displaced from solutions of its salts by many metal –e.g., Zinc or Iron.

\[
\begin{align*}
Zn + CuSO_4 & \rightarrow Cu + ZnSO_4 \\
Fe + CuSO_4 & \rightarrow Cu + FeSO_4
\end{align*}
\]

The familiar experiment of dipping a knife blade into copper sulphate solution, with consequent formation of layer of copper on the blade; is an example of this; copper will, in its turn, displace silver, gold or platinum from their solution since these metals are still lower in the electro-chemical series, e.g.\(^1\)

\[
Cu + 2AgNO_3 \rightarrow Cu(NO_3)_2 + 2Ag
\]

1.6 Uses of copper:

Next to iron, copper\(^{(1)}\) is the most useful metal we have. Enormous quantities are used in the electrical industries, for household utensils and for brewery vessels. Large quantities are used for the fire boxes of locomotive boilers and for steam pipes in stationary plant. Copper nails rivets and sheeting are (or were) used for sheathing wooden ships. Also use it in constituent of many alloys. Copper is notable in having extensive use in the pure condition, most metal require to have their properties modified by the addition of small quantities of other substances in order to make them most useful. Many compound of copper have important uses.
Stability of copper in air and water coupled with its excellent conductivity makes it very use metal.

1. For making vacuum pans, heating\textsuperscript{(9)} utensils and conductor coils.
2. For manufacturing electric goods, wires.
3. In coinage.
4. For covering the bottoms of the wooden ships.
5. In copper plating, electrotyping.
6. For manufacturing allys.
7. Copper salts largely used as insecticides.

1.7 Copper Compounds:

(a) Copper Oxides and Hydroxides:

Copper furnishes three oxides whose\textsuperscript{(1)} existence is established:

\begin{align*}
\text{Cuprous oxide} & \quad \text{Cu}_2\text{O} \\
\text{Cupric oxides} & \quad \text{CuO} \\
\text{Copper dioxides} & \quad \text{CuO}_2
\end{align*}

Of which only the first two are of any particular importance. In addition, oxides of the formula \text{CuO}_2 and \text{Cu}_4\text{O} have been reported, but the evidence is indecisive.

Theoretically two hydroxides would be expected to exist corresponding to cuprous oxide and cupric oxide respectively. Actually cuprous hydroxide seems not to exist. A yellow precipitate is first obtained in the preparation of cuprous oxide (equation) below:
\[ \text{Cu} + \text{CuO} \rightarrow \text{Cu}_2\text{O} \]

Which rapidly turns into the red cuprous oxide itself. This yellow precipitate has been thought by some to be cuprous hydroxides; but it generally supposed to be a colloidal "mixture" of cuprous oxide and water of no fixed composition.

When a solution of Sodium and Potassium hydroxides is added to a cold solution of cupric salt, a pale blue, gelatinous precipitate of cupric hydroxide is formed:

\[ \text{CuSO}_4 + 2\text{NaOH} \rightarrow \text{Cu(OH)}_2 \downarrow + \text{Na}_2\text{SO}_4 \]

(b) Salts of Copper:

The equilibrium between cuprous and cupric salts; copper forms two series of salts, corresponding to the oxides cuprous oxide and cupric oxide, and known consequently as the cuprous and cupric salt.

There is still some doubt concerning the true molecular formula of cuprous salts. The vapor density of cuprous chloride corresponds to a formula Cu\(_2\)Cl\(_2\) event at 1600°C. On the other hand, the iodide is CuI at 1000°C and the freezing points of solutions of cuprous compounds in organic solvents indicate similar differences. The probable conclusion seems to be that univalent copper and the ion \( \text{Cu} \) do exist, but that the cuprous compounds have a marked tendency to form double molecules.

The equilibrium between the cuprous and cupric salts is interesting. The soluble cuprous salt decompose in the solution
in water into cupric salt and copper, e.g. cuprous sulphate, which can be made in absence of water, decomposes at once in water with cupric sulphate and copper. On the other hand, cupric salts of acids whose cuprous salts are insoluble decomposes in water into the cuprous salt which precipitated, e.g., cupric iodide or cyanide and cyanogenes being evolved also. Thus:

\[
\text{Cu}_2\text{SO}_4 = \text{CuSO}_4 + \text{Cu}
\]

\[
2\text{CuI}_2 \rightarrow 2\text{CuI} + \text{I}_2
\]

In general it may be said that cuprous salts cannot exist in contact with water unless they are either insoluble or combined in a complex.

Cupric salts of acids whose cuprous salts are insoluble are similarly unstable in presence of water, but can sometimes obtained in the form or co-ordination compound with organic substances, e.g., Cupric iodide forms a stable co-ordination with ethylene diamine:

![Coordination Compound Diagram]

Similar considerations apply to the soluble cuprous salts. These facts are interpreted in term of Ionic Theory as follows.
The interchange between cuprous and cupric salts is represented by the equilibrium:

\[ 2Cu^+ \]

Hence, a soluble cuprous salt will furnish a solution containing much Cu ion and the equilibrium will tend to move to the right. Conversely, when the cupric salt of an acid whose cuprous salt is insoluble is dissolved in water, cuprous ions will be removed by precipitation, and the equilibrium will be moved to the left. The stability conferred by the formation of complexes and co-ordination compounds is similarly due to the removal of, or non-formation of, ions of one or other kind.

c - Complexes of Copper:
The M\(^1\) complexes are mainly\(^{(10)}\) of the type M[CuX\(_2\)] in which the covalence of the metal is limited to two and of which all the elements provide. Examples Of the M\(^{II}\) complexes K\(_2\)CuCl\(_4\).2H\(_2\)O has a tetragonal unit cell with features deriving from both CuCl\(_2\).2H\(_2\)O and CuCl\(_2\).

The Cu\(^{II}\) complexes CsCuCl\(_3\) consist of Cs\(^+\) ions and infinite chain (CuCl\(_3^{2-}\))\(_n\) ions. The coordination in these is planar but the sharing of corners by the CuCl\(_3\) units gives them spiral arrangement.

1.8 The tripstive state:-
Copper (III):- The existence of simple\(^{(11)}\) compound of copper has not been definitely established, but a number of compounds contain copper (III) in anionic complexes have been obtained.
The complexes represented in these compound include the cuprate (III) ion \( \text{CuO}_2^- \) the hexa-flurocuprate(III) ion \([\text{CuF}_2]^-\), Potassium cuprate (III) \( \text{KCuO}_2 \) is obtained as a steel – blue product by heating a mixture of \( \text{CuO} \) and \( \text{K}_2\text{O} \) in dry oxygen atmosphere at 400 to 450°C. The product has a characteristic X-ray pattern.

**1.9 Spectra and Magnetic properties:-**

Because of the relatively of low\(^{12}\) symmetry (i.e, less than cubic) the environment in which the \( \text{Cu}^{+2} \) ion is characteristically found, detailed interpretation of the spectra and magnetic properties are somewhat complicated, even through one is dealing with the equivalent of a one - electron case. Virtually all complexes and compounds are blue or green. Exception are generally caused by strong ultraviolet bands - change - transfer bands – tailing off into the blue and of visible spectrum, they causing the substances to appear red or brown. The blue or green colour is due to the presence of an absorption band in the 600-900 nm region of spectrum.

**1.10 Organo complexes:**

The organo cuprate ([RC\(_6\)H\(_3\) CH\(_2\)NMe\(_2\) CuLi],\(^{13}\) isolated from the reaction between copper (1) bromide and the corresponding aryl- lithium, has been shown to have a tetra-meric structure with the copper and lithium atoms joined by aryl bridges.

**1.11 Copper Proteins:-**
Three type of Cu$^{II}$ in proteins have been$^{(14)}$ characterized by e.p.r and visible spectroscopy; type-1 Cu$^{II}$, which is responsible for the bright blue colour of the 'blue' protein, and having absorption at ~ 600 nm of very high extinction coefficient and an abnormal e.p.r. spectrum; type-2 Cu$^{II}$, non blue with a normal e.p.r signal; and type-3 e.p.r, insensitive Cu$^{II}$, associated with an absorption at ~ 330 nm.

1.12 Gold, Silver & Copper

The elements (Cu, Ag and Au) all have one$^{(8)}$ electron outside a completed $d$ shell. They show only slight similarities in properties and considerable differences. All three metals have the same crystal structure (cubic close-packed). They conduct electricity and heat particularly well, and they tend to be noble (unreactive). The only ions which exist in solution (apart from complexes) are Cu$^{+2}$ and Ag$^+$. The most stable oxidation state varies; Cu(+II), Ag(+I) and Ag(+III). Copper is produced on a large scale and 11 million tones were used in 1992, mostly as the metal and in alloys. Copper is biological important in various oxidase enzymes, as an oxygen carrier in invertebrates and in photosynthesis. There is great interest in various mixed oxides of copper which act as superconductors.

1.13 Effect of co masking on completeness of precipitation

As interference occur in quantitative$^{(15)}$ and quantitative analysis, so it's difficult to precipitate ions pure, so to avoid this
interference some substance which make a complex with metal used which called *masking*:

Prevention of precipitation of any given ion by \(^{(16)}\) combining it in a complex of a low degree of dissociation is known as masking. Masking is widely used in analytical practice.

For example when Co\(^{++}\) is detected as the complex thiocyanate \([\text{Co}(\text{CNS})_4]^-\) the solution must be free from Fe\(^{+++}\) ion, which give an intensely colored compound with CNS\(^-\) ions. Therefore if Fe\(^{+++}\) ions are present, NH\(_4\)F or (NaF) is added to form the stable complex. It is also possible to remove Fe\(^{+++}\) ions by addition of tartaric or citric acids, which form fairly stable complexes, (i.e., of a low degree of dissociation) with Fe\(^{+++}\) ions.

Of the common elements which are usually \(^{(15)}\) associated with copper ores, those that interfere with the iodometric determination are iron, and antimony. Trivalent iron is reduced by iodide

\[
2\text{Fe}^{+3} + 2\text{I} \rightleftharpoons 2\text{Fe}^{+2} + \text{I}_2
\]

But by the addition of excess of fluoride, the iron (III) is converted into the complex \([\text{FeF}_6]^-\). That it has no oxidizing action upon the iodide.

A more general approach \(^{(17)}\) to increasing the selectivity of extraction and analysis is the adding of *masking agent*. These are competing complexing agents that form charged complexes that are more stable for certain metals. EDTA and
cyanide ion are commonly used as masking agents. Thus, although Cu$^{+2}$ forms a more stable complex oxine than VO$_2^{+2}$ does, the vanadium may be extracted in the presence of copper by adding EDTA, which forms an even more stable complex with copper (Cu—EDTA)$^{-2}$.

The selectivity of an extraction can often be controlled by proper pH adjustment. For example, cadmium could be separated from Bi, Sn$^{+2}$, Pb, Zn, Ti, $^{2+}$ and Hg at pH = 10.

1.14 Detection and Determination of Copper:

A. Qualitative:

Copper salts in solution are easily (1) recognize by their blue colour, which is rendered more intense by the addition of ammonia. In qualitative analysis, copper is precipitate as sulphide. Copper ferroycyanide is also a characteristic copper salt.

Copper can also be detected by means or certain organic reagents (e.g., cupron, a-benzoin oxine, and salicyladoxime).

When a few drops of a 1 present solution of cupron in alcohol are added to a slightly ammonical solution of copper salt a green precipitate or ($C_{14}H_{11}O_{2}N$)Cu is formed. This is a sensitive test for copper. Lead, iron, aluminum, cobalt and nickel do not interfere if soluble titrate is also present. This condition may be secured by addition of tartaric acid. When a solution of copper salt is made slightly alkaline with sodium hydroxide, and then made acid with a considerable excess of
acetic acid a yellowish precipitate of the complex Cu(C\textsubscript{7}H\textsubscript{6}O\textsubscript{2}N\textsubscript{2} is formed on addition of O-SC.C present.
Solution of salicyladoxime, this is an extremely sensitive test, and other elements which might interfere do not do so provided that sufficient acetic acid is present.

**B. Quantitative:**

Copper is very conveniently determined volumetric by addition of excess potassium iodide solution to a solution containing a known amount of the material to be analyzed. The iodine liberated is then titrated with a standard solution of sodium thiosulphate in the absence of any free acid other than acetic. Usually a slight excess of sodium carbonate is added, the excess being removed by addition of acetic acid.

\[
2\text{CuSO}_4 + 4\text{KI} \rightarrow 2\text{CuI} + 2\text{K}_2\text{SO}_4 + \text{I}_2
\]

Copper may be determined gravimetrically by electrolysis on to a previously weighed platinum dish, or by precipitations as sulphide. The former method is slow though accurate; the later suffer from the drawback that the ignition of the precipitated sulphide must be carried out in an atmosphere or hydrogen.

The reactions of copper with cupron and salicyladoxime described above can also be applied to it's determination. Copper can detect and determine by atomic absorption spectroscopy.

**C. Iodometric Determination Of Copper**
In volumetric analysis\textsuperscript{(16)} one of the most important applications is iodometry, in which determination of copper ions, widely used in analysis of alloys, ores, etc….This determination is based on the following reaction:

\[ 2\text{Cu}^{+2} + 4\text{I} \rightarrow 2\text{CuI} + \text{I}_2 \]

This is an oxidation reduction reaction, the equation illustrate that each cupric ions Cu\textsuperscript{+2} ions gain an electron to form the I\textsuperscript{-} ions, and the cupric ions is reduced to a cuprous ions Cu\textsuperscript{+} ions, which is then precipitated in the form of the sparingly soluble \textbf{cuprous iodide} CuI (solubility product~10\textsuperscript{-12}). Therefore, the oxidation grams equivalent of copper and CuSO\textsubscript{4}.5H\textsubscript{2}O in this case are equal to the gram-molecule (249.79g CuSO\textsubscript{4}.5H\textsubscript{2}O) respectively.

The values of the standard oxidation potentials of the systems Cu\textsuperscript{2+/+} (+0.17V), and I\textsubscript{2}/2I\textsuperscript{-} (+0.54V), might suggest that the reaction should proceed in the reverse

A large excess of KI is needed to make this revisable reaction proceed sufficiently fully in the required direction; the greater the excess of KI, the lower the Cu\textsuperscript{++} concentration and the higher the oxidation potential of the Cu\textsuperscript{2+/+}/Cu\textsuperscript{+} system.

Although H\textsuperscript{+} ions do not take part in this reaction, it is helpful to have faintly acid solution in order to suppress hydrolysis of cupric salts, which lowers the oxidation potential of Cu\textsuperscript{2+/+}/Cu\textsuperscript{+} system and slows down reaction.
Thiosulphate ion is a moderately \(^{(18)}\) strong reducing agent that has been widely used to determine oxidizing agents by an indirect procedure that involves iodine as an intermediate. With iodine, thiosulphate ion is oxidized quantitatively to tetrathionate ion, the half-reaction being:

\[
2S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} + 2e^-
\]

The quantitative aspect of this reaction with iodine is unique. Other oxidants oxidize the tetrathionate ion, wholly or in part to sulfate ion. Sodium thiosulfate, Na\(_2\)S\(_2\)O\(_3\), one of the few reducing agents that are stable toward air-oxidation. An example of this procedure is the determination of sodium hypochlorite in bleaches.

The reactions are:

\[
2\text{Cu}^{2+} + 2\text{I}^- \rightarrow 2\text{Cu}^+ + \text{I}_2
\]

\[
2S_2O_3^{2-} + \text{I}_2 \rightarrow S_4O_6^{2-} + 2\text{I}^-
\]

The quantitative conversion of thiosulfate ion to tetrathionate ion shown in the equation above requires a pH smaller than 7. If strongly acidic solutions must be titrated, air-oxidation of the excess iodide must be prevented by blanketing the solution with an inert gas, such as carbon dioxide or nitrogen.

A copper metal sample is\(^{(17)}\) dissolved in nitric acid to produce Cu (II), and the oxides of nitrogen are removed by adding H\(_2\)SO\(_4\) and boiling to SO\(_3\) fumes. The solution is
neutralized with NH$_3$ and then slightly acidified with H$_3$PO$_4$. [The H$_3$PO$_4$ also complexes any iron (III) that might be present and prevents its reaction with I$^-$.] Finally, the solution is treated with excess KI to produce CuI and an equivalent amount of I$_3^-$, which is titrated with standard Na$_2$S$_2$O$_3$ solution, using starch indicator. KSCN is added near the end point to displace absorbed I$_2$ on the CuI by forming a layer of CuSCN. For best accuracy, the Na$_2$S$_2$O$_3$ is standardized against high-purity wire, since some error occurs from reduction of copper (II) by thiocyanate.

D. Determination of Copper by Direct Titration with EDTA using fast sulphon black F indicators:

This indicator is virtually specific$^{(15)}$ in its color reaction with copper in ammonical solution; it forms colored (red) complex with only copper and nickel, but the indicator action with nickel is poor.

E. Photometric Titration of Copper (II) with EDTA:

The titration of copper-ion solution with EDTA may be carried out photometrically at wavelength 745nm at this wavelength the copper EDTA complex has considerably greater molar absorption coefficient than the copper solution alone. The pH of the solution should be about 2-4. Iron (III) interferes (small amounts may be precipitated with sodium fluoride solution): tin (IV) should be masked with 20 percent aqueous tartaric acid solution. The procedure may be
employed for the determination of copper in brass, bronze, and bell metal without any pervious separations except the removal of insoluble lead sulphate when present.

F. Gravimetry:

(i) Determination of copper as copper (I) thiocyanate

This an excellent method, since must thiocyanates of other metals are soluble. Separation may thus be effected from bismuth, cadmium, arsenic, antimony, tin, iron, nickel, cobalt, manganese and zinc. The addition of 2.3g of tartaric acid is desirable for the prevention of hydrolysis when bismuth, antimony, or tin are present. Excessive amounts of ammonium salts or of the thiocyanate precipitant should be absent, as should also oxidizing agents, the solution should only be slightly acidic, since the solubility of the precipitate increase with decreasing pH. Lead mercury, the precious metal, selenium, and tellurium interfere and contaminate the precipitate.

The reaction may represented as:

\[
2\text{Cu}^{+2} + \text{HSO}_3^- + \text{H}_2\text{O} = 2\text{Cu}^+ + \text{HSO}_4^- + 2\text{H}^+
\]

\[
\text{Cu}^+ + \text{SCN}^- = \text{CuSCN}
\]

(ii) Determination of copper by cupron:

Also copper (I) can determinte by benzoin-\(\alpha\)-oxim (cupron) is a specific reagent for determination of copper in ammoinical solution. A green, heavy, and readily filterable precipitate is obtained.
This insoluble in water, dilute ammonia solution acetic acid, tartaric acid and ethanol, is slightly soluble in concentrated ammonia and readily soluble in mineral acids. Separation of the precipitate can thus be effected from iron and other metals whose hydroxides are not precipitated in tartrate solutions. Separation can also be made from cadmium, zinc, cobalt, and nickel, which are not precipitated in ammonia solutions.

(iii) **Estimation of copper as cupric oxide in a solution of copper sulphate:-**

Copper is precipitated as Cu(OH)$_2$ by adding a hot solution of NaOH or KOH to hot solution of copper salts, which containing little Cl$^-$ ions. The precipitation is apply in a hot condition and in a presence of hydrochloric acid, in order to enhance the rapid formation of granular precipitate. Use of phenolphthalein checks excessive addition of alkali. The treatment of ash with a drop of concentrated nitric acid is necessary to check cupric oxide from reduction during the ignition. The precipitate on heating changed to black or dark brown cupric oxide.

\[
\text{CuSO}_4 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SO}_4 + \text{Cu(OH)}_2
\]

\[
\text{Cu(OH)}_2 \overset{\text{heating}}{\rightarrow} \text{CuO} + \text{H}_3\text{O}^+ 
\]

1.15 **Methods for determination of Micro amount of copper:**

a. **Electrochemical Analysis or Method:**
Copper may be deposited from either sulphric or nitric solution, but usually, a mixture of the two acids is employed. If such solution is electrolyzed with an e.m.f of 2-3 volts the following reactions occur:

Cathode: \( \text{Cu}^{+2} + 2e \rightarrow \text{Cu} \)

\[
2\text{H}^+ + 2e \rightarrow \text{H}_2
\]

Anode: \( 4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4e \)

The acid concentration of the solution must not be too great, otherwise the deposit of the copper may be in a complete or the deposit will not adhere satisfactorily to the cathode. The beneficial effect of nitration ion due to depolarizing action at the cathode:

\[
\text{NO}_3^- + 10\text{H}^+ + 8e \rightarrow \text{NH}_4^+ + 3\text{H}_2\text{O}
\]

The reduction potential of the nitrate ion is lower than the discharge potential of hydrogen, and therefore, the hydrogen is not liberated in the free state. The nitric acid must be free from nitrous acid as the nitrite ion hinders complete deposition and introduces other complications. The nitrous acid may be removed by boiling the nitric acid before adding it, or by the addition of urea to the solution:

\[
2\text{H}^+ + 2\text{NO}_2^- + \text{CO(NH}_2\text{)}_2 \rightarrow 2\text{N}_2 + \text{CO}_2 + 3\text{H}_2\text{O}
\]
The action is rapid, and the acidity of the electrolyte is unaffected. The error due to nitrous acid is increased by the presence of a large amount of iron; iron is reduced by the current to iron (II) state, whereupon the nitric acid is reduced. This error may be minimized by the proper regulation of the pH and by the addition of ammonium nitrate instead of nitric acid, or, best by the removal of the iron prior to electrolysis, or by complexation with phosphate or fluoride.

The solution must be free from the following, which either interfere or lead to an unsatisfactory dispositive: silver, mercury, bismuth, selenium, tellurium, arsenic, chloride, antimony, tin, molybdenum, gold, and the platinum metals, thiocyanates, chloride, oxidizing agent such as oxides of nitrogen or excessive amounts of iron(III) nitrate or nitric acid.

The electrolytic deposit should be Salmon-pink in color, silky in texture, and adherent. If it is dark, the presence of foreign elements and / or oxidation is indicated. Spongy or coarsely crystalline deposits are likely to yield high results; they arise from the use of too high current densities or improper acidity and absence of nitrate ion.

b. Colorimetric

(i) Various methods are available (16) for colorimetric determination of copper. The ammonia and ferrocyanide methods are the most useful.
The reagent used in the ammonia method for proceeding the color is NH$_4$OH solution, which give a series of blue ammonia complexes of different co-ordination numbers with the Cu$^{+2}$ ion. Usually in colorimetric determinations, the complexes [Cu(NH$_3$)$_6$]$^{++}$ are formed. For example:

$$\text{Cu}^{+2} + 4\text{NH}_4\text{OH} \rightarrow [\text{Cu(NH}_3\text{)}_4]^{+2} + \text{H}_2\text{O}$$

The instability constant of [Cu(NH$_3$)$_4$]$^{+2}$ is $5 \times 10^{-14}$.

Nickel and cobalt, which formed colored complex with ammonia interfere with determination of copper by the ammonia method. Cations which formed insoluble hydroxides with ammonia, such as, Fe$^{+3}$, Al$^{+3}$, Mn$^{+2}$, Pb$^{+2}$, Sn$^{+2}$, Bi$^{+3}$, Hg$^{+2}$, etc… also interfere.

Moderate amounts of these cations can be separated from Cu$^{+2}$ ion, by precipitating with ammonia.

The ferrocyanide method is based on the reaction of Cu$^{+2}$ ions with potassium ferrocyanide; K$_4$[Fe(CN)$_6$], as follow:

$$\text{Cu}^{2+} + [\text{Fe(CN)}_6]^{4-} \rightarrow \text{Cu}_2[\text{Fe(CN)}_6]$$

The cupric ferrocyanide formed is sparingly soluble substance, which forms a red-brown precipitate at considerable concentration of Cu$^{+2}$. In very diluted solutions a colloidal solution of Cu$_2$[Fe(CN)$_6$], yellow-brown to yellow color is formed instead of a precipitate. This color specially in very diluted (yellow) solutions, persists for a long time without appreciable changes of intensity.
(ii) **Determination of copper by biscyclohexanone oxalylidihydrazone:**

Small quantities of copper\(^{(15)}\) may be determined by the diethylidithiocarbamate method or by the "neocuproins" an extraction being necessary in both cases. In another simple procedure, the copper is complexed with biscyclohexanone oxalylidihydrazone and the resulting blue color is measured by a suitable spectrophotometer within the range 570-600nm. The solution measured should contain not more than 100μg of copper.

**C. X-Ray Fluorescence:**

The absorption of X-rays produces\(^{(20)}\) electronically excited ions that return to their ground state by transitions involving electrons from higher energy levels. Thus, an excited ion with a vacant K shell is produced when lead absorbs radiation of wave lengths shorter than 0.14 Å°; after a brief period, the ion returns to its ground state via a series of electronic transitions characterized by the emission of X-radiation (Fluorescence) of wavelength identical to those that result from excitation produced by electron bombardment.

**(i) Qualitative and Semiquantitative Analysis:**

Figure (1) illustrates an interesting qualitative application of the X-ray fluorescence method. Here the untreated sample, which was excited by radiation from an X-ray tube, was subsequently recovered unchanged. Note that the abscissa for
wavelength dispersive instrument is often plotted in terms of the angle $2 \Theta$, which can be readily converted to wavelength with knowledge of the crystal spacing of the monochromator equation below.

$$n\lambda = 2d \sin \theta$$

Where $d$ of is the interplanar distance of the crystal. Identification of peaks is then accomplished by reference to tables of emission lines of the elements.

Figure (2) is a spectrum obtained with an energy dispersive instrument. With such equipment, the abscissa is generally calibrated in channel number of energy in keV. Each dot represents the number of counts accumulated in one of the several hundred channels.
Qualitative information, such as that shown in fig (1) and (2), can be converted to semiquantitive data by careful measurement of peak heights. To obtain a rough estimate of concentration, the following relationship is used:

\[ P_x = P_s W_x \]
Where $P_x$ is the relative line intensity measured in terms of number of counts for a fixed period, and $W_x$ is the weight fraction of the desired element in the sample. The factor $P_s$ is the relative intensity of the line that would be observed under identical counting conditions, if $W_x$ where unity. The value of $P_s$ is determined with a sample of the pure element of a standard sample of known composition.

(ii) Quantitative Analysis:

Modern X-ray fluorescence instruments are capable of producing quantitative analysis of complex materials with precision that equals or exceeds that of the classical wet chemical methods or other instrumental methods. For the accuracy of such analysis to approach this level, however, requires either the availability of calibration standards that closely approach the sample in overall chemical and physical composition or suitable methods for dealing with matrix effects.

(iii) Diffraction of X-Rays:

In common with other type of electromagnetic radiation, interaction between the electric vector of X-radiation and the electrons of the matter through which it passes result in scattering. When X-rays are scattered by the ordered
environment in a crystal, interference (both constructive and destructive) take place among the scattered rays because the distances between the scattering centers are of the same order of magnitude as the wavelength of the radiation, diffraction is the result.¹

1.16 Objective :

* Quantitative determination of copper in Malachite by classical and instrumental methods

(i) Titrimetry  (ii) Gravimetry  ( iii ) Atomic absorption and ( iv) X- Ray fluorescence, and to compare the results with those reported in the literature.

CHAPTER TWO

EXPERIMENTAL

2.1 Malachite Sample :
About 250 gm of Malachite sample was obtained from

_Geological Research Center._

**2.2 - Chemicals:**

- Hydrochloride acid (HCl, M. w = 35.5, specific gravity = 1.16g/ml, ASSAY = 36%).
- Nitric acid (HNO₃, M. w = 62.07, specific gravity = 1.0g/ml, ASSAY = 70%)
- Sulphuric acid (H₂SO₄, M. w = 98.05, specific gravity = 1.84g/ml, ASSAY = 98%)
- Acetic acid (CH₃COOH, M. w = 60.05, specific gravity = 1.05g/ml, ASSAY = 99.5%)
- Perchloric acid (HClO₄, M. w = 100.46, ASSAY = 70-72%)
- Conc. Ammonia (NH₄OH, m. w = 17, specific gravity = 0.9g/ml, ASSAY = 30%)
- Potassium iodide ((KI, M. w = 166, ASSAY = 99%).
- Sodium thiosulphate (Na₂S₂O₃.5H₂O, M. W = 248.17, ASSAY = 99%).
- Sodium Hydroxide (40.00, ASSAY = 98%)
- Silver Nitrate (M. wt = 169.87, ASSAY = 99%)
- Barium Chloride (M. wt = 244.28, ASSAY = 99-102%)
• Potassium Thiocynate (M. wt = 97.18, ASSAY = 98%, density = 1.89g/ml at 20°, B.p (decomposition 500°C, M. p =137°C, PH value = 6.0-8).

• Ammonium fluoride (NH₄F, M. wt = , ASSAY = 99.0%)

• Zinc dust (Zn, M.wt = 65, ASSAY 99%)

• Phenolphthalein indicator:

• Starch indicator: India – Qualid Kems COMP, pH 6-7.5, Chloride (Cl) 0.04 %, Lossing on drying at 105°C 10%

2.3 Reagents

2M acetic acid: 11.5 ml was taken from the concentrated acid and made up to 100 ml in volumetric flask.

2M sulphuric acid: 10.868 ml was taken from the concentrated acid and made up to 100 ml volumetric flask, were dilute with distilled water.

72% of perchloric acid: 72 ml was taken from the concentrated

1:1 hydrochloric acid: 100 ml was taken from the concentrated and mixed with 100 ml of water.

1:1 ammonium hydroxide: 200 ml of concentrated ammonia solution was taken and mixed with 200 ml of water.

Starch indicator: 3 gm of starch was dissolve in 50 ml water and heated until boiled.
Phenolphthalein indicator: 1gm of Phenolphthalein indicator was dissolved in 50 ml ethanol.

10 % Sodium hydroxide: 10 gm of Sodium hydroxide was dissolved in 100 ml water.

0.05 M sodium thiosulphate: 6.204gm was dissolved in water and made up to 500 ml volumetric flask.

10% Potassium Thiocynate: 10gm of Potassium Thiocynate was dissolved in 100 ml water.

0.1 M Silver nitrate: 1.08 gm of Silver nitrate is dissolved in water and mark up to 100 ml volumetric flask.

0.1 M Barium chloride: 2.44 gm of Barium chloride is dissolved in water and mark up to 100 ml volumetric flask.

2.4 Equipments

1- Atomic Absorption Spectrophotometer: Japan, Shimadzu, Model 6800.

2- X-ray Fluorescences Spectrophometer UK

3- Oven: UK, Genlab, model MINO/50

4- Furnace: UK, DAIHAN LABTECH co; ltd

2.5 Total analysis of Malachite

A - Determination of silica in malachite:
The silicate was determined by fusion of sample with sodium carbonate and weighing the residue.

**Procedure:**

1.002g of the finely powdered dry malachite was weighed and placed in crucible, 6g of anhydrous sodium carbonate was added, mixed well by glass rod, covered by little amount of sodium carbonate, and the mixture was fused for 30 minutes and allowed to cool. The fusion was covered with water, left over night, warmed on the water bath until the content was well disintegrated, by a pipette 25 cm$^3$ of concentrated hydrochloric acid was added into covered container, warmed until carbon dioxide has ceased. Continue the evaporation to dryness, crushing all lumps with a glass rod. The residue was leaved for an hour at 100 - 120° C to dehydrate. Moisten the residue with 5 cm$^3$ concentrated hydrochloric acid, 75 cm$^3$ of water was added to remove salts of iron, aluminum, and other metals which may be present and filter through ash less filter paper. Washed with warm dilute hydrochloric acid, and finally with a little hot water (the filtrate was kept). Fold up the moist filters, and place them in a weighed platinum crucible. Dried the paper with a small flame, char the paper, and burn off the carbon over a low flame; care was taken, that none of the fine powder is blown away. When all the carbon had been oxidized, covered the crucible, and heated for an hour at 1200° C in order to complete the
dehydration. Allowed to cool in desiccators, and weighed. The ignition was repeated three times until the weigh is constant.

**Calculation:**

\[
\text{percentage of } \text{SiO}_2 = \frac{\text{wt of the residue}}{\text{wt of the sample}} \times 100\% 
\]

**B – Determination of copper:**

Determination of copper by iodometry method

**Principle:**

\[
2\text{Cu}^{2+} + 2\text{I}^- \rightarrow 2\text{Cu}^+ + \text{I}_2 \\
2\text{S}_2\text{O}_3^{2-} + \text{I}_2 \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{I}^- 
\]

**Procedure:**

The previous filtrate was made up to 250 cm\(^3\) in volumetric flask. Shaked well, then 100 ml was taken to titration flask, concentrated ammonia solution was added, till intensive blue color was obtained, then the solution was neutralized by 2N acetic acid (pale green color), excess amount of potassium iodide was added (dark brown), the solution was titrated with the standard 0.05M sodium thiosulphate solution until the brown color of the iodine is fades, then 2 cm\(^3\) of starch was add (blue color), and continue the addition of thiosulphate solution until the color disappear, and the volume was recorded.

The titration was repeated with another 100 cm\(^3\) of the malachite solution.
Calculation:

No of mole of $\text{Cu}^{2+} = \text{M} \times V \times 10^{-3}$

No of mole of $\text{S}_2\text{O}_3 = \text{No. of mole of } \text{Cu}^{2+}$

Wt of the $\text{Cu}^{2+} = \text{No of moles x Awt}$

Percentage of $\text{Cu} = \frac{\text{wt of } \text{Cu}^{2+} \text{ in the sample}}{\text{Wt of the sample}} \times 100$

C- Treatment of copper by the classical wet chemical method

Procedure:

1.002 g of powdered dry malachite was weighed out, dissolved in 15 ml of concentrated nitric acid, heated until dryness with stirring, 20 cm$^3$ of 2M sulphuric acid was added, heated for 30 min, filtered, and washed by distilled water.

Conc. ammonia solution was add to the filtrate until intensive blue color was obtained, then 2N acetic acid solution was added till pale green color was obtained, the solution was titrated against 0.05M sodium thiosulphate solution as mentioned in the previous method.

- The previous wet method was repeated, but by using a masking (citric acid) before titration. Weight of sample is 1.102g.

Calculation:

No of mole of $\text{Cu}^{2+} = \text{M}.V \times 10^{-3}$

No of mole of $\text{S}_2\text{O}_3 = \text{No of mole of } \text{Cu}^{2+}$

Wt of the $\text{Cu}^{2+} = \text{No of moles x Awt}$
Percentage of Cu = \( \frac{\text{wt of Cu}^{+2} \text{ in the sample}}{\text{Wt of the sample}} \times 100\% \)

D - Determination of copper by gravimetry:

**Principle:**

\[
\text{CuSO}_4 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SO}_4 + \text{Cu(OH)}_2 \downarrow \quad \text{(Blue ppt)}
\]

\[
\text{Cu(OH)}_2 + \text{heating} \rightarrow \text{CuO} \downarrow + \text{H}_3\text{O}^+ \quad \text{Dark brown}
\]

**Procedure:** To estimate copper as cupric oxide.

2.068 g malachite was treated by wet classical method. To the filtrate (Cu\(^{2+}\)) an equal volume of distilled water was added and 1 ml of conc hydrochloric acid, covered the beaker by watch glass and boiled the contents of beaker. A few drops of phenolphthalein were added, then a hot solution of 10% NaOH was slowly added with constant stirring, until clear liquid becomes light pink in color. A blue ppt is obtained. The beaker is covered and boiled for 3 – 5 min. on boiling Cu(OH)\(_2\) partially changes to dark brown CuO. After ppt had settled, filtered of the ppt and washed with hot distilled water, until last filtrate becomes free from alkali (no effect on red litmus paper), continue the washing till the filtrate becomes free S\(\text{O}_4^{2-}\) and Cl\(^-\) ions (tested with BaCl\(_2\) and AgNO\(_3\) solution, respectively)
The ppt was transferred and burned the filter paper to a clean ash. The crucible was cooled and one drop of conc. HNO₃ was added followed by heating the crucible first gently then on full flame. The crucible was ignited, the ignition was repeated until constant weight was obtained.

**Calculation:**

\[
\text{CuO} \rightarrow \text{Cu} \\
79.75 \rightarrow 63.5
\]

Conversion Factors = \( \frac{\text{Cu}}{\text{CuO}} = \frac{63.57}{79.57} = 0.7957 \)

Wt of Cu⁺⁺ = Conversion Factor x wt of the ppt CuO

\[
\text{Percentage} = \frac{\text{wt of the Cu}^{++}}{\text{wt of the sample}} \times 100\%
\]

**E- Determination of copper gravimetry:**

**Principle:**

\[
\text{CuCO}_3 \cdot \text{Cu(OH)}_{2(s)} \rightarrow 2\text{CuO} \ (s) + \text{CO}_2(s) + \text{HO}_2(g)
\]

Green Malachite → Black Solid + Clear gas + Clear gas

**Procedure:**

1.5g of malachite was weighed out and placed in a dry crucible and heated for five minutes at maximum flame temperature. Allowed to cool, weighed. The process of heating repeat five times until the weigh was constant.

**Calculation:**

\[
\text{CuO} \rightarrow \text{Cu} \\
79.75 \rightarrow 63.5
\]
Conversion Factors = \[
\begin{align*}
Cu &= 63.57 = 0.7957 \\
CuO &= 79.57
\end{align*}
\]

\[
\text{Wt of } Cu^{++} = \text{Conversion Factor} \times \text{wt of the ppt CuO}
\]

\[
\text{Percentage of } Cu = \frac{\text{wt of the } Cu^{++}}{\text{wt of the sample}} \times 100\%
\]

**F - Determination of copper by reduction:**

**Principle:**

\[
Fe + Cu^{++} \rightarrow Fe^{+++} + Cu
\]

**Procedure:**

5.385 g of well powdered of malachite was weighed out and dissolved first by 20 ml of 1:1 HCl decanted, and then another portion of HCl was added till the solution become free from the green colour. Filtered, iron dust was added to the filtrate and excess amount of HCl 1:1 till the evaporation of gas is stopped.

Filtered and weighed the copper metal weigh.

**Calculation:-**

\[
\text{Percentage of } Cu = \frac{\text{wt of the } Cu^{++}}{\text{wt of the sample}} \times 100\%
\]
G - Volumetric Determination of copper in an ore:

**Principle:**

\[
2\text{Cu}^{2+} + 2\text{I}^- \rightarrow 2\text{Cu}^+ + \text{I}_2
\]
\[
2\text{S}_2\text{O}_3^{2-} + \text{I}_2 \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{I}^-
\]

**Procedure:**

0.6210 g of the dry, finely ground malachite was weighed out in a pyrex flask. 15 cm³ of 72 percent of perchloric acid were added slowly. The flask was heated gently in the fume cupboard for 5 min, and allowed to cool for 4 min. 50 ml of distilled water were added carefully through a funnel, mixed well and boiled the solution for 5 min, cooled to room temperature. Dilute with ammonia (1:1), drop wise until the solution smells slightly of ammonia. 20 ml of ammonia fluoride was added shacked well until the ppt dissolve. 3 g of A. R potassium iodide were added to the solution shake well and titrated at once with standard 0.05M sodium thiosulphate, 2 ml of starch solution were added when the brown color of iodine decreases in intensity. The addition of the thiosulphate solution was continued until the blue color becomes faint. Then 20 cm³ of 10 percent aqueous potassium thiocynante solution was added, and then the titration was complete.

H - Determination of copper by atomic absorption:

**Procedure**

1.005 g of powdered malachite was weigh out, dissolved in HNO₃ conc., heated, until dryness, diluted with distilled water, filtered, and transferred to 250 volumetric flask, 5 ml of this
solution was made up to 50 ml with distilled water. The atomic absorption was measured using atomic absorption apparatus.

The same solution was used for measuring iron and gold.

**Calculation:**

To determine the concentration of Fe:

The concentration of Fe in 5 ml = Reading concentration \( \times 50 = C \times 5 = X \) ppm

The concentration of Fe in 250 ml:

\[
X \times 250 = Y \text{ mg/ml}
\]

\[
\times \frac{1000}{1000}
\]

The concentration Fe in g/250 ml:

\[
\frac{Y}{1000} = Z \text{ g/250ml}
\]

percentage of Fe = \( \frac{Z}{\text{Wt of sample}} \) \times 100%

Concentration of Cu⁺:

Assume the final concentration: - (A)

The concentration of Cu in 5 ml = \( A \times 50 = C \times 5 = X \) ppm

The concentration of Cu in mg per 250 ml:

\[
X \times 250 = Y \text{ mg/250 ml}
\]

\[
\times \frac{1000}{1000}
\]

The concentration of Cu in g per 250 ml

\[
\frac{X}{1000} = Z \text{ mg/250 ml}
\]

percentage of Cu = \( \frac{Z}{\text{Wt of the sample}} \) \times 100%
I - Determination of copper by X-ray fluorescence:

A powder of malachite was used to determine the copper quantitatively and qualitatively.
CHAPTER THREE
RESULTS & DISCUSSION

Results: Table illustrate the total results (2)

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>64.99 %</td>
<td>Gravimetry</td>
</tr>
<tr>
<td>Fe</td>
<td>0.564</td>
<td>Atomic Absorption</td>
</tr>
<tr>
<td>Au</td>
<td>0.019</td>
<td>Atomic Absorption</td>
</tr>
<tr>
<td>Cu</td>
<td>4.00%</td>
<td>Without mask - Volumetric</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.2% Without mask - Volumetric</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>3.70 By Mask (NH4 F) _ Volumetric</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.71 By Mask (Citric Acid ) _Volumetric</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>5.20 Without Mask (Reduction to Cu) _ Gravimetric</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.28 Without Mask (Ppt as CuO) - Gravimetric</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>3.72 By Mask (Citric Acid) (Ppt as CuO) _ Gravimetric</td>
</tr>
<tr>
<td></td>
<td>2.7</td>
<td>By ignition - Gravimetric</td>
</tr>
<tr>
<td></td>
<td>4.5</td>
<td>Atomic Absorption</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>XRF</td>
</tr>
</tbody>
</table>
3.1 Results: Table (3)

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>64.99 %</td>
<td>Gravimetry</td>
</tr>
<tr>
<td>Fe</td>
<td>0.564</td>
<td>Atomic Absorption</td>
</tr>
<tr>
<td>Au</td>
<td>0.019</td>
<td>Atomic Absorption</td>
</tr>
</tbody>
</table>

Table (3): Illustrate percentage of metals rather than copper, the higher percentage of silica in Malachite agree with many minerals ores contain high percentage of silica. Iron is mainly found with copper in ore (chalcopyrite), iron found as iron (III) due to the air oxidation. The percentage of iron is so small this refer to the area of collection. Gold exist with copper in native, gold usually found in small amount, therefore treatment will be difficult by classical methods, also gold treat by cyanide and we avoid this because of the high toxicity of cyanide.

Tables illustrated the concentration (%) of Cu$^{+2}$ by various methods:

Table (4.a) Volumetric

<table>
<thead>
<tr>
<th>% Copper</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.00%</td>
<td>Without mask</td>
</tr>
<tr>
<td>4.2%</td>
<td>Without mask</td>
</tr>
</tbody>
</table>

Table (4. b) Volumetric

<table>
<thead>
<tr>
<th>% Copper</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.70</td>
<td>By Mask (NH$_4$F)</td>
</tr>
<tr>
<td>3.71</td>
<td>By Mask (Citric Acid)</td>
</tr>
</tbody>
</table>
Table (4 a and b): Small different between the percentages of copper by using iodometry method by using masking and without masking, masking of iron used unable iron reacting as oxidizing agent, the small different means that iron exist in a small amount in malachite. This result is similar to the result of atomic absorption. since iodometry is the excellent method for determination of the copper, as seen in the pervious chapter that using of masking is so important to remove any oxidising agent ex (Fe).

Table (5) Gravimetric

<table>
<thead>
<tr>
<th>% Copper</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.20</td>
<td>Without Mask (Reduction to Cu)</td>
</tr>
<tr>
<td>4.28</td>
<td>Without Mask (Ppt as CuO)</td>
</tr>
<tr>
<td>3.72</td>
<td>By Mask (Citric Acid) (Ppt as CuO)</td>
</tr>
<tr>
<td>2.7</td>
<td>By ignition</td>
</tr>
</tbody>
</table>

Table (5): High percentage of Cu by reduction with Fe refer to that may the first filtrate don't pure. Some impurities from the crude ore was precipitated with the pure copper, to overcome this problem the first filtration may repeat until the filtrate be clear, other problem may be the reason some substance may precipitate other than copper so, the conditions of the experiments be may controlled. The results of precipitation of copper as cupric oxide without masking, high percentage is observed, usually in gravimetric
water is absorbed in the surface of molecules, due to this the result is a high yield. By masking the result is typical to those obtained by iodometry, so masking an important factor in analysis.

The result of ignition seems to be the accurate one in gravimetry methods, because ignition only (without treatment with a solution) give a chance to dehydrate the ore.

**Table (6) Spectroscopy**

<table>
<thead>
<tr>
<th>% Copper</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5</td>
<td>Atomic Absorption</td>
</tr>
<tr>
<td>4.0</td>
<td>XRF</td>
</tr>
</tbody>
</table>

**Table (6)**: Illustrate result obtained by atomic absorption, in atomic no interference, no contamination, small amount can be detect, so the excellent results obtain by this method.

- The quantity of the Fe is so small, but it may effected as oxidizing agent.

**Qualitative analysis by X-Ray fluorescence**: Copper is observed at \( k_\alpha = 8 \) and \( k_\beta = 8.5 \), when compare with the standard table of elements it is found typical to value of \( k_\alpha \) and \( k_\beta \) of copper.

Iron is observed at \( k_\alpha = 6 \) and \( k_\beta = 6.5 \), when compare with the standard table of elements it is found typical to value of \( k_\alpha \) and \( k_\beta \) of copper.
**X-Ray Fluorescence** also a good methods for analysis of ore, the result is near to those obtained by atomic absorption. Qualitatively copper and iron was detected

- **The sum of percentages** of element in malachite ore is less than 100%, this due to evaporation of carbon dioxide, when treated the ore by acids or in heating. Also hydroxide remaining in the solution.
Conclusion

The study shows that: The percentage of copper in the analyzed sample about 4-5 %. The percentage which was determined by different methods show similar results. This results is also similar to that obtained by Corporation of Geological Center.
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Appendix

- Calibration curves
- Results of atomic Absorption of Fe, Cu, Au
- Qualitative Result of x-ray fluorescence