

DETERMINATION OF COPPER IN COPPER ORES
USING VARIOUS ANALYTICAL TECHNIQUES

BY

HASSAN, UMAR FAROUK

A DISSERTATION SUBMITTED TO

FEDERAL UNIVERSITY OF TECHNOLOGY, MINNA

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE
AWARD OF THE DEGREE OF MASTER OF TECHNOLOGY,
M.TECH IN ANALYTICAL CHEMISTRY

SUPERVISOR: DR. A.A. FAROQ

JANUARY, 1997

DECLARATION

I hereby declare that this dissertation entitled "DETERMINATION OF COPPER IN COPPER ORES USING VARIOUS ANALYTICAL TECHNIQUES" has been written by me and that it is a record of my own research work. It has not been presented before in any previous application for a higher degree.

HASSAN, UMAR FAROUK

The above declaration is confirmed by:

DR. A.A. FAROQ
(Supervisor)

Date:.....

CERTIFICATION

This dissertation titled "DETERMINATION OF COPPER IN COPPER ORES USING VARIOUS ANALYTICAL TECHNIQUES" by HASSAN, UMAR FAROUK meets the regulations governing the award of the degree of Master of Technology of Federal University of Technology, Minna and is approved for its contribution to scientific knowledge and literary presentation.

DR. A. A. FAROQ
(Supervisor)

Date:.....

DR. M.A.T. SULEIMAN
(Head of Department)

Date:.....

Professor D.O. ADEFOLALU
(Dean, Post-Graduate School)

Date:.....

External Examiner

Date:.....

TABLE OF CONTENTS

Dedication	i
Acknowledgement	ii
List of Figures	iii
List of Tables	iv
Abstract	v
CHAPTER ONE	
1.0 Introduction	1
1.1 The nature of an ore and copper	1
1.2 Colorimetric analysis	7
1.3 Titrimetric analysis	10
1.4 Gravimetric analysis	11
1.5 Aims and Objective	12
CHAPTER TWO	
2.0 Literature Review	13
CHAPTER THREE	
3.0 Experimental and Results	21
3.1 Reagents	21
3.2 Dissolution of Copper Ores	21
3.3 Colorimetric Determination	22
3.3.1 Standard 0.10 mol dm ⁻³ copper (II) chloride dihydrate	22
3.3.2 Selection of a suitable wavelength	22
3.3.3 Colorimetric Determination of copper in the two or samples	27
3.4 Titrimetric Determination	30
3.4.1 Ammonia-Ammonium chloride pH ₁₀ buffer	30
3.4.2 0.10 mol dm ⁻³ zinc tetraoxo sulphate (VI) heptahydrate	30
3.4.3 0.05 mol dm ⁻³ EDTA	31
3.4.4 Eriochrome Black T indicator	31
3.4.5 Fast Sulphon Black F indicator	31
3.5 Standardization of EDTA	31
3.5.1 Titrimetric Determination of copper in the two ore samples	32
3.6 Gravimetric Determination	35
3.6.1 0.2 mol dm ⁻³ Tetraoxo Sulphate (VI) acid	35
3.6.2 Saturated Trioxo Sulphate (IV) acid	36
3.6.3 10% (m/v) Ammonium Thiocyanate solution	37
3.6.4 0.1% (m/v) Ammonium Thiocyanate solution	37
3.6.5 20% (v/v) Industrial Methylated spirit	37
3.7 Gravimetric Determination of copper in the two ore samples	38
3.8 Statistical Analysis of Results	40

CHAPTER FOUR

4.0	Discussion of Results	44
4.1	Introduction	44
4.2	Percentage of copper in ore samples	44
4.3	Comparison of Results	48
4.4	Conclusion	49
	References	50

DEDICATION

This Dissertation is dedicated to my parents, HAJIYA FATIMAT, Late ALHAJI HASSAN as well as my children; Hassan, Halimat, Khashiyatu and Saratu respectively.

ACKNOWLEDGEMENT

I wish to express my profound gratitude and appreciation to Dr. A.A. Farouq for his tireless efforts, encouragement, assistance and meaningful suggestions both during the conduct of the investigation and write-up of the thesis. The same appreciation is extended to the Head of Department of Chemistry, Dr. M.A.T. Suleiman and other members of staff in the department for the assistance rendered to me during the pursuit of this program.

Appreciation is also gratefully extended to my mother, Hajiya Fatimat Hassan for her moral and financial support as well as all members of my late father's family who have in one way or the other showed great concern for me.

I am also grateful to Dr. E.K. Tsado for his useful suggestions on statistical analysis. I am deeply indebted to all my course mates, colleagues and friends, especially Garba Aliyu and Alhaji Abubakar, K. I wish to commend Mr. Steve Aluko for a good typing work.

Finally, I owe a great debt to my household members, especially Mrs. Kulthum Farouk, who have again encouraged, assisted and tolerated me for the period spent away from them.

HASSAN, UMAR FAROUK

LIST OF FIGURES

FIGURE		PAGES
1.0	Block diagram of the essential components of a colorimeter	9
3.0	Graph of absorbance of $4 \times 10^{-3} \text{ mol dm}^{-3}$ $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution against wavelength (nm)	24
3.1	Graph of absorbance of $10 \times 10^{-3} \text{ mol dm}^{-3}$ $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution against wavelength (nm)	25
3.2	Graph of absorbance of 6.00 cm^3 of malachite ore per 100 cm^3 of solution against wavelength (nm)	26
3.3	Calibration graph of absorbance of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution against concentration (mol dm^{-3})	28
3.4	Apparatus used for the generation of saturated trioxosulphate (IV) acid	36

LIST OF TABLES

TABLE	PAGES
3.0 Colorimetric percentage of copper in Ore samples	29
3.1 Titrimetric percentage of copper in malachite ore sample	33
3.2 Titrimetric percentage of copper in covellite ore sample	34
3.3 Gravimetric percentage of copper in ore samples	39
3.4 Anova of the colorimetric percentage of copper in each ore sample	40
3.5 Anova of the titrimetric percentage of copper in each ore sample	41
3.6 Anova of the gravimetric percentage of copper in each ore sample	42
3.7 Anova of the mean percentage of copper in ores for colorimetric, titrimetric and gravimetric determinations	43
4.0 Percentage of copper in malachite ore based on the three analytical techniques	46
4.1 Percentage of copper in covellite ore based on the three analytical techniques	47

ABSTRACT

Two different geological copper ore materials comprising malachite and covellite were analyzed for the percentage of copper using three different analytical techniques, namely, colorimetry, titrimetry and gravimetry respectively.

The analysis reveals that the mean percentages of copper in malachite sample using colorimetric, titrimetric and gravimetric techniques are 63.50, 63.50 and 61.63 respectively, while the average percentages of copper in the covellite ore sample were found to be 42.33, 42.86 and 39.51% respectively.

The techniques could be used for the routine determination of the percentage of copper in copper ores.

CHAPTER 1

1.0 INTRODUCTION

1.1 An ore is any mineral or mixture of minerals from which it is feasible to extract a metal. The metals may be present as native elements or more commonly as oxides, sulphides, sulphates, silicates or other compounds. Minerals of little or no value which occur with ore minerals are called gangue. Some gangue minerals may not be worthless in that they are used as byproducts, for instance, limestone for fertilizer or flux, pyrite for making tetraoxosulphate (VI) acid and rock for road material [1-6].

Whether or not the recovery of a metal is economically worthwhile depends, among other things, upon the richness and extent of the mineral deposits, the state of the technology and the type of mineral or minerals. It is now profitable to mine ores containing as little as 0.25% copper [6,7].

Copper is a member of the group of metals that are collectively known as the coinage metals. Copper occurs principally as mineral compounds in which ^{63}Cu constitutes 69.1% and ^{65}Cu , 30.9% of the element. Copper is widely distributed in all continents and is present in most living organisms. The high affinity of copper for sulphur is the main factor that determines its manner of occurrence in the earth's crust [8,9].

Copper shows a strong tendency to combine with all available sulphur during the crystallization of rocks [8]. The total content of copper in the earth's crust is comparatively small, which is 0.01% by mass, but it occurs more frequently than other

metals in the uncombined state, the copper nuggets reaching a considerable size. Wherever free copper is found, brightly coloured copper ore is also usually found, so that primitive men were guided to the right minerals and were consequently able to wrest copper from them by roasting and reduction processes [2,4,5,10-12].

By far the greatest part of the world's copper is obtained from sulphide ores. These are chalcocite, Cu_2S ; Covellite, CuS ; Chalcopyrite, CuFeS_2 ; bornite, Cu_5FeS_4 ; and enargite, $\text{Cu}_3[\text{AS},\text{Sb}]_4\text{S}_4$. Copper is also commonly found in oxidized ores. These include: Cuprite, Cu_2O ; tenorite, CuO ; malachite, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$; azurite, $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$; chrysocolla, $\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$; and brochantite, $\text{Cu}_4(\text{OH})_6\text{SO}_4$ [3,9,13-15].

Sulphide ores are of greater importance than the oxidized ores because they yield 80% of all the copper produced. Copper occurs in over 30 enzymes and proteins. Ascorbic acid oxidase is a copper plant enzyme which catalyses the reduction of oxygen to water and the oxidation of ascorbic acid to dihydroascorbate [7,16-20].

Copper is essential to all forms of life. In particular, human need for copper was established in 1928. However, problems arise when it is deficient or in excess. In some cases, intake of essential elements is even more critical than for toxic elements. Mechanisms therefore appear available in biological systems, that protect against small excesses of essential elements [7,17,20,21]. Copper deficiency is an indication of reduced protein and enzyme activity. The symptoms of this are: anaemia, loss of hair pigments, reduced growth and reduced

arterial elasticity. Menkes kinky hair disease in children is due to a deficiency of cytochrome oxidase, which is an enzyme that catalyses a reaction in the electron transport system. The disease is fatal by the age of 3-5 years. Copper deficiency also results in kwashiorko, a decrease in the number of leucocytes, skeletal defects and degeneration of the myelin sheaths of nerve cells. Ruptures and aneurysms of the aorta becomes more likely. Medical research evidence suggests that an imbalance in the amount of copper and zinc leads to a heart disease known as coronary artery disease. A high zinc to copper ratio also increases the deposition of fatty substances in the blood vessels [17-21].

The daily human consumption is between 2-5mg. The required amount for a child is 1-1.6mg per day, for adults is 2mg per day, while less than 0.3mg per day produces deficiency. About 32% of the copper consumed is absorbed, but this varies. For instance, high calcium and iron intake reduces copper absorption. Copper is mainly distributed in the liver for storage, kidneys, intestines, blood, muscle and brain [9,17,18].

Amine complexes of cupric chlorate, cupric dithionate, cupric azide and cuprous acetylide are explosive, but are of no industrial or public health importance. In this regard, copper acetylide has been found to be the cause of the explosions in acetylene plants and therefore the use of copper in the construction of these plants has been discouraged [9].

Fragments of copper metal or copper alloys that lodge in the eye can cause a condition known as chalcosis, which may lead to uveitis, abscess and loss of the eye. Also, workers who spray

vineyards with bordeaux mixture may suffer from pulmonary lesions, a condition known as vineyard sprayers lung as well as copper-laden hepatic granulomas [9].

Copper and its salts have been found to be remarkably non-toxic to mammalian tissues. However, cases of acute and chronic human toxicity has been reported [22,23].

In acute copper poisoning, works of chemical reference contain statements to the effect that soluble salts of copper are poisonous. This is true in practical terms only if such solutions are used with misguided or suicidal intent. In the former instances, Copper (II) tetraoxosulphate (VI) known as bluestone or blue vitriol, is generally ingested in gramme quantities before it can be toxic. Nausea, vomiting, diarrhoea, sweating and rarely convulsions, coma and death may result. Ingestion of smaller amounts of copper salts dissolved from the walls of copper pots and vessels by the action of carbonated water or citrus juices seldom produces symptoms and does not represent a threat to life. The symptoms that occur are mild nausea and vomiting and this is related to acute gastroenteritis [9,17,22].

An increased concentration of ceruloplasmin in the blood causes Wilson's disease. Chronic human toxicity does not represent a major health hazard, although there have been reports of its possible occurrence in infants resulting from contaminated water or water pipes. Chronic human toxicity is extremely rare, except in those individuals who inherited a set of autosomal recessive genes producing an abnormal increase in body copper and in whom, as a consequence, hepatolenticular degeneration, otherwise known as Wilson's disease develops. A very high

concentration of copper is also found in the brain of a person who suffers from Wilson's disease [18,22].

A normal individual absorbs a scant amount of copper, sufficient to meet the body's essential needs and an excess copper is readily eliminated. Copper, in small amounts, is a trace element essential for the activity of such mammalian metalloenzymes as ceruloplasmin, cytochrome oxidase, dopamine and tryosinase. Molybdenum intake has been found to alter the amounts of copper excess necessary to produce toxicity [22].

Some important sources that are rich in copper are, shell fish, kidneys, liver and nuts, while poor sources are dairy products, sugar and honey. Other sources of copper are wine, roofing materials, cooking utensils, coins, pigments, insecticides, fungicides, algacides, moluscicides and dental materials. Soft water or water with a low pH value, can also leach appreciable amounts of copper from pipes [9,17,24].

Copper is one of the most important non-ferrous metals, whose usefulness is accounted for by its combination of high electrical conductivity, high thermal conductivity, ease of casting, extrusion, rolling and drawing to produce wire, tubing and strip; low corrosion rate of copper when used for food preparation, excellent alloying characteristics, high aesthetic appeal and low toxicity to humans. It is one of the first metals to have been used by humans due to its fairly abundant supply [8,11,13,25,26].

The multifarious uses of copper springs directly from its workability, and as an electrical conductor. Over 75% of copper output is used in the electrical industries. Perhaps the thermal

Electrical conductivities of copper are second only to those of silver. Technically, copper comes second only to iron in abundance [9,25-27].

Copper has been employed as a bactericide, molluscicide and fungicide for a long time and is of importance in the control of schistosomiasis. The addition of copper to lake water acts as an important deterrent to the transmitting of the disease by the infection of snails that act as a host for the responsible parasite [8].

Medical uses range from a copper intra-uterine device for contraceptive purposes to copper drugs in cancer therapy. Copper hexafluoroarsenate (VI) is a powerful emetic and has been used clinically as such in the treatment of intoxications [8,9].

The resistance to salt water corrosion of admiralty brass, which contains 71% copper, 28% zinc and 0.75-1.00% impurities led to the extensive use of this alloy in ships and condenser tubing.

Since 1963 there has been a steady replacement of admiralty brass by copper-nickel alloys. The resistance to corrosion of copper by food and its non-toxicity in dilute solutions have encouraged its use for food preparation.

The corrosion rates of copper coupled with the ease of casting, bending and of soldering resulted in the extensive use of copper tubing for domestic water pipe. Copper radiators in automobiles use the high thermal conductivity of copper and the ease of mechanical working and brazing [8,24,28].

Livestock and poultry feeds are frequently supplemented with copper either to promote growth or to provide antibiotic activity. Copper (II) tetraoxo sulphate (VI) is also used to

supplement pastures deficient in the metal. Also, copper (II) tetraoxo sulphate (VI) neutralised with hydrated lime known as bordeaux mixture is used for the prevention of mildew in vineyards. Copper (II) oxide is used as a component of paint for ship bottoms [9].

Copper is used for the absorption and mobilization of iron required to make haemoglobin. Copper serves the same oxygen-carrying function in the blood of certain marine animals that iron serves in higher animals, hence it is an essential constituent of haemocyanin, the colouring matter in the blood of some moluscs and arthropods [7,16,17].

Native copper once widespread in the United States, is now mined in quantity only in Michigan. The grade of ore used for copper production has been going steadily downwards as the richer ores have become exhausted and the demand for copper has grown. The threshold level for an average ore in the United States contains less than 1.0% copper, but the average is higher in other countries. The following threshold levels of copper in various ores have also been reported: 4.0, 5.0, 66.43 and 79.67% respectively [13,14,29,30].

There are vast amounts of copper in the ground, available for future use if ores of still lower grades are utilized and there is no prospect of exhaustion for a long time to come [13].

1.2 COLORIMETRIC ANALYSIS:

This is based on the variation of the colour of a system with change in the concentration of some component. The colour is usually due to the formation of a coloured compound by the

addition of an appropriate reagent, or it may be inherent in the desired constituent itself. The intensity of the colour may then be compared with that obtained by treating a known amount of the substance in the same manner [31].

A colorimeter is a type of visible spectrophotometer that covers only, or primarily, the visible region (380-750 nm). In visual colorimetry, natural or white light from the source strikes a diffraction grating and is dispersed into its component colours like a rainbow. Light of a wavelength range of only a few nanometers (8-20 nm) passes through a slit and strikes the cell containing the sample. Some of the light is absorbed and the rest is transmitted to the phototube and ultimately gives a readout [32].

When the eye is replaced by a photoelectric cell, thus largely eliminating the errors due to the personal characteristics of each observer, the instrument is termed a photoelectric colorimeter [31].

The choice of a colorimetric determination depends upon the following:

a colorimetric method will often give more accurate results at low concentrations than the corresponding titrimetric or gravimetric procedure. It may also be simpler to carry out;

it can frequently be applied under conditions where no satisfactory gravimetric or titrimetric procedures exist, such as in certain biological substances; and,

there is often no serious sacrifice of accuracy over the corresponding gravimetric or titrimetric procedures provided the experimental conditions are rigidly controlled [31].

The block diagram of the essential components of a colorimeter are shown in figure 1.0

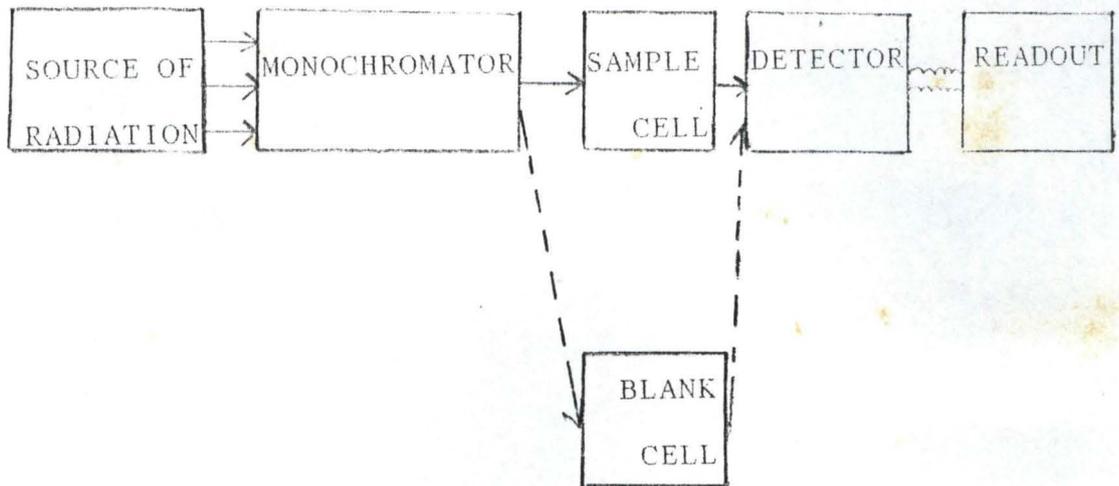


Fig. 1.0: A block diagram of the essential components of a colorimeter

1.3 TITRIMETRIC ANALYSIS

This refers to the quantitative chemical analysis carried out by determining the volume of a solution of accurately known concentration which is required to react quantitatively with a measured volume of a solution of the substance to be determined [31].

A titration is performed by adding exactly the volume of a standard solution needed to react with an unknown quantity of a second substance. The standard solution is called the titrant, the volume of titrant needed for the titration is carefully measured by means of a burette and the solution being titrated is termed the titrand. The point at which this occurs is called the equivalent point or the theoretical end point [31,32].

The completion of the titration is detected by some physical change, produced by the standard solution itself, such as the faint pink colour formed by potassium tetraoxo manganate (VII) solution or, more usually, by the addition of an auxiliary reagent, known as an indicator [31].

Titrimetric methods are capable of a high precision and wherever applicable possess obvious advantages over gravimetric methods. They need simpler apparatus, and are, generally quickly performed; tedious and difficult separations can often be avoided [31].

This method is only applicable to solutions containing up to 25mg copper ions in 100.00 cm³ of water. If the concentration of copper is too high, the intense blue colour of the copper (II) amine complex masks the colour change at the end point. If difficulty is experienced with an end point then it is better to

start with a smaller portion of the test solution, and to dilute this to 100.00 - 150.00 cm³ before following the experimental procedure [31].

The following are some chief requirements that a titrimetric analysis must fulfil.

The reaction should be relatively fast, and stoichiometric. Some method must be available for determining the point in the titration at which a stoichiometric amount of titrant has been added and the reaction is complete. Finally, the reaction should be quantitative [31,32].

1.4 GRAVIMETRIC ANALYSIS:

It is the quantitative determination of a substance by precipitation followed by isolation and weighing of the precipitate [32].

A gravimetric estimation, when performed with care is capable of a high degree of accuracy. The reasons for the continuing use of this method, despite the disadvantage that, it is generally somewhat time-consuming are enumerated below.

It is accurate and precise when using modern analytical balances. Possible sources of error are readily checked, since filtrates can be tested for completeness of precipitation and precipitates may be examined for the presence of impurities. It has the important advantage of being an absolute method, that is, one involving direct measurement without any form of calibration being required and finally determinations can be carried out with relatively inexpensive apparatus, the most expensive requirements being a muffle furnace and, in some cases, platinum crucibles [31-33].

This method of determination of copper as copper (I) thiocyanate is an excellent method, since most thiocyanates of other metals are soluble. The essential experimental conditions with respect to this method are: slight acidity with respect to hydrochloric acid or tetraoxo sulphate (VI) acid, the presence of a reducing agent, such as trioxosulphate (IV) acid or ammonium hydrogen trioxosulphate (IV), to reduce copper (II) to copper (I); a slight excess of ammonium thiocyanate solution, since a large excess increases the solubility of the copper (I) thiocyanate due to the formation of a complex thiocyanate ion; and the absence of oxidising agents [31].

1.5 AIMS AND OBJECTIVE:

The aim of this project is to determine the percentage of copper in two copper ore samples by three different analytical methods: Colorimetric, titrimetric and gravimetric and to compare the results in order to find the method that is most sensitive.

Based on the result, one may be able to highlight the possibility of the presence of copper in commercial quantity at the locations where the samples were taken.

CHAPTER 2

2.0 LITERATURE REVIEW

Much work has been done on the determination of copper in different constituents. Using automated analytical control system, the operation and performance characteristics of a computerized quality control system consisting of localized, group and centralized analyzers for a copper smelting plant were carried out [34]. Up to 1321 samples were analyzed during each 8 hour shift. It was also reported that the maximum total analysis time was 30 minutes and up to 8 elements were determined simultaneously.

The direct determination of copper in solids by direct current argon plasma emission spectrometry with sample introduction using laser ablation has been reported [35]. The emission intensity was dependent on sample preparation technique, particle size, laser pulse rate and copper anion. The system was also used to directly determine copper in pelletized ore samples with 2.0 - 6.0 % relative standard deviation, a detection limit of $20 \mu\text{g g}^{-1}$ and acceptable accuracy.

A comparison of isotope dilution mass spectrometric methods for the assay of copper in copper ore reference materials has been reported [36]. Isotope dilution inductively coupled plasma mass spectrometry was found to be an excellent method for the determination of the concentration of copper in copper ore and is capable of a relatively high precision for a number of elements in inorganic matrices.

The study of the amenability of low-grade copper ores to bacterial leaching has been carried out. In this, a *Thiobacillus ferrooxidans* mutant, *sulfobacillus thermosulfidoxidans*, *sulfolobus* and mixed cultures of different origins leached 44.0 - 79.0, 36.5 - 70.7, 41.1 - 81.5 and 17.7 - 18.9 % copper from three different ores, *in vitro*. The method is economically feasible, since the acid consumption was less than 15 kg per ton for all non carbonate ores [37].

Tetrabutyl ammonium bromide/thenoyl trifluoro acetone/methyl isobutyl ketone extraction for atomic absorption spectrometric determination of cobalt, nickel and manganese in copper ores and concentrates has been studied [38]. They also reported an extraction - atomic absorption spectrometric method of determination of cobalt, nickel and manganese in metallurgical copper materials containing considerable amounts of copper, iron, lead, zinc and aluminium.

The optimization of the density of a sampling network by gradually increased spacing has been reported [39]. The optimization density of a sampling network in prospecting for ores, including the determinations of iron, copper, antimony, gold and silver was reported to depend mainly on the degree of the ore distribution heterogeneity and that the distances between sampling points could vary from 2.0 - 50.0 m.

The composition and textures of Cu-Zn-Fe sulfide ores has been studied [40]. It was reported that quartz veins in volcanic rocks contain sphalerite, pyrite and chalcopyrite, with minor amounts of native gold, galena, covellite and chalcocite.

A deep-seated base metal ore occurrence has been studied in relation to the geological pattern of ore accumulation [41]. It was also reported that, in the elongate subvolcanic body copper porphyry ore were found, accompanied by a skarnous copper ore accumulation, where the high-grade ores occur. The deep-seated ore mineralization represents a peculiar type of porphyric copper ore deposit, where a central copper ore area is zonally surrounded by a complex ore mineralization.

The use of a Neutron source SO-I for the determination of the major component in copper and barite ores and their enrichment products has been studied [42]. In the determination, copper and barium were determined in copper ore and barite, respectively by activation with about 10^7 thermal neutrons $\text{cm}^{-2} \text{S}^{-1}$ for 15 minutes from a neutron source. It was reported that the copper determinations were correlated for aluminium and manganese interference, the barium determinations for aluminium interference and that the sensitivities were 0.03g copper and 1.5g barium.

The geology and exotic copper mineralization in the vicinity of copper Butte has been carried out [43]. It was also reported that chrysocolla and copper bearing wad, limonite and clays occur and that possibly 50.0 - 100.0 million tons of materials were present with copper of about 0.77%. The source of the copper was uncertain and a hidden sulfide ore body may also exist nearby.

The determination of the composition of some sulfide materials by using the laser microspectral analyzer, LMA-1 has been studied [44]. It was reported that nickel, cobalt, silver,

bismuth, antimony and copper were determined in pyrrhotite, pyrite, chalcopyrite, pentlandite and galena samples with the LMA-1 analyzer and the correlations between the distributions of certain elements were also determined.

The factors controlling the localization of mineralizations has been reported [45]. The report indicated that the assessment was based on the examination of the general geology, the lead, copper, zinc, silver and antimony contents in shales, and the ore mineral paragenesis in quartz veins. The minerals of interest were found to be chalcopyrite, sphalerite, galena and pyrite.

It has been reported that the central virginia volcanic-plutonic belt is a host for massive sulfide deposits [46]. The report shows that there are local concentrations of sphalerite and other, base minerals within the major pyrite deposits [Zn 1.0 - 12.5, Cu 1.0 - 2.0 and lead less than 5.0 % respectively].

Scanning electron microscope has been used in evaluating metallurgical plant performance [47]. It was reported that the quantitative evaluation of minerals by scanning electron microscopy was improved by using a computer-controlled image analyzer with a digital scan generator for beam position control and an automated motor-driven stage for sample position. The quantitative evaluation of minerals by scanning electron microscopy was used to study the flotation of a Cu-Pb-Zn ore and a tin ore containing cassiterite, pyrite and pyrrhotite.

The study of the conditions of lead extraction by fatty acids for the analysis of mineral raw materials has been studied [48]. It was reported that bismuth and lead were determined in

various ores and ore concentrates by methods involving extraction from sulfosalicylic acid solutions (for masking iron, aluminium, titanium, tin and antimony) at pH of 5.0 - 5.5 by C₇₋₉ carboxylic acids, re-extraction and chelatometry with 0.05 mol dm⁻³ complexon III. The extraction of bismuth, lead, copper, zinc, barium, strontium, calcium and magnesium by C₇₋₉ carboxylic acids was studied as a function of pH.

A colour reaction of bivalent transition metal ions with bromopyrogallol red in the presence of surfactants has been used for the spectrophotometric microdetermination of copper, zinc, cadmium and manganese [49]. The result shows that the sensitization mechanism of the systems are considered to be the synergistic effect of chelation, association and micelle solubilization. The methods were applied to determine these metals in pure aluminium, cast aluminium, nickel alloys, copper ores, waste water and drinking water respectively.

The direct spectrophotometric determination of copper in aluminium-base alloy with 4-[5 chloro-2-pyridylazo]-1, 3-diaminobenzene [5-Cl-PADAB] has been reported [50]. In the determination, the colour reaction of copper (II) with 4-(5 chloro-2-pyridylazo)-1, 3-diaminobenzene was investigated and the optimum conditions for the detection of copper were determined. They reported that Beer's law was obeyed in the range of 0-30.0 µg copper per 25.0 ml at 527.00 nm and that the recovery was 99.0 - 102.0 %.

Flameless atomic absorption determination of noble metals after liquid-liquid extraction by a mixture of bis(2-ethylhexyl) dithiophosphate and p-octylaniline was studied [51]. In this

study, noble metals were determined in samples containing copper, such as Cu - Ni sulfide ores, by graphite-furnace atomic absorption spectrometry after preconcentration by extraction from 2.0 - 3.0 mol dm⁻³ HCl into 0.05 mol bis (2-ethylhexyl) dithiophosphate - 0.25 mol p - octylaniline in methyl phenol. It was also reported that the detection limits were Au 0.0005, Ag 0.0001, Pt 0.015, Pd 0.0005, Rh 0.002 and Ru 0.015 Ppm in 10.0 g samples.

The determination of silver, antimony, bismuth, copper, cadmium and indium in ores, concentrates and related materials by atomic absorption spectrometry after methyl isobutyl ketone extraction as iodides has been reported [52]. The report described the methods for determining ca 0.2 µg g⁻¹ or more of Ag and Cd; 0.5 µg g⁻¹ or more of Cu and 5.0 µg g⁻¹ or more of Sb, Bi and In in ores, concentrates and related materials.

A study of photometric complexometric titration using ethylene diamine tetrapropionic acid (EDTP) in copper titration without adding indicator has been carried out [53]. The report indicates that copper reacts with ethylene diamine tetrapropionic acid to form a complex with an apparent stability constant of 8.0 at pH 4.5. The sensitive method requires no prior separation and is meant to determine copper in ores and cast alloys using photometric detection at 640.00 nm.

A new selective colour reaction for copper using a new colour reagent, 2-(4,5-dimethylthiazol-2-ylazo)-5-(dimethylamino) aniline for the determination of copper in copper ores, lead powder, corn meal, water and soil respectively without interference has been reported [54]. The new reagent forms a

1:2 metal-ligand complex with copper and can be used in the spectrophotometric determination of copper without interference from 50-fold excess nickel, 500-fold excess cobalt and large amounts of iron and common anions.

Atomic absorption spectroscopy using flame atomiser has been used for the rapid, low-cost analysis of a copper slag for 13 elements [55]. The samples were dissolved with 3:1.5:2 HCl-HF-HNO₃ in a heated plastic pressure vessel and that boric acid was added to dissolve the matrix effect. The average relative standard deviation was found to be 1.83 %.

A model for correcting the matrix effect on portable x-ray fluorescence analyzer has been reported [56]. This method was successfully applied in the analysis of tin ores and copper ores. In this, the matrix correction method for x-ray fluorescence analysis was based on the linear relation between the mass absorption coefficient of incident radiation and the reciprocal of the intensity of compton scattering.

In a related analysis of copper ore, x-ray fluorescence with a programmable appliance and measuring procedure was used for the rapid, industrial, on site analysis of copper and other ores [57]. This method permits the simultaneous determination of up to 8 elements and the sample preparation as well as the evaluating program are presented for the determination of copper and iron in copper ores.

Similarly, direct reading x-ray spectrometer model SRM-18 was reported to have been used for the analysis of stainless steel [58]. The report indicated that silicon, phosphorus, titanium, chromium, nickel, manganese, vanadium, copper,

molybdenum and tungsten were rapidly determined within an analysis time of 40 seconds by computerized x-ray fluorescence analysis with the SRM-18 quantometer.

An x-ray fluorescence express analysis of Cu-Mo ores using a semi-conductor detector has also been reported [59]. The method was rapid and used for the determination of copper and molybdenum in Cu-Mo ores with a sensitivity of up to 10^{-4} % and a relative error of less than 5.0 % by using a Si(Li) detector, ^{109}Cd excitation source and an 800-channel analyzer LP-4840.

The development and verification of methods for the x-ray spectral analysis of slurries of Cu-Ni ore beneficiation products has been studied [60]. It was reported that copper, iron, nickel and solids were determined in slurries of Cu-Ni ore beneficiation products by x-ray fluorescence spectrometry.

The experimental testing of the prototype of the BARS-2 x-ray spectrometric application for the rapid determination of copper, zinc and iron in Cu-Zn ores and concentrates has been studied [61]. The report indicates that Ni-Co and Cu-Ni differential filters were used for the separation of the copper and zinc radiation and that the filters for copper and zinc were balanced according to iron and copper respectively.

CHAPTER 3

3.0 EXPERIMENTAL AND RESULTS:

In the preparation of all the solutions, chemicals of analytical reagent grade purity and distilled-deionised water were used. All the glass wares were thoroughly washed with soap solution, repeatedly rinsed with distilled-deionised water and the solution to be used therein.

3.1 REAGENTS:

For the dissolution of copper ore samples, 12.0 mol dm^{-3} of tetraoxo sulphate (VI) acid was used. This was prepared by adding 65.22 cm^3 of concentrated tetraoxo sulphate (VI) acid to 15.00 cm^3 of water in a beaker which was surrounded with ice. On cooling, the resulting solution was quantitatively transferred into a 100 cm^3 volumetric flask and made up to the mark with water.

3.2 DISSOLUTION OF COPPER ORES:

1.0g of ground malachite and covellite copper ores were each dissolved in 20.00 cm^3 of $12.00 \text{ mol dm}^{-3}$ tetraoxo sulphate (VI) acid in covered beakers. The solutions were heated to complete the dissolution, cooled, transferred quantitatively into two separate 250 cm^3 volumetric flasks and each was made up to the mark with water. Colorimetric, titrimetric and gravimetric determinations of copper were separately carried out using the solutions of the ore samples.

3.3 COLORIMETRIC DETERMINATION

For colorimetric determination, 3.00 cm³, 6.00 cm³ and 9.00 cm³ each of the stock solutions prepared in section 3.2 were measured into six different 100 cm³ volumetric flasks using a burette. To each of the flasks was then added 5.00 cm³ of concentrated ammonia solution. The content of the flasks were thoroughly agitated and made up to the mark with water.

3.3.1 STANDARD 0.10 mol dm⁻³ COPPER (II) CHLORIDE DIHYDRATE

4.2625g of Copper (II) chloride dihydrate was dissolved in 30.00 cm³ of water in a beaker. The resulting solution was quantitatively transferred into a 250 cm³ volumetric flask and made up to the mark with water.

From the above 0.10 mol dm⁻³ standard solution; 4.00 cm³, 6.00 cm³, 8.00 cm³, 10.00 cm³ and 12.00 cm³ were each measured into five different 100 cm³ volumetric flasks using a burette. Each volumetric flask was then treated as in section 3.3 above.

A blank solution was also prepared by measuring 5.00 cm³ of concentrated ammonia solution into a 100 cm³ volumetric flask and made up to the mark with water.

3.3.2 SELECTION OF A SUITABLE WAVELENGTH

A suitable wavelength of maximum absorbance was determined using 4.00 cm³ and 10.00 cm³ of the diluted standard solutions prepared in section 3.3.1 as well as 6.00 cm³ of the diluted malachite solution prepared in section 3.3.

Using a corning 253 colorimeter and two matched 1.00cm rectangular cuvettes, the absorbance of the solutions were

measured at a varied wavelength of 20.00 nm over a wavelength range of 400.00 to 700.00 nm. The blank solution was used to standardise the machine at every 20.00 nm wavelength interval.

The absorbance values obtained for the three different solutions were separately used in plotting graph of absorbance against wavelength as shown in figures 3.0, 3.1 and 3.2 respectively. By extrapolation, a suitable wavelength of 600.00nm was obtained in each case.

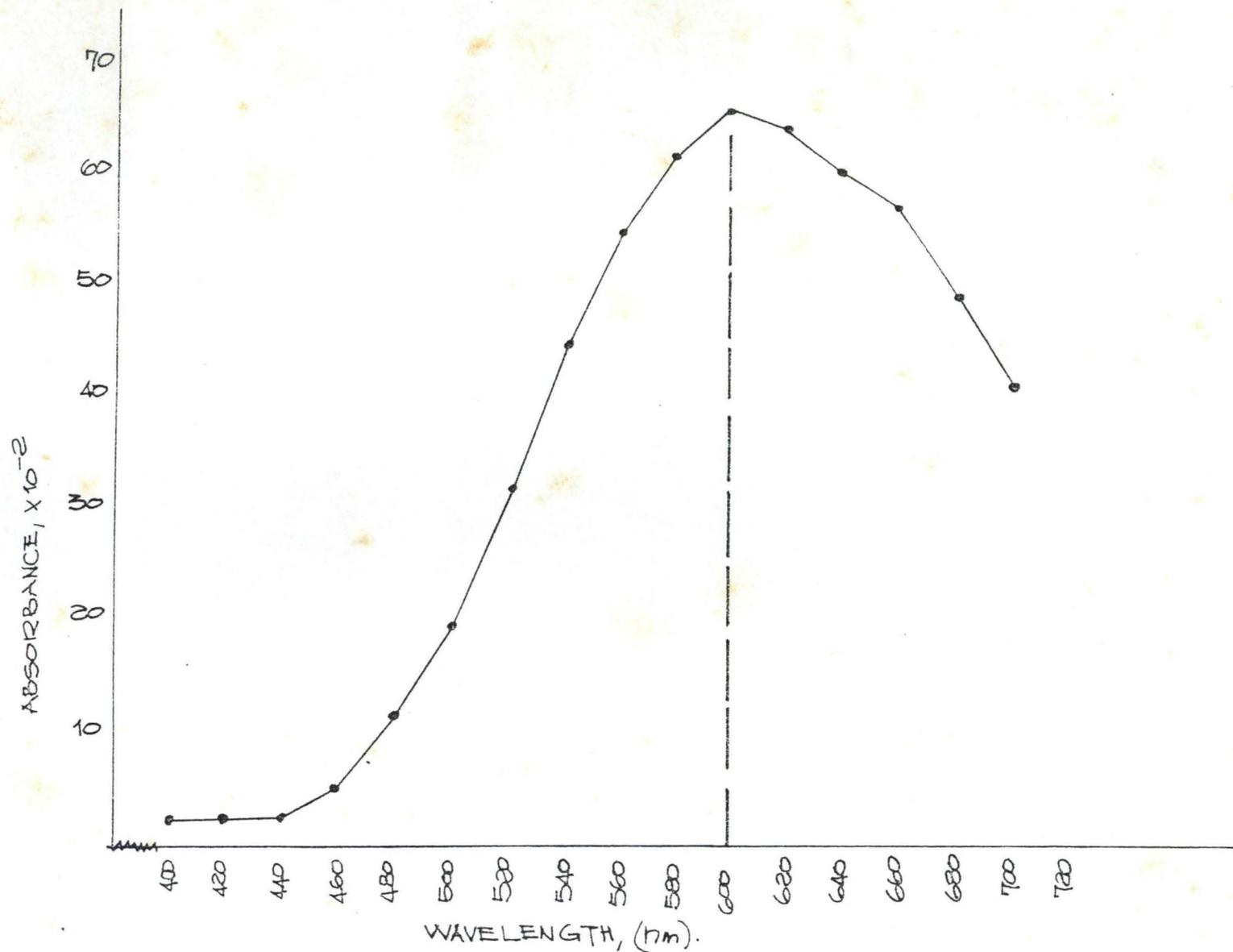
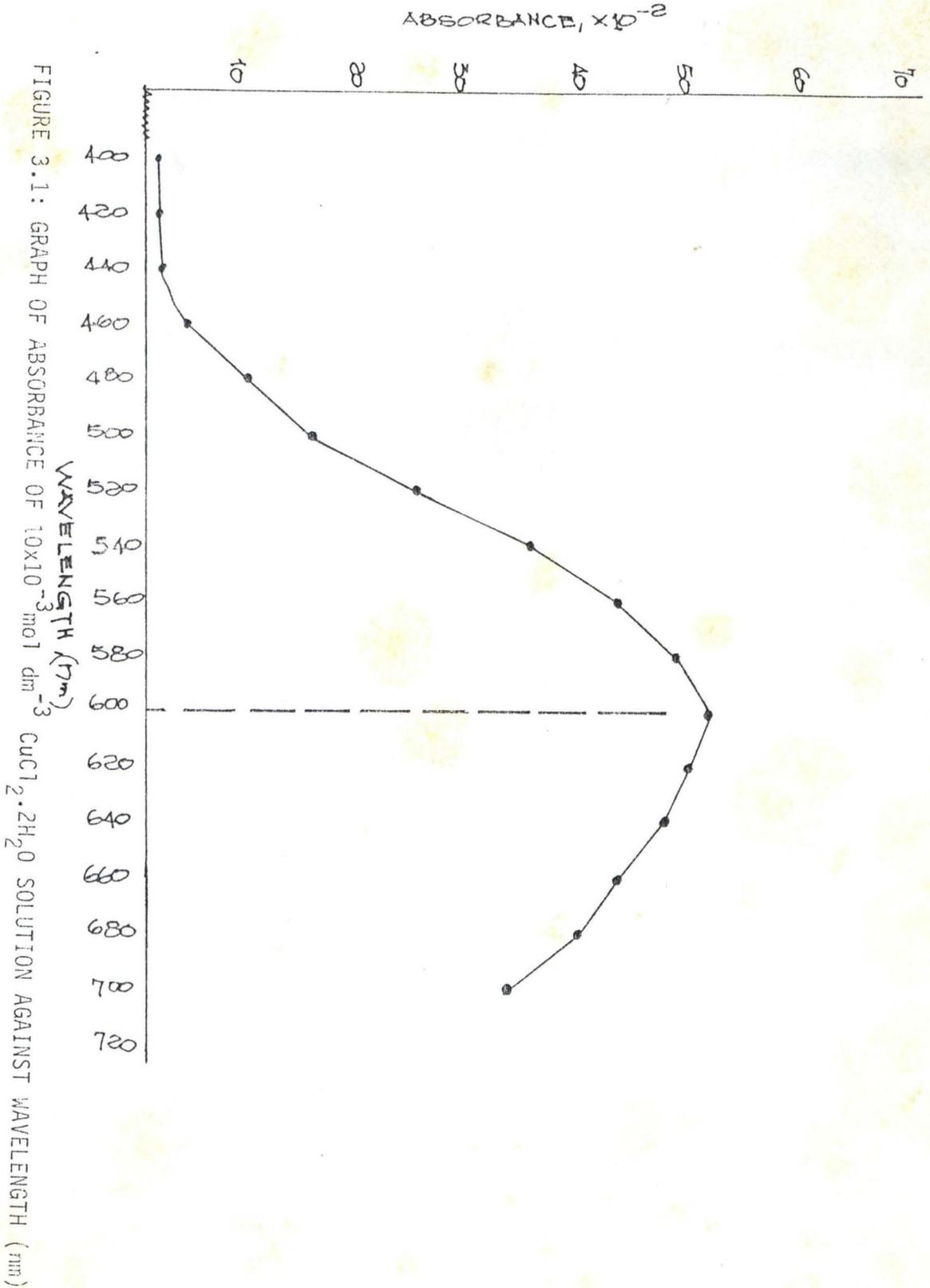


FIGURE 3.0: GRAPH OF ABSORBANCE OF $4 \times 10^{-3} \text{ mol dm}^{-3} \text{ CuCl}_2 \cdot 2\text{H}_2\text{O}$ SOLUTION AGAINST WAVELENGTH (nm)



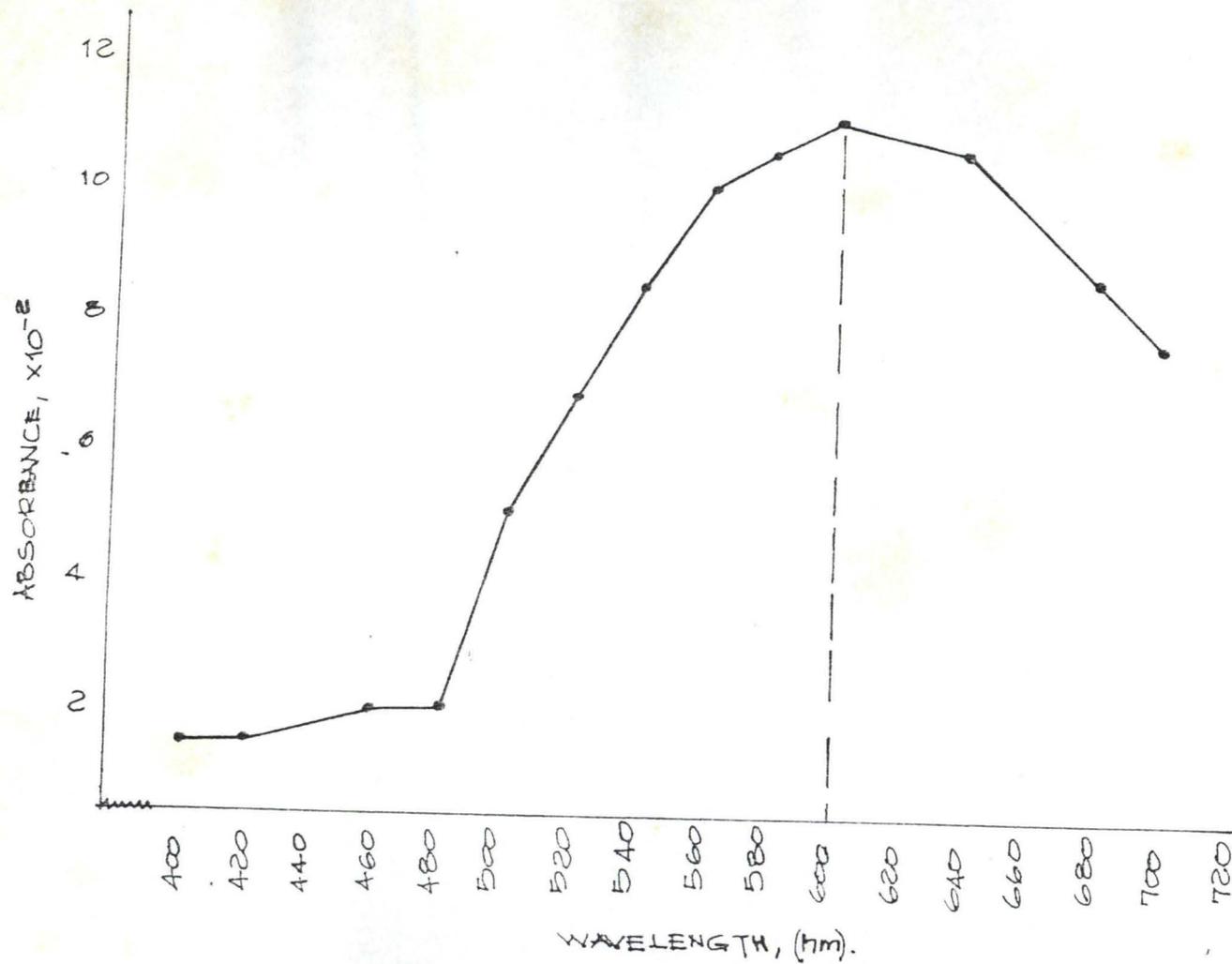


FIGURE 3.2: GRAPH OF ABSORBANCE OF 6.00 cm³ MALACHITE ORE PER 100 cm³ OF SOLUTION AGAINST WAVELENGTH (nm)

3.3.3 COLORIMETRIC DETERMINATION OF COPPER IN THE TWO ORE SAMPLES

The absorbances of the various copper standards were measured in a matched 1.00 cm rectangular cuvette at 600.00 nm using the blank solution to standardise the corning 253 colorimeter to zero.

The absorbance values obtained were used in plotting a calibration graph of absorbance against concentration of copper as shown in figure 3.3.

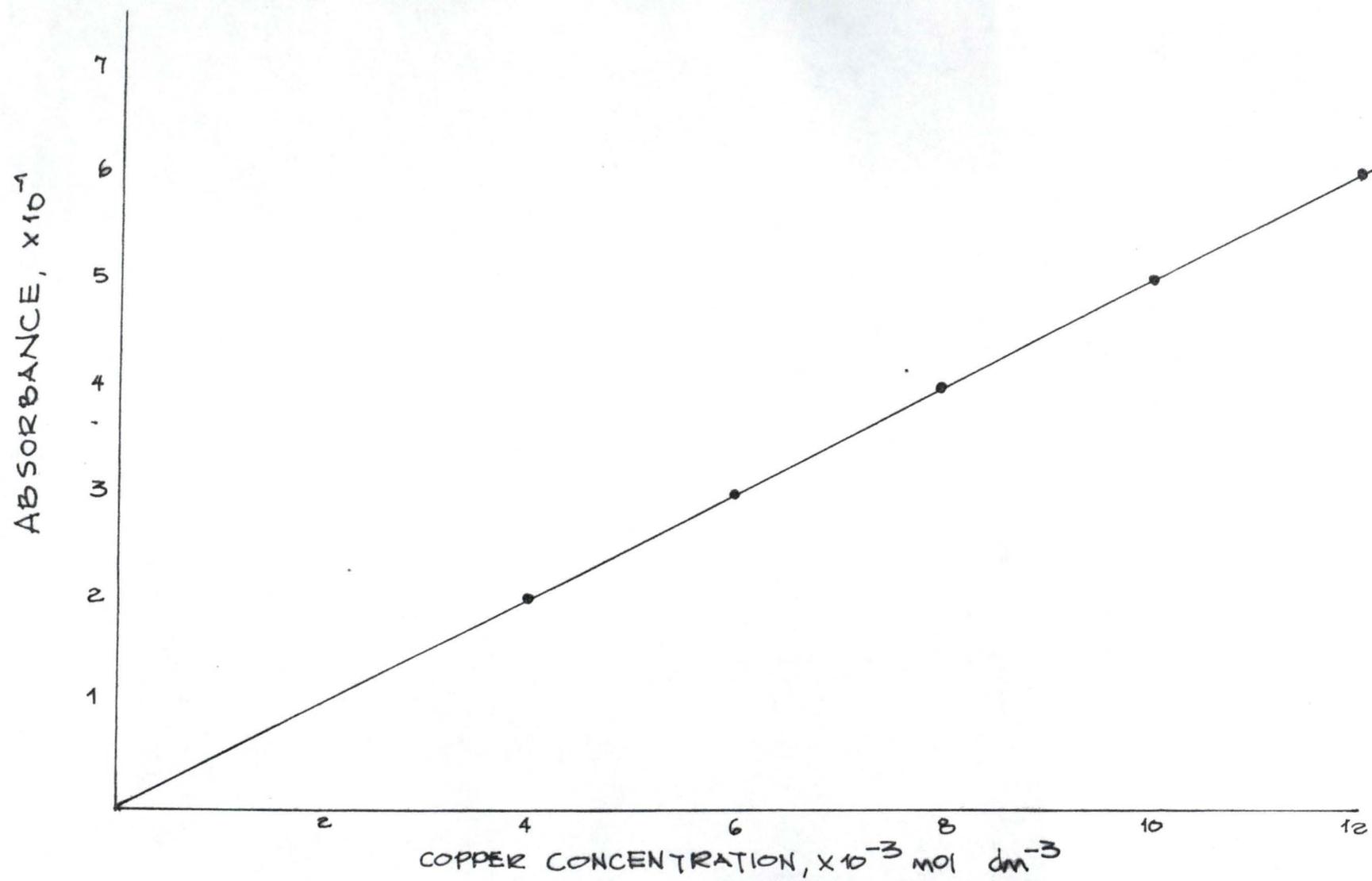


FIGURE 3.3: CALIBRATION GRAPH OF ABSORBANCE OF $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ SOLUTION AGAINST CONCENTRATION (mol dm^{-3})

The absorbance values for the solutions of malachite and covellite ores under investigation were taken and their corresponding concentrations were determined from the calibration graph in figure 3.3.

The percentage of copper in each of the original copper ore sample were then calculated and tabulated as shown in table 3.0.

Table 3.0: Colorimetric Percentage of Copper in Ore Samples

Ore	Volume of the sample solution taken (cm ³)	Concentration (x10 ⁻³ mol dm ⁻³) read from the calibration graph	Percentage copper
Malachite	3.00	1.20	63.50
Malachite	6.00	2.40	63.50
Malachite	9.00	3.60	63.50
Covellite	3.00	0.80	42.33
Covellite	6.00	1.60	42.33
Covellite	9.00	2.40	42.33

3.4 TITRIMETRIC DETERMINATION

For the titrimetric determination of copper in the two copper ore samples analyzed, the following solutions were prepared.

3.4.1 AMMONIA-AMMONIUM CHLORIDE pH_{10} BUFFER

7.0g of ammonium chloride was dissolved in 57.00 cm^3 of concentrated ammonia solution, transferred quantitatively into a 100 cm^3 volumetric flask and made up to the mark with water. Several of the solutions were made and transferred into a plastic container for subsequent use.

3.4.2 0.10 mol dm^{-3} ZINC TETRAOXO SULPHATE (VI) HEPTAHYDRATE

7.175g of zinc tetraoxo sulphate (VI) heptahydrate was dissolved in 100.00 cm^3 of water in a beaker. The resulting solution was quantitatively transferred into a 250 cm^3 volumetric flask and diluted to the mark with water. The solution was transferred into a plastic container for subsequent use.

3.4.3 0.05 mol dm^{-3} EDTA

18.612g of dried disodium dihydrogen ethylene diamine tetraacetate dihydrate was dissolved in 100.00 cm^3 of water in a beaker. The resulting solution was quantitatively transferred into a 1 dm^3 volumetric flask. The solution was thoroughly mixed by agitating the flask and made up to the mark with water. The solution was transferred into a plastic container for use.

3.4.4 ERIochrome BLACK T INDICATOR

0.20g of the dyestuff was dissolved in 15.00cm³ of triethanol amine in a beaker, followed by the addition of 5.00cm³ of absolute ethanol to reduce the viscosity. The resulting solution was transferred into an indicator bottle for use.

3.4.5 FAST SULPHON BLACK F INDICATOR

0.5g of the solid was dissolved in 15.00cm³ of water in a beaker. The resulting solution was quantitatively transferred into a 100cm³ volumetric flask and diluted to the mark with water.

3.5 STANDARDIZATION OF EDTA

10.00 cm³ of 0.10 mol dm⁻³ zinc tetraoxo sulphate (VI) heptahydrate solution was transferred into a 250cm³ conical flask using a burette, followed by the addition of 50.00cm³ of water and 5.00cm³ of ammonia-ammonium chloride pH₁₀ buffer. A cloudy suspension was formed which disappeared on agitating the flask.

Two drops of eriochrome black T indicator was added to the conical flask and titrated with the EDTA solution with constant agitation until the colour changed from mauve to a clear blue colour. The experiment was repeated until concurrent titre values were obtained.

3.5.1 TITRIMETRIC DETERMINATION OF COPPER IN THE TWO ORE SAMPLES

In view of the reasons advanced in section 1.3, the stock solution was diluted before carrying out the direct titrimetric determination of copper in the two ore samples. The dilutions were carried out by measuring 10.00cm^3 of the stock solution into a 100cm^3 volumetric flask and made up to the mark with water. Several of the the dilutions were made for both ores.

For each of the diluted copper ore solutions, 25.00cm^3 of the diluted solution was pipetted into a 250cm^3 conical flask. 25.00cm^3 of distilled-deionised water was added, followed by 5.00cm^3 of concentrated ammonia solution and 5 drops of the indicator fast sulphon black F.

The whole content of the flask was uniformly mixed by agitation and then titrated with 0.05 mol dm^{-3} EDTA solution until the end point. The end point was the change of colour from blue to dark green. The experiment was repeated several times for both the malachite and covellite ore samples analyzed.

The percentage of copper in malachite ore is shown in table 3.1

Table 3.1: Titrimetric percentage of Copper in malachite Ore sample

ORE REPLICATES	PERCENTAGE COPPER
1	63.50
2	63.50
3	63.50
4	63.50
5	63.50
6	63.50
7	63.50
8	63.50
9	63.50
10	63.50

=====

The percentage of copper in covellite ore is shown in table 3.2.

Table 3.2: Titrimetric percentage of Copper in covellite Ore sample

ORE REPLICATES	PERCENTAGE COPPER
1	42.86
2	42.86
3	42.86
4	42.86
5	42.86
6	42.86
7	42.86
8	42.86
9	42.86
10	42.86

=====

3.6 GRAVIMETRIC DETERMINATION

For the gravimetric determination of copper in the two ore samples, the following solutions were prepared.

3.6.1 0.2 mol dm⁻³ TETRAOXO SULPHATE (VI) ACID

About 5.50cm³ of concentrated tetraoxo sulphate (VI) acid was added to 25.00cm³ of water in a beaker surrounded with ice. On cooling, it was quantitatively transferred into a 500cm³ volumetric flask and made up to the mark with water.

3.6.2 SATURATED TRIOXO SULPHATE (IV) ACID

A fresh saturated solution of trioxo sulphate (IV) acid was prepared using the apparatus shown in figure 3.4

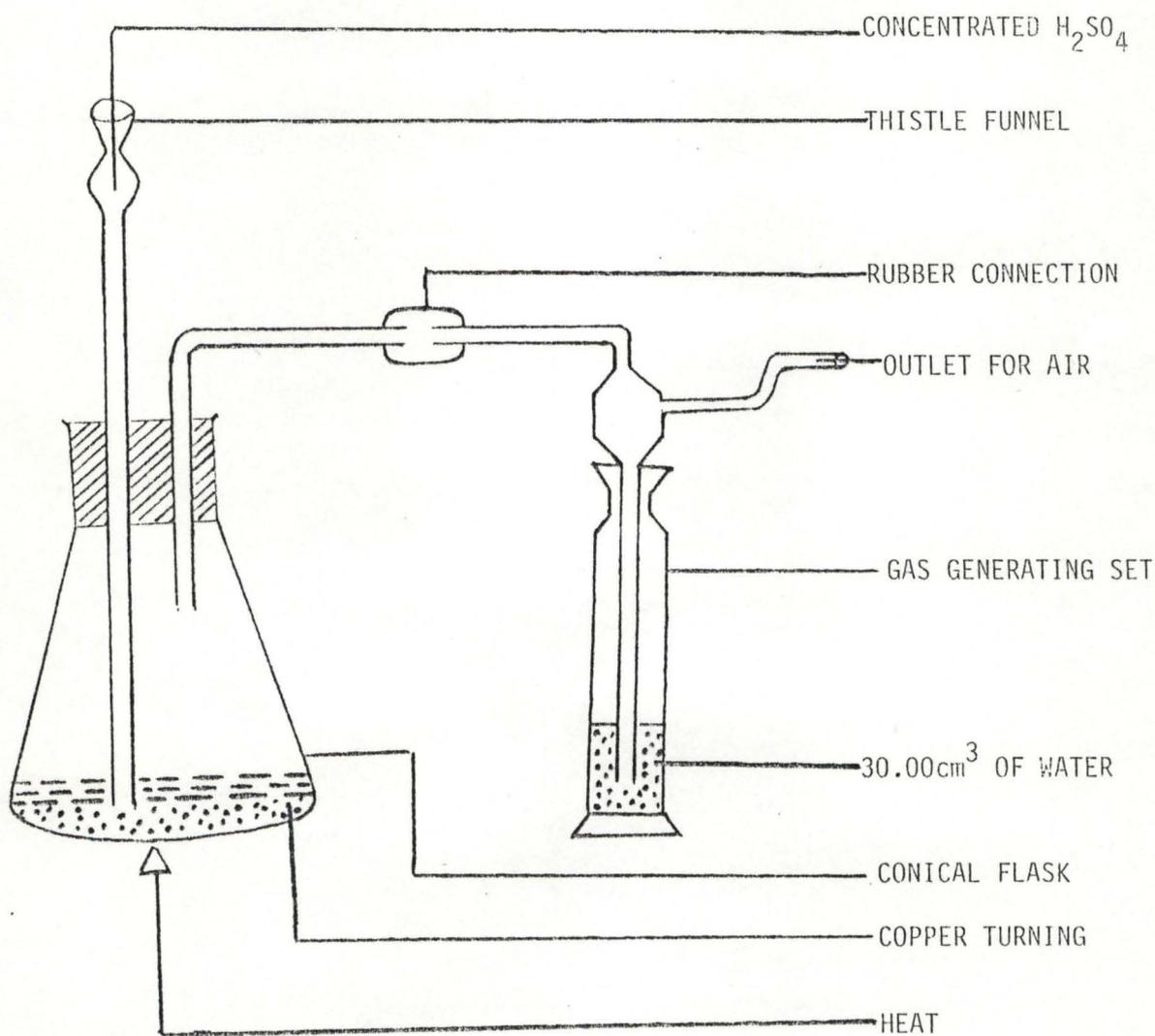
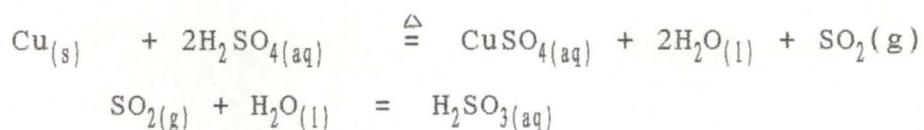


Fig. 3.4: Apparatus used for the generation of saturated Trioxo Sulphate (IV) Acid

A mixture of 20.00cm³ of concentrated tetraoxo sulphate (VI) acid and 11.684g of copper turnings were heated for 45.0 minutes on a heating mantle. The sulphur (IV) oxide liberated was collected over 30.00cm³ of water forming a saturated solution of the acid.

Equations:



3.6.3 10% (m/v) AMMONIUM THIOCYANATE SOLUTION

10g of ammonium thiocyanate was dissolved in 25.00cm³ of water in a beaker. The resulting solution was quantitatively transferred into a 100cm³ volumetric flask and made up to the mark with water. A fresh solution was always prepared.

3.6.4 0.10% (m/v) AMMONIUM THIOCYANATE SOLUTION

0.10g of ammonium thiocyanate was dissolved in 15.00cm³ of water in a beaker. The resulting solution was quantitatively transferred into a 100cm³ volumetric flask and made up to the mark with water.

3.6.5 20% (v/v) INDUSTRIAL METHYLATED SPIRIT

About 21.10cm³ of industrial methylated spirit was added to 20.00cm³ of water in a 100cm³ volumetric flask. The resulting solution was made up to the mark with water.

3.7 GRAVIMETRIC DETERMINATION OF COPPER IN THE TWO ORE SAMPLES

50.00cm³ of the stock solution of copper ore was pipetted into a 500cm³ beaker. 25.00cm³ of 0.2 moldm⁻³ tetraoxo sulphate (VI) acid was added into the beaker, followed by 25.00cm³ of the freshly prepared saturated trioxo sulphate (IV) acid solution. From a burette was also ran in slowly with stirring an excess, 5.00cm³ of the 10% ammonium thiocyanate solution.

The beaker was covered with a watch glass and allowed to stand overnight. A white precipitate of copper (I) thiocyanate and a colourless supernatant solution, which smells of sulphur (IV) oxide was formed within an hour.

The white precipitate of copper (I) thiocyanate was filtered the following day on a weighed number 3 sintered glass crucible available, instead of number 4. The residue of copper (I) thiocyanate was washed 10 times with cold 0.10% ammonium thiocyanate solution and 5 drops of the saturated trioxo sulphate (IV) acid solution.

The precipitate was then washed several times with 20% industrial methylated spirit. The precipitate was finally dried to a constant mass in the oven at 110°C.

The experiment was repeated 5 times for each of the two copper ores analyzed. The percentage of copper in the two ore samples as determined from the mass of the precipitates obtained are shown in table 3.3.

Table 3.3: Gravimetric percentage of copper in ore samples

ORE REPLICATES	MASS OF COPPER (I) THIOCYANATE PRECIPITATE (g)	PERCENTAGE COPPER
Malachite 1	0.2358	61.62
2	0.2359	61.64
3	0.2359	61.64
4	0.2359	61.64
5	0.2357	61.59
Covellite 1	0.1512	39.51
2	0.1511	39.48
3	0.1510	39.46
4	0.1513	39.54
5	0.1513	39.54

3.8 STATISTICAL ANALYSIS OF RESULTS

Statistics, when correctly used is an essential tool for the analyst. The use of statistical methods can prevent hasty judgements being made on the basis of limited information [32].

Table 3.4: Anova of the Colorimetric percentage of copper in each ore sample

SOURCE OF VARIATION	df	SS	MS	CALCULATED F	TABULAR $F_{0.01}$
BLOCK	2	0	0		
TREATMENT	1	672.25	672.25	0	98.50
ERROR	2	0	0		
TOTAL	5	672.25			

The tabular F value at the 1% level of significance for the given degrees of freedom is 98.50. The calculated F value [0] is lower than 98.50, hence there is no significant difference in the colorimetric percentage of copper obtained.

Table 3.5: Anova of the Titrimetric percentage of copper in each ore sample

SOURCE OF VARIATION	df	SS	MS	CALCULATED F	TABULAR $F_{0.01}$
BLOCK	9	0	0		
TREATMENT	1	2130.05	2130.05	0	10.60
ERROR	9	0	0		
TOTAL	19	2130.05			

The tabular F value at the 1% level of significance for the given degrees of freedom is 10.60. The calculated F value [0] is lower than 10.60, hence there is no significant difference in the titrimetric percentage of copper obtained.

Table 3.6: Anova of the Gravimetric percentage of copper in each ore sample

SOURCE OF VARIATION	df	SS	MS	CALCULATED F	TABULAR $F_{0.01}$
BLOCK	4	1.74×10^{-3}	4.35×10^{-4}		
TREATMENT	1	1223.24	1223.24	923196.98	21.20
ERROR	4	5.3×10^{-3}	13.25×10^{-4}		
TOTAL	9	1223.24			

The tabular F value [21.20] is very much lower than the calculated F value [923196.98] at 1% level of significance for the given degrees of freedom. Hence, the percentage of copper obtained differ very significantly at the 1% level of significance.

The least significance difference test when carried out gives an $LSD_{0.01}$ value of 0.106. The difference in the percentage of copper in the two ores is therefore very highly significant at 1% level of significance. This is because the difference in the percentage of copper is greater than the $LSD_{0.01}$.

Table 3.7: Anova of the mean percentage of copper in ores for colorimetric, titrimetric and gravimetric determinations

SOURCE OF VARIATION	df	SS	MS	CALCULATED F	TABULAR $F_{0.01}$
BLOCK	2	8.254	4.127		
TREATMENT	1	681.174	681.174	1211.40	98.50
ERROR	2	0.5623	0.2812		
TOTAL	5	689.990			

The calculated F value [1211.40] is very much greater than the tabular F value [98.50] at 1% level of significance. Hence, the mean percentages of Cu in the two ore samples differ very significantly at the 1% level of significance.

The least significance difference test when carried out gives an $LSD_{0.01}$ value of 4.297. The difference in the mean percentage of copper in the two ores is therefore very highly significant at 1% level of significance. This is because the difference in the percentage mean of copper is greater than the $LSD_{0.01}$.

CHAPTER 4

4.0 DISCUSSION OF RESULTS

4.1 INTRODUCTION

Although copper metal occurs in the free state in some parts of the world, the supply available from such sources is quite insufficient to meet the world's need for copper. The majority of copper obtained today are from various sulphide ores [24].

One of the most important industrial processes is the extraction of a metal from its ore. In most cases, the process begins with heterogeneous rock and ends with the recovery of a pure metal. Our industrial society consumes huge quantities of copper each year, nearly all of which are produced by chemical processes [62].

Before any metallurgical industry could embark upon extraction processes, the concentration of the desired metal must be sufficiently high to make its extraction chemically feasible and economically competitive. Ores of low metal concentration are worked only if they can be processed comparatively easily and inexpensively or if the metal product is scarce and valuable. The required concentration varies greatly from metal to metal. For copper it is 1.0% or even less [5,7].

4.2 PERCENTAGE OF COPPER IN ORE SAMPLES

Two copper ore samples; malachite and covellite were determined for percentage copper using colorimetric, titrimetric and gravimetric analytical techniques respectively.

Colorimetric determination of copper in malachite ore sample gave a value of 63.50%, whereas in covellite ore sample, it was 42.33%.

The percentage of copper in malachite ore sample as determined using volumetric method was found to be 63.50%, whereas for covellite ore, it was 42.86%.

The gravimetric method of determination for the percentage of copper in malachite ore sample was found to be between 61.59 to 61.64%, whereas that of covellite ore was between 39.46 to 39.54% with mean values of 61.63 and 39.51% respectively.

This therefore indicates that the percentage of copper as determined is within the acceptable limits, hence these ores from the unknown mines could be profitably mined. This is because, it is now profitable to mine ores containing as little as 0.25 or 1.0% of copper [5.7].

Table 4.0: Percentage of Copper in malachite ore based on the three analytical techniques

Colorimetric Determination (% Cu)	Titrimetric Determination (% Cu)	Gravimetric Determination (% Cu)
63.50	63.50	61.62
63.50	63.50	61.64
63.50	63.50	61.64
	63.50	61.64
	63.50	61.59
	63.50	
	63.50	
	63.50	
	63.50	
	63.50	
Mean (\bar{x})	63.50	61.63

Table 4.1: Percentage of Copper in covellite ore based on the three analytical techniques

Colorimetric Determination (% Cu)	Titrimetric Determination (% Cu)	Gravimetric Determination (% Cu)
42.33	42.86	39.51
42.33	42.86	39.48
42.33	42.86	39.46
	42.86	39.54
	42.86	39.54
	42.86	
	42.86	
	42.86	
	42.86	
	42.86	
	42.86	
Mean (\bar{x})	42.33	39.51

4.3 COMPARISON OF RESULTS

In the two ore samples, analysis have shown that there was a good agreement between the results obtained for colorimetric and titrimetric determinations of copper as shown in tables 4.0 and 4.1.

Inspite of the numerous advantages offered by gravimetric method, the high accuracy and sensitivity associated with the method in general and in particular to the determinations of copper, since most thiocyanates of other metals are soluble, the percentage of copper as determined in comparison with those obtained for colorimetric and titrimetric methods is lower. This may be due to the use of number 3 sintered glass crucible available for filtering instead of number 4. Sintered glass crucible number 3 has a wider pore size (20-30 μm) than that of number 4 (5-10 μm) [31].

Since it is now profitable to mine ores containing as little as 0.25 or 1.00% of copper, the two ore samples; malachite and covellite as determined could therefore be profitably mined. Based on the results of the current studies, malachite ore could be more profitably mined than covellite ore since lower-grade ores (covellite ore) increases production cost.

The threshold level for an average ore in the United States is less than 1.00% copper, but the average could be higher in other countries. The threshold level of copper in various ore samples also ranges from about 1.00 to 79.67% [13,14,29,30]. Comparatively, this study has shown that the mean percentage copper in the two ore samples is very much higher than some of the threshold levels. The reason may be, there is a high

distribution of copper in the unknown mines where the samples were obtained.

4.4 CONCLUSION

Colorimetric, titrimetric and gravimetric determinations of copper in the two ore samples gave a high percentage of copper in comparison with some of the threshold levels. In conclusion, the two ore samples could therefore be profitably mined, but malachite ore with a higher copper content could be more profitably mined than covellite ore.

There was a good agreement between colorimetric and titrimetric results. However, there was a slight difference between the results obtained in gravimetric determination with those of the other two methods. It is therefore not possible to determine which of the methods of determination is most accurate among these three methods. Hence, further work could be carried out on the gravimetric determinations of copper in ore samples using a number 4 sintered glass crucible required in the procedure.

REFERENCES

1. Barton, P.B. and Roedder, Jr. E. "McGraw-Hill Encyclopaedia of Science and Technology", Vol. 19, P. 611, McGraw-Hill Inc., New York, 1982.
2. Dillard, C.R. and Goldberg, D.E. "Chemistry: Reactions, Structure and Properties", P. 485, Collier-Macmillan Publ., New York, 1973.
3. Kneen, W.R., Rogers, M.J.W. and Simpson, P. "Chemistry: Facts, patterns and principles", Pp 294-520, The Eng. Lang. Book Society and Addison-Wesley Publs. Ltd, London, 1982.
4. Oganesian, E.T. "Chemistry: A Refresher Course", P. 214, Mir. Publs., Moscow, 1989.
5. Mortimer, C.E. "Chemistry: A Conceptual Approach", 4th Edition, Pp. 637-638, D. Van Nostrand Co.; New York, 1979.
6. Yoder, C.H.; Suydam, F.H. and Snavely, F.A. "Chemistry", P. 614, Harcourt Brace Jovanovich Inc.; New York, 1975.
7. Whitten, K.W. and Gailey, K.D. "General Chemistry". Pp 556-557, CBS College Publ., USA, 1981.
8. Tuddenham, W.T. and Dougall, P.A. "Kirk-Othmer Encyclopaedia of Chemical Technology". Pp 316-318, John Wiley and Sons Inc.; New York, 1985.
9. Scheinberg, H.I. "Encyclopaedia of occupational health and society". Vol. 1A-K, Pp 546-548, International Labour Organisation, Geneva, 1989.
10. Glinka, N.L. "General Chemistry", Vol. 2, Pp 238-240, Mir. Publs. (English translation), Moscow, 1981.

11. Rochow, E.G. "Modern Descriptive Chemistry". P. 177, W.B. Saunders Co.; London, 1977.
12. Mahan, B.H. "College Chemistry". Pp. 575-576, Addison-Wesley Publ. Co., Inc., London, 1966.
13. Butts, A. "McGraw-Hill Encyclopaedia of Chemistry". Pp 221-226, McGraw-Hill Book Co.; New York, 1983.
14. Science Teachers Association of Nigeria (STAN). "Chemistry for Senior Secondary Schools". P. 260, Heinemann Educational Books Ltd., Nigeria, 1987.
15. Hicks, J. "Comprehensive Chemistry". 3rd Edition, Pp 562-575, Macmillan Press Ltd., London, 1982.
16. Sienko, M.J. and Plane, R.A. "Chemistry", 5th Edition. Pp 387-388, McGraw-Hill International Book Co.; Tokyo, 1976.
17. Fergusson, J.E. "Inorganic Chemistry and the Earth Chemical Resources, their extraction, use and Environmental Impact". Vol. 6, pp 348-349, Pergamon Press Ltd., England, 1982.
18. Wolfe, D.H. "General, Organic and Biological Chemistry". P. 252, McGraw-Hill Book Co., New York, 1986.
19. Holum, J.R. "Fundamentals of General, Organic and Biological Chemistry". P. 686, John Wiley and Sons Inc., New York, 1978.
20. Bloomfield, M.M. "Chemistry and the living Organism" 5th Edition, Pp 90-92, John Wiley and Sons Inc., New York, 1992.
21. Berlow, P.P.; Burton, D.J. and Routh, J.I. "Introduction to the chemistry of life". P. 62, Saunders College Publ., Winston, 1982.

22. Ricksecker, R.E. "McGraw-Hill Encyclopaedia of Science and Technology". Vol. 3 (Cha-cyst), Pp 632-640, McGraw-Hill Inc.; New York, 1982.
23. Butts, A. "McGraw-Hill Encyclopaedia of Science and Technology", 2nd Edition. Pp 476-477, McGraw-Hill Inc.; New York, 1987.
24. Jones, M.M.; Johnston, D.O.; Nettekville, J.T.; Wood, J.L and Joesten, M.D. "Chemistry and Society". Pp 249-546, CBS College Publ., USA, 1987.
25. Liptrot, G.F. "Modern Inorganic chemistry", 4th Edition, Pp 405-406, Bell and Hyman Ltd., London, 1983.
26. Dickson, T.R. "Introduction to Chemistry", 6th Edition, P. 61, John Wiley and Sons Inc., New York, 1991.
27. Steedman, W.; Snadden, R.B. and Anderson, I.H. "Chemistry for the Engineering and Applied Sciences", 2nd Edition, Pp 158-159, Pergamon Press Inc., New York, 1980.
28. Russel, J.B. "General Chemistry", P. 674, McGraw-Hill Inc. Singapore, 1988.
29. Carmichael, R.S. "Practical Handbook of Physical Properties of Rocks and Minerals", Pp 88-89, CRC Press Inc. Florida, 1990.
30. Wilson, J.G. and Newall, A.B. "General and Inorganic Chemistry", 2nd Edition, Pp. 580-588, Cambridge University Press, London, 1970.
31. Jeffery, G.H.; Bassett, J.; Mendham, J. and Denney, R.C. "Vogel's Textbook of Quantitative Chemical Analysis", 5th Edition, Pp 417-672, Longman Group Ltd., United Kingdom, 1988.
32. Fritz, J.S. and Schenk, G.H. "Quantitative Analytical

Chemistry", 4th Edition, Pp 46-117, Allyn and Bacon Inc., London, 1979.

33. Lambert, J. and Muir, T.A. "Practical Chemistry", 3rd Edition, P.421, Heinemann Educational Books Ltd., London, 1978.
34. Khmaro, V.V.; Bregman, I.I.; Ogol, A.F. and Li, I.E. Tsventn. Met. 11, 103-6 (1986) [C.A. 106: 95039P (1987)].
35. Mitchell, P.G.; Snadden, J. and Radziemski, L.J. Appl. Spectrosc. 41 (1), 141-8 (1987) [CA. 106: 95175e (1987)].
36. Beary, E.S.; Brletic, K.A; Paulsen, P.J. and Moody, J.R. Analyst 112 (4), 441-4 (1987) [CA 106: 188077q (1987)].
37. Grudeva, V.I. and Grudev, S.N. Zesz. Nauk. Akad. 128, 41-50 (1986) [CA 106: 99148w (1987)].
38. Rozanska, B. and Lachowicz, E. Talanta 33 (12), 1027-9 (1986) [CA. 106: 95121j (1987)].
39. Treger, M. Geol. Pruzkum 27(5), 134-6 (1985) [CA. 106: 76426 (1987)].
40. Al-sari, A.M.; Al-shanti, A.M. and El-Mahdi, O.R. Bull. Fac. Earth Sci. 6, 578-85 (1984) [CA 106: 7679u (1987)].
41. Cseh Nemeth, J. Foldt. Kozl. 105, 692-708 (1975) [CA 86: 58142q (1977)].
42. Barkhatova, I.I.; Bakhtadze, L.V; Gambaryan, R.G.; Gurkov, V.A. and Tokvi, I.G. Vses Nauchno-Issled. Inst. Yad. Geofiz. Geokhim. 19, 47-54 (1974) [CA 86: 182560p (1977)].
43. Phillips, C.H. Spec. Publ. N.M. Geol. Soc. 6, 174-9 (1976) [CA 86; 192675u (1977)].
44. Atamanova, S.P. Gorn. Porod. Kol'sk. Poluostrova 1, 64-7 (1980) [C.A. 97: 16294n (1982)].

45. Gutierrezmaroto, A. and Monseur, G. *Commun. cient. soc. Esp. Mineral.* 2, 199-219 (1981) [C.A. 97: 58776b (1982)].
46. Pavlides, L.; Gar, J.E. and Cranford, S.L. *Econ. Geol.* 77(2), 233-72 (1982) [C.A. 97: 9323t (1982)].
47. Mckee, D.J. *Proc. Int. Congr. Appl. Mineral. Miner. Ind.* 2, 103-16 (1985) [C.A. 103: 145213b (1985)].
48. Galkina, L.L. *Zavod. Lab.* 51(3), 11-14 (1985) [C.A. 103: 31699 (1985)].
49. Xu, Q.; Zhou, Z. and Yin, Z. *Fenxi Huaxue* 13(3), 170-5 (1985) [C.A. 103: 204989j (1985)].
50. Zhou, Z.; Tang, L. and Shi, Y. *Zhejiag Gongxuyuan xuebao* 26, 12-18 (1985) [C.A. 103: 188755x (1985)].
51. Yukhin, Yu. M.; Udalova, T.A. and Tsimbalist, V.G. *Zh. Anal. Khim* 40(5), 850-4 (1985) [C.A. 103: 81042k (1985)].
52. Donalson, E.M. and Wang, M. *Talanta* 33(3), 233-42 (1986) [C.A. 105: 34721n (1986)].
53. Chen, H.; Zhou, S.; Yang, G. and Chen, Y. *Fenxi Ceshi Tongbao* 4(1), 39-43 (1985) [C.A. 105: 164057m (1986)].
54. Gao, J.; Huang, Y. and Hui, F. *Ziran kexueban* 20(3), 86-91 (1984) [C.A. 102: 55243m (1985)].
55. Matthes, S.A. *Bur. Mines* 1, 12 (1980) [C.A. 94: 76122c (1981)].
56. Cheng, Y. and Liu, L. *Hejishu* 11, 1-6 (1986) [C.A. 106: 168023r (1987)].
57. Kiraly, J. *Analysenverfahren* 3, 137-9 (1983) [C.A. 103: 152907j (1985)].
58. Gimmel'Ferb, A.G. and Podkopaeva, O.A. *Zavod. Lab.* 51(8), 84-5 (1985) [C.A. 103: 171134w (1985)].

59. Vyropaev, V.Ya.; Purehvkhaïdav, D. and Sirazhet, Kh. Report 7(17), 18 (1975) [C.A. 86: 100364r (1977)].
60. Bondarenko, A.V. and Ol'Khovoi, V.A. Obogashch. Rud. 26(6), 24-8 (1981) [C.A. 97: 65641g (1982)].
61. Lomonosov, G.G.; Kuzin, V.F.; Kulikova, A.A. and Mechetin, V.G. Izv. Vyssh. Uchebn. Zaved. 19(8), 139-41 (1976) [C.A. 86: 65047r (1977)].
62. Masternton, W.L.; Slowinski, E.J. and Walford, E.T. "Chemistry in the Laboratory". P. 197, Holt, Rinehart and Winston Publs, New York, 1980.