Technological University Dublin

ARROW@TU Dublin

Masters

Science

1993-01-01

# Aspects of Gold Recovery from an Indigenous Ore

Cormac Patrick McNamee

*Technological University Dublin*

## Recommended Citation

McNamee, C. (1993). *Aspects of gold recovery from an indigenous ore*. Masters dissertation. Technological University Dublin. doi:10.21427/D7Q314

The National University
of
Ireland

A Dissertation for the M.Sc.
in
Chemistry

# Aspects Of Gold Recovery From An Indigenous Ore

By
Cormac Patrick McNamee

May 1993

# CONTENTS

# ACKNOWLEDGEMENTS

I wish to express my most sincere thanks to Dr.Barry Foley for his great wisdom, support, encouragement and technical expertise throughout the course of this project. His technical advice and help were greatly appreciated. Thanks also to Dr. Peter Kavanagh for all his help during this project.

A very special word of thanks to Mr. Sean McGee and Dr.John Cassidy for their help and co-operation. Thanks also to Professor David Brown for his help.

I would also like to thank all the staff and post-grads who worked in the Chemistry Department throughout the course of my work.

Finally, I would like to express my most sincere gratitude to my mother and family without whose support I could not have succeeded.

Cormac Patrick McNamee

Cormac Patrick McNamee

# SUMMARY

This project involved the investigation into the basic electrochemistry of the thiourea-formamidine disulphide redox couple and an estimation of the formal potential, $E^{o'}$ for the couple. By carrying out optimisation experiments on the leaching of gold from an ore sample from the Avoca mine in Co. Wicklow, the optimum leaching conditions were determined for maximum gold extraction.

The effects of various organic and inorganic species on the adsorption of gold onto activated carbon and modified peat were investigated with the use of factorial designed experiments. The Langmuir Isotherm model was applied to estimate the capacity of the carbon for these species.

Finally, a quick reverse-phase High Performance Liquid Chromatography technique was developed for the estimation of thiourea and formamidine disulphide in leach slurries.

# CHAPTER 1

## GOLD

### 1.1 Introduction

Gold was probably the first metal known to and used by humans, since it occurs in nearly pure form, and its colour weight and brightness make it easily distinguishable from the sand and gravel with which it is usually associated. Lexicographers trace the word "gold" to an old Gothic term meaning yellow;and the symbol Au is from Latin "Aurum".

The indestructibility, rarity and appearance of gold have been important in world history. The thirst for gold which was synonymous with wealth, prompted many of the early voyages of discovery and conquest, and "Gold rushes" opened up the American west and helped to settle Alaska. The possession of gold has been a symbol of wealth from the earliest times.

Alchemy, the search for the philosopher's stone which would transmute base metals into gold, while futile, contributed, if not theoretical, at least factual knowledge to the advancement of chemistry, metallurgy and medicine.

Gold is distributed widely throughout the world, normally in very low concentrations and generally in the native form. It is usually alloyed with silver and often with some copper. The only compounds of gold found in nature are the tellurides, containing varying amounts of gold, silver and tellurium. The total occurrence in the lithosphere is very low, estimated at around 5E-7 percent. Seawater contains gold, the amounts depending on depth and location. The average is estimated to be about $0.02\mu g/dm^3$, but the enormous amount of seawater in the world results in a total of perhaps 70 million tons of gold in the ocean.

Furthermore, offshore exploration of the continental shelf indicates that gold is present on the ocean floor. The total is conservatively estimated to be perhaps 10 billion tons of gold. There is no practical means of exploiting this at present but the possibilities for the future should not be entirely discounted.

Native gold is found in both lode and alluvial deposits. The largest gold deposits are in the Witwatersrand and the Orange Free State of the Union of South Africa; where the gold is present in deep mines as veins and stringers in a matrix of pyrite and quartz sand. Many pyrite and pyrrhotite minerals which are worked for their copper, lead, zinc or nickel content also contain some gold, which is recovered as a valuable by-product. In some areas, erosion of primary deposits over geological time has freed native gold, resulting in native nuggets and flakes found in the sand and gravel of river beds. Discovery of such deposits stimulated the famous gold rushes of California and the Yukon. Gold is found in nearly every country of the world. The leading producer by far has been the republic of South Africa. Canada, the United States, the Soviet Union and Australia are also important producers and many other countries produce smaller but significant amounts. In the United States, about 5% of the total production is from placer mining (the panning of gold so well known to devotees of "westerns"), and about 55% from gold and silver ores, and 40% as a by-product of mining for base metals such as copper and lead.

Gold, like silver and the other precious metals, is quoted and sold in troy ounces: 1 troy oz. = 31.1g. Its purity may be expressed, like that of silver, in "fineness" that is, in parts per thousand. However, a special system is also used, in which the unit is the karat (k or kt). A karat is a unity of purity equal to 1/24 of 100%; i.e. 18kt gold is 75% pure etc.

## 1.2 Uses

The principal use of gold is as a monetary standard, even though many countries are not on the "gold standard". Gold is universally prized, the amount available is usually constant, and its value is high enough that large quantities are not needed for most transactions. It is estimated that half the world's gold is held by private persons as a hedge against inflation. The United States, reversing a long-standing policy, now allows private ownership of gold bullion.

Thus much of the gold supply is unavailable for use by industry and this poses an economic problem because industrial uses, especially in the electronics industry and allied industries, are increasing, and the price of gold has risen to unprecedented levels. Once controlled by the U.S treasury at 35$/troy oz. (1.125$/g), the price of gold has increased from that level by 4 or 5 times. In spite of this and in spite of many efforts to find cheaper alternatives, gold remains indispensable in many electronic and electrical components.

In 1972, non-monetary uses of gold totalled about 227tne, of which 60% was in jewellery and arts, 10% in dentistry and 30% in industrial applications. Both jewellery and industrial applications include gold used in electroplating.

Jewellery is made of gold ranging from 21 to 10 kt or even lower. Gold can also be bonded to base-metal cores producing "gold filled" or rolled gold plate. The process is called "cladding".

Electrical and electronic devices use gold-plated electrical contacts to ensure reliable performance. Printed circuits, contacts and connectors are representative of the items that are gold-plated in the electronics industry. Gold is preferred to silver or copper because it does not oxidise or tarnish to form interfering films which affect contact resistance or solderability. Transistor bases and integrated circuits are gold-plated because it withstands corrosion in semiconductor production. It is ductile, easily soldered and welded and does not "poison" semiconductor materials. For aerospace applications, gold has the highest values of infra-red emissivity and reflectivity which protects both people and instruments from radiation in space. The telephone system is a large user of relays which require extreme reliability, long life and low electrical noise. Gold plating is the surest known means of securing these properties.

The dental profession is a major user of gold. Its non-corrodibility in oral media and its good casting qualities recommend it for this use. The chemical industry uses some gold for corrosion-resistant equipment. Gold-palladium alloy thermocouples are used in jet-aircraft engines and in industrial equipment. Gold leaf, produced mechanically, by vacuum evaporation or by electroplating is widely used for decorative purposes.

Much of the gold used in these applications is recoverable when the item has reached the end of its working life and owing to the high price of gold, this recovery has become increasingly important.

Gold has also been used in medicine for the treatment of arthritis and radioactive colloidal gold has some use in cancer therapy.

**Table 1.1** Properties of gold

| **Properties** | |
|---|---|
| Atomic Number | 79 |
| Atomic Mass | 196.9665 |
| Crystal Structure | FCC |
| Melting point °C | 1063 |
| Boiling point °C | 2809 |
| Density g/cm$^3$ | 19.302 |
| Electrical resistivity $\mu$Ohm-cm,0°C | 2.06 |
| Tensile strength,annealed, MPa | 124 |
| Hardness, Vickers | 25 |
| Standard Electrode Potential, E°, 25°C<br>$Au^+ + e^- \longrightarrow Au^0$ | +1.68 V |

Some properties of gold are summarised in table 1.1. Gold is an extremely noble metal as shown by its standard electrode potential. It does not react with sulphur, selenium, nitrogen or carbon at any temperature and hydrogen is essentially insoluble in it. Tellurium forms a number of intermetallic compounds which appear in some ores.

Halogens, if completely dry, show little or no reaction with gold at room temperature except for bromine. In the presence of moisture, bromine reacts vigorously, chlorine and iodine somewhat less so. Fluorine reacts strongly at red heat but not below 110°C.

Mercury readily amalgamates with gold; contact with mercury and mercury salts (in either the +1 or +2 state) should be avoided since they may cause cracking of stressed gold alloys; ferric chloride and nitric acid solutions may have similar effects.

All three coinage metals (copper, silver and gold) have a single s electron outside a complete d-shell. In spite of this similarity in electronic structure, there are few similarities among the three metals and it is not clear why this is the case.

## 1.3 Production

Gold usually occurs in veins or placer deposits, which, if not already of fine size, must be crushed. It can then be separated by gravity concentration, by amalgamation or by cyanidation. In some ores where the gold is present as the telluride or intimately mixed with sulfides, preliminary roasting may be required. In the amalgamation process, the pulp of crushed ore and water is passed over amalgamated copper plates to which the particles of gold adhere. The gold amalgam is scraped off at intervals, the excess mercury squeezed out and the remainder distilled off.

### Cyanidation

Recovery of gold by the cyanidation process is by far the most important commercial process. In 1890, MacArthur and the Forrest brothers found that cyanide was a good solvent for gold[1]. Cyanide leaching or heap leaching can be used to treat ores, concentrate or calcine on a large scale. The ore or tailings are leached with a solution of sodium cyanide or the less expensive calcium cyanide together with some lime. The solution is aerated to provide oxygen to oxidise the gold metal to its cation $Au^+$. The cation then complexes with the cyanide ion to form sodium cyanoaurite,

$$4Au + 8CN^- + O_2 + 2H_2O \dashrightarrow 4[Au(CN)_2]^- + 4OH^- \quad [2].$$

The rate of dissolution is directly proportional to the oxygen content of the gas used for aeration. A problem with the cyanidation process is the relatively slow dissolution kinetics[3].

The resulting solution is deoxygenated, clarified and mixed with zinc dust which precipitates the gold. Sulphuric acid is added to dissolve residual zinc and most of the copper. The residue is washed, dried and melted with material which promote the fusion of gold and silver. This gold and silver alloy is then cast into moulds for analysis.

If the silver content is low, the gold can be recovered by refining in a chloride solution. This is known as the "Wohlwill" process. The doré metal (gold which contains more silver than gold) dissolves anodically and the silver chloride which would otherwise coat the anode, is made to slough off by superimposing an alternating current on the electrolytic current. The process is rather slow however, and has been replaced by the "Miller Process". This process involves chlorination of the precious-metal mixture. The base metals are converted to chlorides which volatilise. Silver forms the chloride which is molten at the temperature of the reaction and can be poured off leaving the gold. After this treatment, the gold has a purity of over 99.5%. The process is not suitable for materials containing platinum metals.

Many other gold recovery processes are in operation on a commercial basis throughout the world such as the "Merill-Crowe" process, carbon-in-pulp (CIP) and resin-in-pulp (RIP).

## Disadvantages of cyanidation

Extraction of gold from gold-bearing ore by cyanidation is the most commonly used method in gold-producing countries. Its generally satisfying technical and economical results make it competitive to other gold extracting methods. High operational costs and environmental restrictions have combined however, to increase smelting costs of precious metals to a level where many mining companies cannot afford to operate.

The major concerns relating to the process are the health and environmental problems associated with it. These problems include the possible formation of severely poisonous hydrogen cyanide gas which can cause paralysis, unconsciousness and respiratory arrest. A few minutes exposure to 300 ppm may result in death. The ingestion or absorption through the skin of cyanide salts can result in severe poisoning. The formation of free forms of cyanide in effluent waters can be fatal to aquatic life [4,5]. Increasing awareness of the problems caused by environmental pollution is expected to result in worldwide tightening of health and safety standards in relation to the use of cyanide. This may severely limit or halt totally the use of cyanide as a leaching agent.

It has been reported that the dissolution of gold is inhibited by the presence of certain metal ions and other species [6,7,8]. Base metals such as copper, zinc and lead cause excessive cyanide consumption. This effect decreases the amount of cyanide available for gold dissolution. Arsenic and antimony react with cyanide solutions in such a way that they reduce the amount of oxygen available for oxidation of gold.

Refractory ores, ores containing base metals, sulfides, pyrite, arsenopyrite and carbonaceous sulfides have been uneconomical to treat because of poor extraction and high reagent consumption [9]. Attempts have been made to overcome this problem by the introduction of a pre-treatment step. Some of these steps have included roasting, oxidative acid leaching, bioleaching and pressure leaching. The presence of carbonaceous material in the ore reduces the leaching efficiency due to adsorption of gold by the carbon. Apart from the added expense of an extra process step, the techniques cause the generation of toxic gases or loss of gold during leaching or bioleaching.

A final disadvantage associated with the use of cyanide as a leaching agent for gold recovery is the relatively slow dissolution of gold by the cyanide species [6,3] resulting in long residence times for economical extraction levels.

The limitations of cyanide for use as a lixiviant for gold have prompted research into the development of an alternative metallurgical process to produce bullion with an efficient, economical and environmentally safe method. This fact is well recognised by the industry and so research into alternative leaching agents has been carried out extensively.

## Thiosulphate

Thiosulphate is a cheap, non-toxic bulk chemical. The solvent action of thiosulphate on gold and silver was observed more than 100 years ago [10]. Several patents have been issued for processes involving ammonium thiosulphate as a lixiviant for precious metals such as Berezowsky et al in 1978 [11] and Kerley in 1981 [12]. Tozawa [13] and co-workers in 1981 also examined gold dissolution in ammoniacal thiosulphate solution. Oxidation of gold in the presence of thiosulphate produces the gold(I) complex $Au(S_2O_3)_2^{3-}$. Alkaline solutions must be used however because thiosulphate disproportionates in acidic solution. The most effective conditions reported for gold extraction using thiosulphate have been the use of oxygen under pressure with high concentration of thiosulphate together with copper as a catalyst in ammoniacal solutions. In 1986, Zipperian et al [14] presented a detailed description of the chemistry and thermodynamics of leaching gold by ammonium thiosulphate. Although oxygen is an effective reagent for cyanidation, it is not electrochemically active at the high potential (above 0.1V) required for thiosulphate. Another disadvantage associated with the use of thiosulphate is that few oxidants are suitable for use in alkaline solution. It is believed that there are no commercial operations for gold leaching using this reagent although thiosulphate was used for at least one in-situ leach project.

### Chlorine

Electrogenerated chlorine can be used for the rapid leaching of gold and silver. Filmer et al [15] concluded that in ores containing more than 0.5% sulphur, chlorine consumption would be excessive. Precipitation of gold from chloride solution and the corrosiveness of acidic chloride solutions are other problems associated with the process [10]. Both gold(III) and gold(I) can be formed depending on the temperature, chloride concentration and the degree of agitation. It was demonstrated at the South African Council for Mineral Technology that the formation of gold(I) posed a number of operational problems during the electrorefining process.

### Bromine

Bromine has been known to be a lixiviant for gold since 1946 as described by Rose [16]. The rate of leaching by bromine is greatly increased when a protonic cation and oxidant are added as described by Kaloscal [17]. It is claimed that the combination leaches gold much faster than cyanide or bromine alone. Bromine leaches gold in both acid and alkaline solutions which is advantageous along with its rapid rate of extraction and non-toxicity. Disadvantages however are likely to be high reagent consumption, interferences in atomic absorption techniques [10] and the requirement of ore bodies of high grade to render the technique profitable.

### Iodine

Of all the halogens, iodine is reported to form the most stable of complexes with gold. The redox potential at which gold dissolves in iodine is about half of that for acidified chlorine but considerably higher than that in cyanide. It does leach over a wide pH range, however, the high reagent cost demands both efficient recycling and recovery.

### Thiourea

Thiourea is a planar organic molecule which dissolves in water to yield a stable form in acidic solutions. It is well known to form a multiplicity of complexes with transition metals [18]. It can act as a ligand by coordination to metals via either the sulphur or nitrogen atoms. The S, N and C atoms of the molecule are all $sp^2$ hybridised. When forming complexes, it is thought that sulphur coordination is preferred [19]. The low basicity of the molecule, however, does not favour coordination via nitrogen-metal bonds. The structure of metal-thiourea complexes depends on the charge on the central metal ion and the size of the central metal ion.

The dissolution of gold in acidic thiourea solutions was first reported by Plaksin and Kozhukhowa [20] in 1941 and was followed up again by the same researchers in 1960 [21]. Hydrometallurgical processes for the extraction of gold have been to date largely based on the use of the soluble anionic ions of gold such as cyanide, sulphite and halide complexes of gold(I). Despite the obvious utility that a cationic species would have in the processing and uses of gold, it is only during the past decades that attempts have been made to take research results to a stage where gold processing technology includes the use of cationic species of gold. Numerous investigations have since examined the use of thiourea as a potential lixiviant for gold in the presence of a suitable oxidant. Lodeischikov [22] described a possible industrial process for the use of acidic solutions of thiourea in the presence of ferric ion for the dissolution of gold in ground ore bodies. In order to have maximum gold recovery, a preliminary acid wash of the ore was recommended. He found that gold recoveries after 8 hours of leaching ranged from 92-98% using 10g/dm$^3$ thiourea, 5g/dm$^3$ sulphuric acid and 3g/dm$^3$ ferric sulphate. It was concluded however that the process would be uneconomical in comparison to the cyanide process except in specialised applications using refractory ores.

Chen (1980) studied acidothioureation of gold using various amounts of oxidant [3]. It was found, using idealised rotating disk experiments, that when the leach solution contained 1% thiourea, 0.5% sulphuric acid and 0.1% ferric ions, that the rate of gold dissolution was over ten times faster than in a solution containing 0.5%

sodium cyanide and 0.05% calcium oxide. Generally it has been recognised that the ferric ion can best speed up the dissolution of gold and that sulphuric acid is more effective than nitric acid or hydrochloric acids. It was also found that the dissolution rate of gold and silver (a very valuable by-product of many gold mines) was increased by increasing the concentration of ferric ion. The dissolution of gold was dependent on the diffusion of thiourea and ferric ion to the gold disk and so the future adoption of acidothioureation to replace traditional cyanidation methods look very promising.

The Institute for Non-Ferrous Metallurgical Industry in China [23] carried out tests on a carbon-bearing clayey ore of the Zhang Jia Kou mine. They found that consumption of sulphuric acid was as high as 135-180kg/tonne of gold concentrate treated, thiourea consumption was 5kg/tonne with a leaching efficiency of 80%. Having calcined the gold concentrate at 680°C, only 70kg of sulphuric acid was needed while thiourea consumption was 1.5-2.2kg/tonne of concentrate treated. A pilot-scale test began in April 1978 on a 100 ppm gold-bearing concentrate. From the results, it was found that precalcining followed by leaching resulted in a recovery that was higher than that observed by cyanidation. They also found that the process was shorter, required less equipment, less space and lower capital investment as compared with the conventional cyanidation process. The calcining step resulted in the calcine becoming loose and porous making the gold more susceptible to attack. It also brought about the oxidation of carbonates and sulfides of iron, lead and copper resulting in the formation of more leachable oxides.

Groenewald (South Africa) in 1977 [24] carried out a comprehensive study on aspects of gold recovery with respect to dissolution, solvent extraction, ion exchange, electrowinning, electroplating etc. He suggested that formamidine disulphide must be assumed to be an active oxidant for gold in thiourea solutions. Addition of formamidine disulphide and hydrogen peroxide produce identical results. The rate of gold dissolution is rapid and increases with increasing concentration of thiourea and oxidant. Because of the faster kinetics associated with thiourea, it should be possible to reduce the reaction time from 24 hours to 5 hours and even 0.5 hours using an acidic solution containing 76g/dm$^3$ thiourea and 15g/dm$^3$ formamidine disulphide. The initial rate of dissolution of gold in a freshly prepared acidic solution of thiourea containing ferric ion as the oxidant is rapid. It also appeared that the oxidation of thiourea by ferric ion did not immediately result in the formation of secondary redox products such as cyanamide and sulphur which retard the rate of gold dissolution by passivation of the gold surface when other oxidants are used. The high extraction however, was accompanied by high consumption of thiourea. He concluded that the high consumption of reagents renders the technique uneconomical compared to the conventional cyanidation techniques. He predicted however that acidic solutions of thiourea could well prove to be an acceptable, less toxic and less corrosive alternative to cyanide, aqua regia or hydrogen bromide/bromine treatments.

The Beherent Engineering Company in Colorado [25] carried out a research effort orientated more towards a practical operational standpoint. It was shown that thiourea can be economically applied to the extraction of precious metals from certain flotation concentrates. High thiourea consumption was experienced due to the operating parameters involved. Several advances were made in understanding the chemistry and control of thiourea leaching, recovery of the precious metals from the leachate and subsequent production of doré. All of the leaching test data showed that most of the extraction during a leaching stage is completed within the first fifteen to thirty minutes of residence time. It was also found that a pre-wash stage could be used to recover copper by electrodeposition and zinc reduction. The work predicted that above a certain % conversion of thiourea to formamidine disulphide, secondary oxidation reactions occur which are irreversible leading ultimately to thiourea decomposition. It has been suggested however that employing copper(II) as an oxidant benefits leaching by producing formamidine disulphide. Therefore a non-pretreated ore would be expected to produce more of the formamidine disulphide oxidant than a pretreated ore as reported by Pesic [26]. Berezowsky and Sefton [27] have also reported an increase in gold extraction due to the presence of copper(II) also in accordance with Deschenes and Ghali [28]. The effect of copper sulphate addition to leach liquors was examined by Sandberg and Huiatt [29]. The results confirmed that the addition of $6g/dm^3$ copper sulphate pentahydrate to the leach doubled the extraction compared to that without copper sulphate addition. Work carried out by Curran [62] on the pretreatment of an ore sample from the Avoca mine site found that after subjecting the ore to various preparatory treatments and performing the leaching in a manner similar to the original sample, the level of gold recovered was dramatically reduced relative to the non-pretreated sample. It was concluded that copper from the ore was mainly responsible for the improvement in gold extraction and the removal of copper plays a major role in decreasing the extraction efficiency.

Hiskey [30] reported that thiourea yields substantially higher levels of silver and gold extraction than does cyanide. The leaching of a bulk concentrate resulted in 83% gold extraction after 4 hours compared with 16% for cyanide after 24 hours of leaching. Although thiourea consumption has been reported as responsible for rendering the process uneconomical by Pyper, Hendrix [31] and Groenewald [32], Schulze [33] described a procedure that effectively reduces the decomposition of thiourea and avoids passivation of the feed material. The procedure involves adding $SO_2$ to the leach system which resulted in the selective reduction of formamidine disulphide to thiourea. Good dissolution rates were reported with relatively dilute thiourea solutions ($3g/dm^3$ Thiourea) and with 50% of the thiourea converted to formamidine disulphide. $SO_2$ additions reduced thiourea consumption from 34.4 to 0.57kg/tonne while at the same time reducing leaching time and increasing gold and silver yields. The presence of sulphur dioxide as a mild reducing agent inhibits the generation of sulphur which passivates the gold surface resulting in poorer extraction. Deschenes and Ghali [28] also used $SO_2$ to reduce thiourea consumption, however gold extraction was not improved.

Bilston, La-Brooy and Woodcock [34] conducted a detailed investigation of the systematic variation of pH, redox potential and thiourea concentration on the gold extraction and thiourea consumption over a specified leaching period. It was found that increasing the acidity of the leach liquor from pH 3.6 to pH 1 increased the gold extraction from 37% to over 90% in 5 hours, however, there was only a limited improvement over pH 5. Thiourea consumption was greatly increased as the redox potential increased from 150 to 200mV versus S.C.E. The initial rate of gold dissolution increased with potential also but the effect on cumulative gold extraction over 5 hours was slight. Thiourea consumption also increased with increased thiourea concentration, rates of gold and silver extraction increased but again the cumulative extraction over 5 hours was marginal. Thiourea consumption increased with increasing acidity also and it is thought that the hydrolysis reaction to form urea and hydrogen sulphide is acid catalysed,

$$CS(NH_2)_2 + H_2O \xrightarrow{H^+} CO(NH_2)_2 + H_2S.$$

According to Shaw and Walker [35], there is also a slow decomposition of thiourea to ammonium thiocyanate,

$$CS(NH_2)_2 \rightleftharpoons NH_4^+ + SCN^-.$$

Below a pH of 2, thiocyanate hydrolyses to ammonium ions and other side reactions also occur.

## 1.4 Basic chemistry of the thiourea system

In order for gold to be dissolved by thiourea, it must be oxidised from the free metal zero state to the +1 oxidation state and thus requires the aid of various oxidants such as iron(III), hydrogen peroxide or formamidine disulphide-itself an oxidation product of thiourea. In acidic solutions, thiourea forms a single cationic complex in contrast with the negatively charged gold complexes formed in most other systems. The bis(thiourea) gold(I) complex forms according to the following equation,

$$Au^0 + 2CS(NH_2)_2 \rightleftharpoons [Au(CS(NH_2)_2)_2]^+ + e^-.$$

The reaction is considered reversible [60] with an electrode potential at 25° of -380mV.

The oxidants used for the dissolution of gold in acidic solutions also oxidise thiourea in successive stages to form a number of products. The oxidation of thiourea to formamidine disulphide (RSSR) is reversible and forms with relative ease in acidic solutions,

$$2CS(NH_2)_2 \rightleftharpoons NH_2C(NH)SSC(NH)(NH_2) + 2H^+ + 2e^-$$

The electrode potential for the reaction is +420mV at 25°C [36]. If the oxidation potential of the solution is too high, formamidine disulphide is irreversibly oxidised to further products which include thiourea, hydrogen sulphide, cyanamide and elemental sulphur. Therefore careful control of the oxidation potential of the thiourea leachate is important to minimise thiourea loss.

$$NH_2(NH)CSSC(NH)NH_2 \text{ ----> } CS(NH_2)_2 + \text{Sulphinic compound.}$$

$$\text{Sulphinic compound ----> } CNNH_2 + S\ .$$

It has been reported that formamidine disulphide acts as an active oxidant for the dissolution of gold. The overall dissolution reaction for gold is,

$$2Au^o + 2CS(NH_2)_2 + RSSR + 2H^+ \text{ ----> } 2Au[CS(NH_2)_2]_2^+$$

The electrode potential for the reaction is 40mV at 25°C [63].

In a sulphate medium, oxidation is produced by the ferric ion,

$$Fe^{3+} + e^{-} \text{ ----> } Fe^{2+} \quad , \quad E^{o} = 770mV.$$

The overall dissolution reaction for gold is therefore,

$$Au^{o} + Fe^{3+} + 2CS(NH_2)_2 \text{ ----> } Au(CS(NH_2)_2)_2^{+} + Fe^{2+}.$$

The electrode potential for the reaction is 390 mV.

It has been reported [24] that the initial rate of gold dissolution in a freshly prepared solution of thiourea containing iron(III) as the oxidant is rapid and is controlled only by the rate of diffusion of oxidant to the surface of the gold. It also appears that the oxidation of thiourea by iron(III) does not immediately yield the secondary redox-reaction products that inhibit the rate of dissolution when other oxidants are used. The most rapid rate of dissolution of gold in acidic solutions of thiourea is therefore obtained with iron(III) as an oxidant. Thiourea however is consumed due to complex formation with iron(III). The reaction between iron(III) and thiourea is slow because of the formation of very stable metal-ligand coordination bonds [61]. The complex $[Fe(III)SO_4(CS(NH_2)_2]^{+}$ was identified in a mixed sulphate thiourea medium [61] and upon completion of the reduction process, the complex $[Fe(II)(CS(NH_2)_2)_2]SO_4$ was also identified.

The formation constant for the reaction of thiourea with iron(III)

$$Fe^{3+} + SO_4^{-} + CS(NH_2)_2 \rightleftharpoons [Fe(III)SO_4(CS(NH_2)_2]^{+}$$

is reported to be $\log \beta = 6.64$ [24].

The formation constant for the gold thiourea complex is much larger

$$Au^{+} + 2CS(NH_2)_2 \rightleftharpoons Au(CS(NH_2)_2)_2^{+}$$

$\log \beta = 21.96$ [30].

Thiourea is known to form a multitude of complexes with transition and non-transition metals. The formation of these complexes during leaching gives rise to reagent consumption which is important from an economic process point of view. The irreversible disproportionation of formamidine disulphide is also a factor which contributes to reagent consumption if the redox potential is too high. It has been speculated that reduction with $SO_2$ may be effective in recovering gold from thiourea solutions.

## Sulphur dioxide

The use of $SO_2$ is an interesting possibility as a reducing agent for formamidine disulphide.Sulphur dioxide is an easily liquified gas with a characteristic pungent odour, it is both unpleasant and physiologically harmful as a choking gas and demands care in use. The gas is moderately soluble in water giving acidic solutions which are weakly reducing

$$SO_4^{2-} + 4H^+ + (x-2)H_2O + 2e^- \dashrightarrow SO_2xH_2O \;, \; E^\circ = +170 \text{ mV.}$$

The acidic solutions of $SO_2$ have been referred to as solutions of sulphurous acid ($H_2SO_3$). However, there is no evidence for the existence of this species in any significant concentrations and the equilibrium in aqueous solutions are best described by the equations

$$SO_2 + xH_2O \rightleftharpoons SO_2xH_2O$$

$$SO_2xH_2O \rightleftharpoons HSO_3^- + H_3O^+ + (x-2)H_2O$$

The first dissociation constant of "$H_2SO_3$" is therefore defined as

$$k_1 = \frac{[HSO_3^-][H^+]}{[\text{tot.dissolved } SO_2] - [HSO_3^-] - [SO_3^{2-}]}$$

Aqueous solutions of $SO_2$ react with alkalis to give two salts; the hydrogen sulphites and the sulphites. The hydrogen sulphite ion undergoes dimerisation to give $S_2O_5^-$ i.e. metabisulphite

$$2HSO_3^- \rightleftharpoons S_2O_5^- + H_2O$$

The equilibrium constant for the dimerisation has a value of 8.8E-2 $dm^3Mole^{-1}$ and hence there is clearly a preponderance of the $HSO_3^-$ form in solution. The solution salts of these species are commonly available and are used as alternatives to $SO_2$ because of greater ease of handling.

For the thiourea system, $SO_2$ does not introduce foreign species that can interfere with the recycle of the thiourea solution. $SO_2$ can help regenerate the thiourea by reducing formamidine disulphide

$$RSSR + 2H_2O + SO_2 \text{ ----> } 2 \text{ Thiourea} + H_2SO_4$$

The reduction of gold in thiourea by $SO_2$ proceeds by the following reaction

$$2Au(CS(NH_2)_2)_2^+ + SO_2 + 2H_2O \text{ ---> } 2Au^0 + 4CS(NH_2)_2 + SO_4^- + 4H^+$$

$$\Delta G = -10.26 \text{ kcal/Mole.}$$

Gold reduction by $SO_2$ is favoured thermodynamically however it may be limited kinetically and may require overpressures of $SO_2$ and elevated temperatures to be accomplished to any significant degree.

## 1.5 Gold recovery

**Cementation**

Since the 1890's, commercial recovery of gold by zinc cementation has been used. The chemistry of the "Merrill-Crowe Process" can be represented by the reaction

$$2Au(CN)_2^- + Zn \text{ ----> } 2Au^o + Zn(CN)_4^{2-}$$

Inhibition of the cementation process occurs due to passivation of the zinc surface by sulphate, sulphide, thiosulphate and ferrocyanide ions. Aluminium has also been used in cyanide medium but is not used for economic reasons [37]. It has been used however for gold recovery from acidic thiourea solutions [38] with aluminium consumption reported at 150mg/litre of solution. Laskonin [39] was the first to use lead powder to recover gold from thiourea solutions. Tataru [40,41] extracted all of the gold from a HCl-thiourea solution with fine lead powder with a consumption of 7.5g/g Au and suggested the following equation for the cementation;

$$2Au[CS(NH_2)_2]_2Cl + Pb \text{ ----> } Pb[CS(NH_2)_2]Cl_2 + 2\ Au^o$$

The Institute of Non-Ferrous Metals in China compared a lead in pulp process with an iron in pulp process [23] and found lead to be better in terms of washing and stripping, faster concentration kinetics along with lower material consumption and capital cost.

Kakovskii [42] suggested iron cementation for thiourea solutions with low gold content. Some regeneration of thiourea was possible, improving the economics of the process.

The U.S.B.M carried out work on recovery with aluminium powder [43] with a recovery of 99.8% of gold and silver and an aluminium consumption of 6.4kg/kg of precious metals. Aluminium was also found to be more effective than activated carbon by Bacon and Donaldson [44]. Lakefield [45] considered an approach which avoided solid/liquid separation. They tried iron wool and found it to be as effective as carbon, recovering almost all of the gold. There was a problem with hydrogen evolution and separation of the wool with the slurry. An iron plate was found to be as fast as activated carbon however iron and acid consumption were reported to be high. They also compared lead foil to lead shot and found lead foil to be slow giving 40% gold recovery in 6 hours and found lead shot to be faster with 62% of the gold recovered in 4 hours. Work being carried out at present involves magnetic separation of steel shavings from an ore slurry and results suggest that it is effective.

## Activated carbon adsorption

The ability of carbon to adsorb gold from chloride solutions was first recorded in 1847 [46]. In 1880,Davis [47] patented the use of wood charcoal for the recovery of gold from liquors resulting from chlorination leaching. In 1894, Johnson [48] patented the use of wood charcoal for the recovery of gold from cyanide solutions. Early practice involved loading activated carbon and selling it to smelters as a gold concentrate but this has been discontinued because of its economical disadvantage compared with the Merill-Crowe process. Zadra [49] suggested the recycling of carbon, electrolysis and recycling of the stripped eluate.

The complete process involves three basic operations for the carbon adsorption process to recover gold and silver from cyanide solutions. The three processes are known as loading, elution and reactivation. Loading can be achieved in clean leach liquors with carbon in column, from leach pulps with carbon in pulp and even when leaching is still in progress with carbon in leach (C.I.L). CIL is used when carbonaceous material in the ore could rob the gold from the pregnant solution [50].

Elution is the step which involves stripping the loaded carbon of its gold. It can be performed at atmospheric or elevated pressures with sodium cyanide-sodium hydroxide solution or with different organic solvents.Work carried out at the Montana College of Mineral Science and Technology U.S.A by Janhunin [51] reported that the use of ethyl alcohol lead to an increase in total gold desorbed or stripped as well as a considerable decrease in elution time.

Reactivation of the carbon is accomplished by heating it to between 600°C and 900°C. Various organic species are adsorbed onto the carbon and are not removed during the elution process. These can cause excessive poisoning with loss of activity for gold adsorption and hence the carbon has to be reactivated periodically. It is usually conducted in rotary kilns. Carbon is fed to the kiln in a wet state and the feed end of the kiln is sealed so that steam generated from the moisture in the carbon passes over the carbon bed and is exhausted from a flue pipe at the discharge thus excluding air from the kiln. The ERGO operation in South Africa treats 30 tonnes of carbon per day through two custom built furnace units operated in parallel.

The first full scale carbon-in-pulp plant was commissioned at the Homestake gold mine in South Dakota. The versatility of the process to treat a wide range of feed materials with high overall gold recoveries along with its relatively low capital and operating expenses have been demonstrated in all major gold-producing countries of the world.

Recovery of gold from thiourea solutions was reported by Gabra [52]. Maximum extraction was 90% in 60 minutes using 20g/dm$^3$ carbon from a solution containing 27 ppm gold. The major drawback of the process was the high loss of thiourea in the leach solution caused by adsorption onto activated carbon (30%). This drawback may be a major limitation of the CIP process to acidic thiourea leachates.

## Electrowinning

This method is usually associated with recovery of gold from cyanide solutions and was developed by the U.S.B.M to recover gold and silver from loaded carbon stripping solutions. The cell design is now known as the Zadra cell [49]. The main advantages in comparison with chemical deposition are a better chemical grade of deposit reducing downstream purification operations and a reduction of chemicals into the solution that is recycled. Most types use porous packed-bed electrodes. Various designs of cell have been developed [53]. Electrowinning can involve separation of the pregnant leach liquor until the gold concentration in the eluant drops to a specified level. The technology of electrowinning in its present state of development cannot be applied to handle liquors that are too dilute or dirty [54]. The basic reactions for the cyanide system are:

$$4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$$

$$Au(CN)_2^- + e^- \longrightarrow Au^0 + 2CN^-$$

The reduction of the gold-thiourea complex occurs according to the following equation;

$$Au(CS(NH_2)_2)_2^+ + e^- \longrightarrow Au^0 + 2CS(NH_2)_2$$

-this is a diffusion controlled reaction with a cathodic potential ranging from -0.15V to -0.35V. Over this region a slight inhibition occurs [24]. Between -0.5V and -0.6V, gold precipitation is accompanied with hydrogen evolution.

## Ion exchange resins

Several research programmes have been aimed at the development of ion exchange resins for gold recovery from cyanide leach pulps and solutions. Abiega, a Russian mine in western Uzbekestan was the first to commercially use a resin-in-pulp (RIP) to recover gold from cyanide pulp [54]. A pilot plant in South Africa is also using RIP [55]. Resins are not usually as susceptible to fouling by organic compounds compared with activated carbons. The resins extract aurocyanide ions by an exchange mechanism. Usually strong base resins with quaternary amine functional groups are used. Copper and iron complexes however displace gold and therefore affect the loading of the resin. Solution composition, pH and gold concentration affect the resin performance.

In the thiourea system, cationic resins adsorb the gold- thiourea complex very strongly. Exchange fibres derived from polyvinyl alcohol have been found to adsorb

100% of the gold from sulphuric or hydrochloric acid solutions. Some inorganic ion exchangers have been examined for the recovery of gold from thiourea solutions.

The lack of selective ion exchange resin, the smaller size of resin beads and the absence of an efficient elution process compared to activated carbon recovery have prevented ion exchange from competing with the major CIP processes.

## 1.6 Toxicity of thiourea

Thiourea has been used both medicinally and commercially in the United States for over 50 years and its toxicological effects are well studied. The lethal dose for humans has been reported as 10g/kg [56]. A consensus of opinions however suggest higher toxicity for laboratory animals than humans [57] but still has a relatively low acute toxic effect on laboratory animals if ingested orally, epidermally or by inhalation. The investigation of the toxic effects of thiourea has been greatly aided by the availability of literature on studies for both animals and humans.

The carcinogenic effects of thiourea have been well studied in laboratory animals. Chronic applications of high doses of thiourea have been shown to produce liver, thyroid and zymbol gland tumors in laboratory rats [58]. Laboratory rats are however carefully bred to be susceptible to cancer and the doses given are extremely high compared to those normally encountered. Evidence suggests that thiourea definitely inhibits the formation of thyroid hormone in man and animals and has been used in medical applications. Treatment of humans with anti-thyroid drugs which include thiourea has not lead to an increase in carcinoma rate [59].

It therefore appears that the use of thiourea in industrial applications is no more dangerous than many other widely used industrial chemicals. The disposal of thiourea can be accomplished by using oxidation techniques similar to those employed in sewage treatment plants. The products of the oxidation are cyanamide, carbon dioxide, nitrogen compounds, sulphur and sulphates. In designing a plant, research would be necessary to determine the best means of disposal into the environment. Thiourea is therefore not restricted by the same toxicity factors as cyanide.

The main benefits associated with the use of acidic solutions of thiourea for the dissolution of gold can be summarised as follows:

(1) Thiourea reaction kinetics for dissolution of gold and silver is of the order of 10 to 12 times greater than cyanidation.

(2) Thiourea is a non-toxic alternative to cyanide

(3) The base metals which cause excessive consumption of cyanide such as lead,copper and zinc have far less effect on thiourea consumption.

(4) Thiourea dissolved in acidic solution may be easily and reversibly oxidised to its first oxidation product (formamidine disulphide) which serves as an active and selective oxidant for gold.

## REFERENCES CHAPTER 1

1. R.J. Adamson(ed.), Gold metallurgy in South Africa, chamber of mines of South Africa, Johannesburg, p.88 (1972).

2. Schulze, R.G., Journal of Metals, 36, 62-65 (June 1984).

3. Chen, C.K., Lung, T.N., and Wan, C.C., Hydrometallurgy, 5, 207-212 (1980).

4. Kirk, R. and Othmer, D., (Eds), Encyclopedia of Chemical Technology, 3rd ed., 7, 317, John Wiley and Sons, New York,(1979).

5. Ecological analysts, Inc., "Cyanide:an overview and analysis of the literature on chemistry, fate, toxicity and detection in surface waters". Report prepared for the inter-industry cyanide group. 2-10, (June 1979).

6. American Cyanamid Co., "Chemistry of cyanidation", mineral dressing notes, No.23, 7, (1978).

7. Naggy, I., McKusic, P. and McCulloch, H.W., Republic of South Africa, national institute for metallurgy project c.28/62, Report No. 38, 4-11., (June 1966).

8. Henley, K.J., Mineral Science and Engineering, 7, No.4, 303-5, (1974).

9. Deschenes, G., IM Bulletin, 79 (895), 76-83, (November 1986).

10. Von Michaelis, H., Engineering and Mining journals 42-47, (June 1987).

11. Berezowsky, R.M.G.S and Sefton, V.B., AIME annual meeting, New Orleans, (February 1979).

12. Kerley, B.J., "Recovery of precious metals from difficult ores" US Patent 4,269,622 (May 26 1981).

13. Tozawa, K., Invi, Y., and Umetsu, Y., "Dissolution of gold in ammonical thiosulphate solution", preprint A81-25, TMS-AIME, (1981).

14. Zipperian, J., Raghavan, S., and Wilson, J., "Summary of presentation by P.J. Wilson". 115th AIME annual meeting New Orleans L.A., (March 1986).

15. Filmer, A.O. et al., "IMM Regional Conference. Proceedings in gold mining, metallurgy and geology", pp.1-8 (October 1984).

16. Rose, T., "Metallurgy of gold", Charles Griffin and Co. London, (1894).

17. Kaloscal, G.I.Z., Australian provisional patent 30201/84, (1980).

18. Stewart, J.E., J. Chem. Phys., 26, 284 (1957).

19. Hanic, F. and Durcanska, E., Inorg Chim. Acta., 293-298, (1969).

20. Plaksin, I. and Kozukhowa, M., Doklady akadomic Nark SSR, 31, 671-674, Russ,(1941).

21. Plaksin, I. and Kozukhowa, M.A., Sb Nauchn. Tr. Inst. Tsvetn. Metall. , 33. 107-109, (1960).

22. Lodeishchikov, V., et al., Nauch. Tr., Inkutsk.Gros. Hauch. Isoled Inst. Redk. Tsvet. Metal, 19, 72-84, Russ,(1968).

23. Wen, C.D., "Studies and prospects of gold extraction from carbon-bearing clayey gold ore by the thiourea process"; Proc. XIV Int. Min. Proc. Cong., 17-23: (Oct 1982).

24. Groenewald, T., "Potential applications of thiourea in the processing of gold", J. S. Afr.IMM; (June1977).

25. Charley, W.R., "Hydrometallurgical extraction of precious metals using thiourea", Practical Hydromet. '83, 7th Annual symposium on uranium and precious metals, ed. G.F. Chlumsky, SME-AIME, New York, (1984).

26. Pesic, B., Final report to the national science foundation Grant No.MSM-8306337, p.91, (July 1986).

27. Berezowsky, R.M.G.S. and Sefton, V.B., "Recovery of gold and silver from oxidation leach residues by ammoniacal thiosulphate leaching". Pres, at 108th Soc. Min. Eng. AIME preprint 79-178, p.17 (1979).

28. Deschenes, G. and Ghali, E. Hydrometallurgy, 20, 179-202, (1988).

29. Sandberg, R.G. and Huiatt, J.L., United States department of the interior, bureau of mines, report of investigation, 9022, (1986).

30. Hiskey, J.B., "Thiourea leaching of gold and silver technology update and additional applications". Minerals and metallurgical processing (November 1984).

31. Hendrix, J.L., Pyper, R.A., "Gold and Silver Leaching, Recovery and Economics", SME-AIME, 83, (1981).

32. Groenewald, T., Hydrometallurgy, 1, 277 (1976).

33. Schulze, R.G., Erzmetall, 39(2), 57(1986).

34. Bilston, D.W., La-Brooy, S.R., and Woodcock, J.T., "Gold and silver leaching from an oxidised gold ore with thiourea under controlled conditions". The Aus. I.M.M., Melbourne branch, symposium on "Extractive Metallurgy", pp.51-60, (November 1984).

35. Shaw, W.H.R., and Walker, D.G., "The decomposition of thiourea in water solutions", J. Am. Chem. Soc., 78:5769-5772, (1956)

36. Preisler, P.W. and Berger, L., The Journal of the Am. Chem. Soc., 69,322-325 (Feb 1947).

37. Hutchings, W., "Laboratory experiments on aluminium and zinc dusts as precipitates of gold in cyanidation practice"; Can. Min. J. 70:10: 74-79; (1949).

38. Van Lierde, A. Ollivier, P. and Lesoille, M., "Développement de nouveau procédé de traitement pour le minerai de Salsigne", Ind. Min., les tech. la, 399-410; (1982).

39. Laskorin, B.N. et al, "The liquid extraction of complex compounds of gold and silver from alkaline solutions"; Dok. Ak. Nauk. SSSR, 39:1170-1172; (1968).

40. Tataru, S., "Précipitation par cémentation de l'or en solutions acides"; Rev. Roam. Chim., 1043-1049; (1968).

41. Tataru, S., "Ion exchange processes for gold recovery"; Rev. Roum. Chim., 19:4:717-725; (1974).

42. Kakovskii, I.A., Khmel'Nilskaya, O.D., Panchenko, A.F. et al., "Thiocarbamide solvent for gold and silver"; Fiz. Kh. Os. Pe. Mi. Syr., 148-55; (1982).

43. Simpson, W.W., Peterson, L., and Sandberg, R.G., "Gold and Silver recovery from thiourea leach solutions"; Pac. Northwest metals and Min. Conf., Portland, Oregon; (April 1984.)

44. Bacon, G., and Donaldson, L., Vancouver, B.C., personal communication ; (July 1985).

45. Yen, W.T., and Wyslouzil, D.M., "Gold recovery from the thiourea leach system"; AIME, Santa Fe, Oct. 14-15; (1985).

46. J. Gross and J. W Scott, "Precipitation of gold and silver from cyanide solution from charcoal", Technical paper 378, US Bureau of Mines, Washington D.C.(1927).

47. W.N. Davis, "Use of carbon for the precipitation of gold from solution and subsequent burning", U.S Pat. 227,963 (25 May 1880).

48. W.D Johnson, "Abstraction of gold and silver from their solution in potassium cyanide", U.S Pat. 522,260 (3 July 1984).

49. Zadra, J.B., Engel, A.L., and Heinen, H.J., "Process for recovering gold and silver from activated carbon by leaching and electrolysis"; U.S.B.M report 4843; (1952).

50. Eisele, J.A., Colombo, A.F., and McClelland, G.E., "Recovery of gold and silver from ores by hydrometallurgical processing"; P.M.M.E and P., U.S.A.; (Feb 1984).

51. W.Janhunin, G.Zucker, H.el-Shall and M.E. el-Dahshan "Effect of some inorganic and organic chemicals on interaction of gold with activated carbon". Journal of Eng. Sci., Vol.13, No.1, (1987).

52. Gabra,G., "Leaching of gold from pyrite and chalcopyrite concentrates using acidified thiourea"; 23rd Ann. CIM Conf. of Met., Quebec; (August 1984).

53. Paul, R.L., Filmer, A.O., and Nicol, M.J., "The recovery of gold from concentrated aurocyanide solutions"; Hydromet. R.D. and plant practice, TMS, AIME, N.Y., 689-704; (1982).

54. Jha, M.C., "Recovery of gold and silver from cyanide solutions: a comparitive study of various processes"; 1st I.S.P.M.R., Reno, Nev.; (June 1984).

55. Flemming, C.A., and Nicol, M.J., "Alternative processes to filtration; carbon-in-pulp and resin-in-pulp in the metallurgical industry"; Hydromet, S.C.I., London, C2-16; (1981).

56. Sakai Chemical Industry Co. Ltd., "Material safety data sheet for thiourea". Supplied by McKesson chemical Co.

57. U.S Institute for Occupational Safety and Health, publication No. 79-100; registry of toxic effects of chemical substances, p.1285 (1978).

58. Fitzhigh and Nelson, Science, 108, 626-8, (1988).

59. Lundbach (Sunalby hospital, Copenhagen) Acta. Med. Scand. 124, 266-281, (1946).

60. Groenewald, T., Journal of Applied Electrochemistry, 5, 71-78 (1975).

61. Maslowska, J., J. Mixed complexes of iron(III), Zess. Nauk. Politechn. Lodz, Chim., vol.20. pp. 5-114, (1969).

62. Curran, A., "Studies into leaching of gold from Avoca Ore", M.Sc. Thesis, Dublin Institute of Technology, (1991).

63. Panchenko, A., et Al., Izv. Akad, Nauk SSR, Met., 6, 32-37 (Russ), (1975).

# CHAPTER 2

# ELECTROCHEMISTRY OF THE THIOUREA-FORMAMIDINE DISULPHIDE COUPLE

## 2.1 Introduction

Careful control of the oxidation/reduction of the thiourea leachate is very important economically to the mining industry. Reagent loss due to the irreversible oxidation of formamidine disulphide is a major factor concerning the feasibility of such a process. The initial thiourea concentration, solution redox potential, pH, type of acid used and the degree of agitation all influence the effectiveness of thiourea leaching and chemical consumption. Formamidine disulphide is the oxidation product of thiourea,

$$2CS(NH_2)_2 \rightleftharpoons RSSR + 2H^+ + 2e^- \quad .....(1)$$

$(E^o = 420 mV$ Vs S.C.E)

Formamidine disulphide itself acts a selective oxidant for gold but if however, the redox potential of the system is too high, formamidine disulphide is irreversibly oxidised to cyanamide, thiourea and elemental sulphur. The potential measured due to the presence of the oxidation/reduction couple is given by the Nernst equation,

$$E = E^{o'} + \frac{RT}{nF} \ln \frac{[oxidised]}{[reduced]} \quad .....(2)$$

$F$ = The Faraday constant.

$T$ = Temperature/K.

$n$ = The number of electrons involved.

$E^{o'}$ = The formal potential.

(Note: $E^{o'}$ is included in the Nernst equation rather than $E^{o}$, the standard electrode potential since $E^{o'}$ is what is actually measured.)

Assuming that formamidine disulphide has not undergone irreversible oxidation and the initial concentration of thiourea is known, it should then be theoretically possible to estimate the % thiourea conversion in a leaching system.

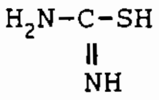
$$\%\ \text{Thiourea Conversion} = \frac{2[\text{RSSR}]\ (100)}{[\text{Thiourea}] + 2[\text{RSSR}]} \qquad \ldots\ldots(3)$$

By following the redox potential during a leaching period, it would be possible to follow the conversion of thiourea to formamidine disulphide with a knowledge of the formal potential. Results indicate (see chapter 3) that there exists an optimum redox potential i.e. an optimum ratio of thiourea to formamidine disulphide, at which the maximum amount of gold can be dissolved in a particular period of time under specified conditions. Hence, by measurement of the redox potential and use of a suitable oxidant or reducing agent, the redox potential could be controlled so that the leaching system operates optimally.

The aim of the following experiments was to determine the formal potential, $E^{o'}$, for the thiourea/formamidine disulphide redox couple and to look at the effects of copper(II) and iron(III) on mixtures of thiourea and formamidine disulphide by following the redox potential. Firstly however, formamidine disulphide had to be synthesised.

## 2.2 SYNTHESIS OF FORMAMIDINE DISULPHIDE DI-HYDROCHLORIDE

The synthesis of formamidine disulphide di-hydrochloride has been described fully by Preisler and Berger [1]. The formamidine disulphide di-hydrochloride was prepared by oxidising thiourea in a solution of the corresponding acid by the slow addition of the theoretical amount of a 30% W/V hydrogen peroxide solution. The mechanism of formamidine disulphide formation has been proposed by Reddy and Krishnan [2] and Gorbachev, Atanasyants and Senatorov [3] to be via a tautomeric form of thiourea,

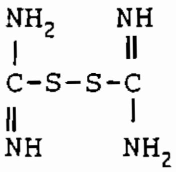


$$H_2N-\underset{\underset{NH}{\|}}{C}-SH$$

is converted to a free radical,

$$H_2N-\underset{\underset{NH}{\|}}{C}-S\cdot \quad + \quad H^+ \quad + \quad e^-$$

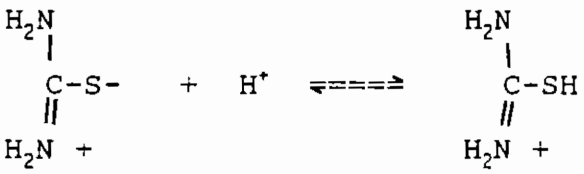
and the free radicals combine to give



$$\underset{\underset{NH}{\|}}{\overset{\overset{NH_2}{|}}{C}}-S-S-\underset{\underset{NH_2}{|}}{\overset{\overset{NH}{\|}}{C}}$$

It is thought that the rate determining step is the charge transfer step to form the free radical. Walter, Ryan and Lane [4] proposed that the following reaction occurs,

(a)



(b)

$$\text{(a)} \quad \underset{\underset{H_2N^+}{\|}}{\overset{\overset{H_2N}{|}}{C}}-S^- \quad + \quad H^+ \quad \rightleftharpoons \quad \underset{\underset{H_2N^+}{\|}}{\overset{\overset{H_2N}{|}}{C}}-SH \quad \text{(b)}$$

In the presence of acid, thiourea may exist as the cation (b), and this could be the intermediate in the formation of formamidine disulphide.

### 2.2.1 Reagents

Thiourea (SKW-Trotsberg)
30% W/V hydrogen peroxide solution (Riedel-De-Haen)
Ethanol (Riedel-De-Haen)
Concentrated hydrochloric acid (Riedel-De-Haen)

### 2.2.2 Experimental details

7.6g of thiourea were dissolved in 75cm$^3$ of 3M HCl. 7.5cm$^3$ of a 30% W/V hydrogen peroxide solution were added very slowly with cooling in ice. 300cm$^3$ of ethanol were added followed by 80cm$^3$ of concentrated HCl. The fine white precipitate formed was filtered on a Buchner funnel and washed slowly with 25cm$^3$ of cold ethanol. The precipitate was left in a desiccator for 24 hours and stored in a freezer to prevent decomposition. The yield was 55%. The melting point was found to be 178.4-179.2°C which corresponds well to the accepted literature value of 177-179°C [5]. The low melting point range suggests that the product was of high purity and sufficiently dry.

Figure 2.1 illustrates the I.R Spectrum of formamidine disulphide in nujol. The band at 721.8 cm$^{-1}$ can be assigned to C=S and N-C-N stretching modes. The bands at 1110 and 1050 cm$^{-1}$ are due to $NH_2$ rocking. The band at 1657.7 cm$^{-1}$ is due to NH bending. The band at 3200 cm$^{-1}$ is due to an N-H vibrational mode.

Figure 2.2 illustrates the $^1$H-NMR spectrum of formamidine disulphide. The peak at 2.5ppm is due to DMSO. The peaks at 3.8 and 9.7ppm are due to $NH_2$ and NH respectively the $NH_2$ peak being twice the integration of the NH peak.

**Figure 2.1** I.R Spectrum of Formamidine Disulphide Dihydrochloride (Nujol Mull).

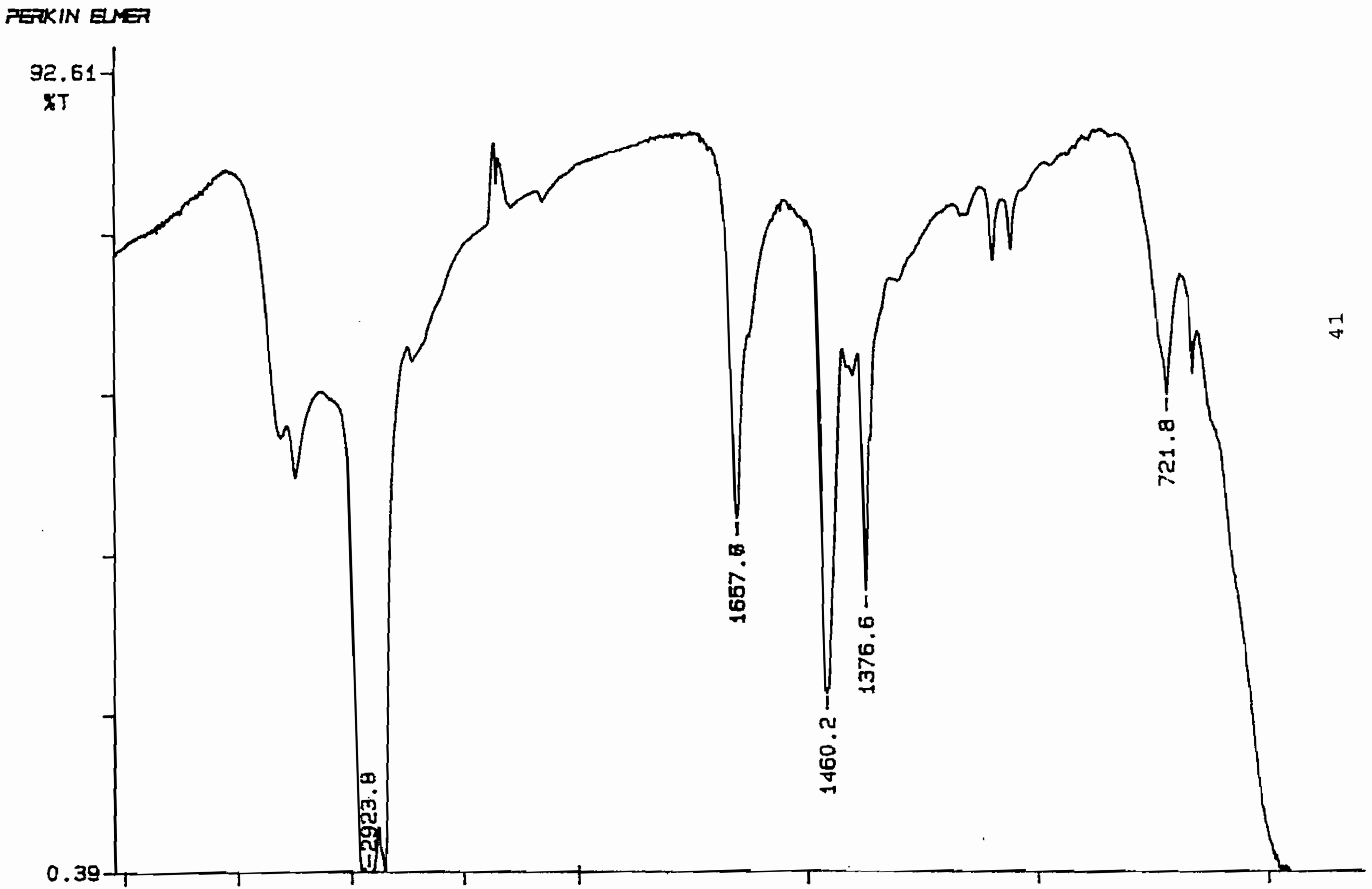
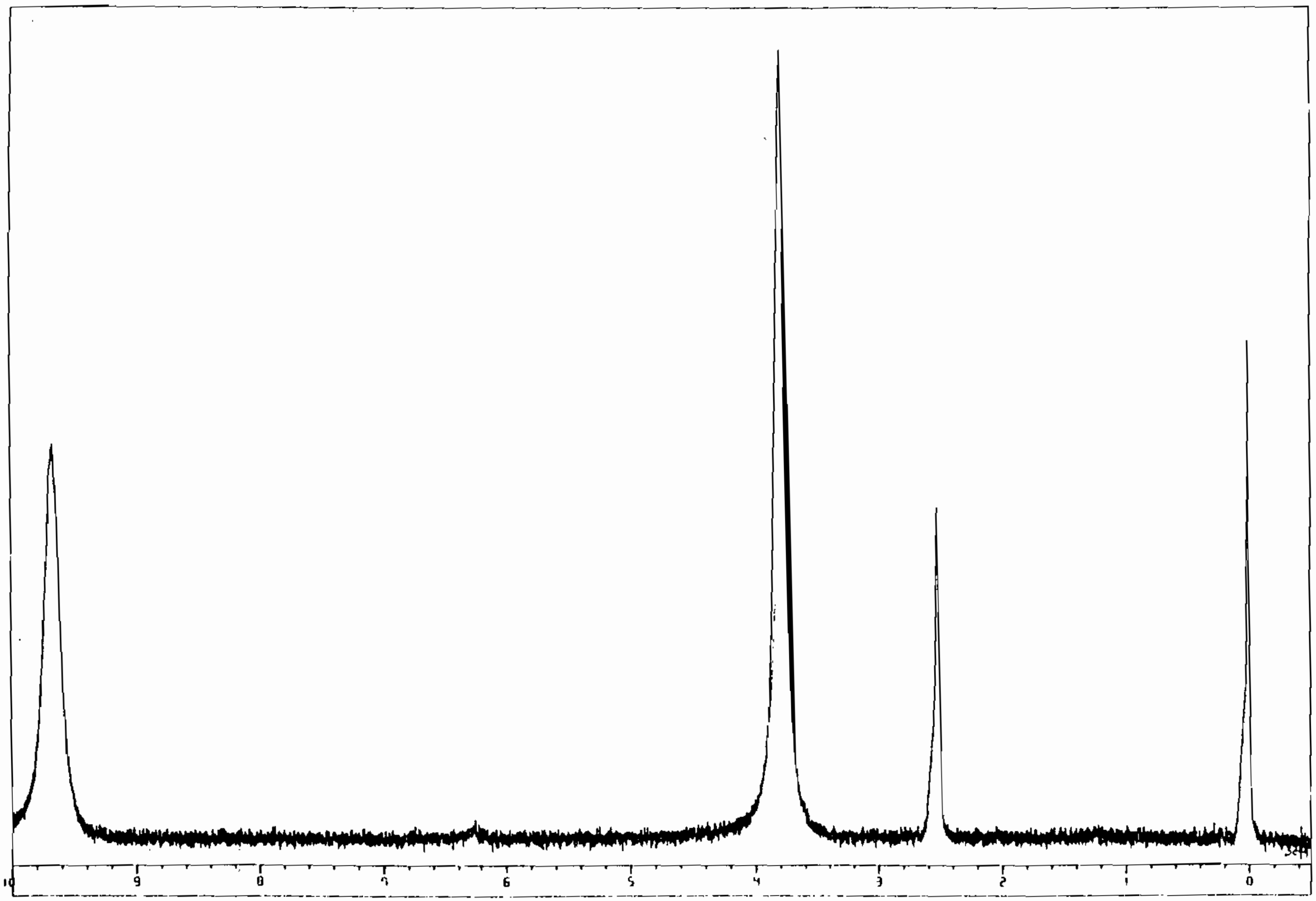


**Figure 2.2** $^1$H-NMR of Formamidine Disulphide Dihydrochloride
Solvent: DMSO-$d_6$
Internal Ref: T.M.S.



## 2.3 ESTIMATION OF THE FORMAL POTENTIAL $E^{o'}$ FOR THE THIOUREA-FORMAMIDINE DISULPHIDE COUPLE

The potential of a theoretically reversible system is governed by the Nernst equation. Applying this equation to the couple yields the following equation,

$$E = E^{o'} + \frac{RT}{2F} \ln \frac{[RSSR]}{[Thiourea]^2} \qquad .....(4)$$

Substituting the values of F, R and T=298K, the following expression is obtained,

$$E = E^{o'} + 0.0296 \log_{10} \frac{[RSSR]}{[Thiourea]^2} \qquad .....(5)$$

Therefore a plot of the measured potential, E, versus the $\log\{[RSSR]/[Thiourea]^2\}$ should yield a straight line of slope 29.6mV and intercept $E^{o'}$, the formal potential. The value of the $\log\{[RSSR]/[Thiourea]^2\}$ can be found by making up known concentrations of the two compounds. The potential, E, was measured using a platinum/saturated calomel electrode combination.

### 2.3.1 Reagents

Solutions of thiourea from thiourea (SKW-Trotsberg)

Solutions of formamidine disulphide from synthesised formamidine disulphide di-hydrochloride.

Copper(II) solutions from copper sulphate pentahydrate (Riedel-De-Haen)

Iron(III) solutions from ferric sulphate (Riedel-De-Haen)

All solutions were made up in 0.01M $H_2SO_4$ from concentrated $H_2SO_4$ (Riedel-De-Haen)

### 2.3.2 Instrumentation

The redox potential of the solutions were measured using a platinum/saturated calomel electrode combination connected to a Hewlett Packard 3468A multimeter.

### 2.3.3 Experimental details

Solutions of thiourea and formamidine disulphide were made up in 0.01M $H_2SO_4$. Four experiments were carried out in which a solution of known concentration of thiourea was added to a solution of known concentration of formamidine disulphide. The solution was stirred continuously with a magnetic stirrer and the potential was measured after each $1cm^3$ addition of thiourea. The new concentrations of both formamidine disulphide and thiourea were calculated in each case. A graph of potential versus $\log\{[RSSR]/[Thiourea]^2\}$ was plotted in each case from which the formal potential was calculated from the intercept. Since the calculation of both thiourea and formamidine disulphide concentration after each addition is quite tedious, a basic computer programme was written to calculate the theoretical concentrations after each thiourea addition. As the amount of thiourea added became large, changes in potential were not as large and so the thiourea was added in larger volume steps of 5 and $10cm^3$.

## 2.4 Results and discussion

The results of experiment #1 are given in table 2.1 and an example of the type of graph obtained is given in figure 2.3.

**Experiment#1**

Initial Conc. of RSSR = 0.00997 Moles/dm$^3$

Initial Conc. of Thiourea = 0.0132 Moles/dm$^3$

Initial Volume of RSSR = 25cm$^3$

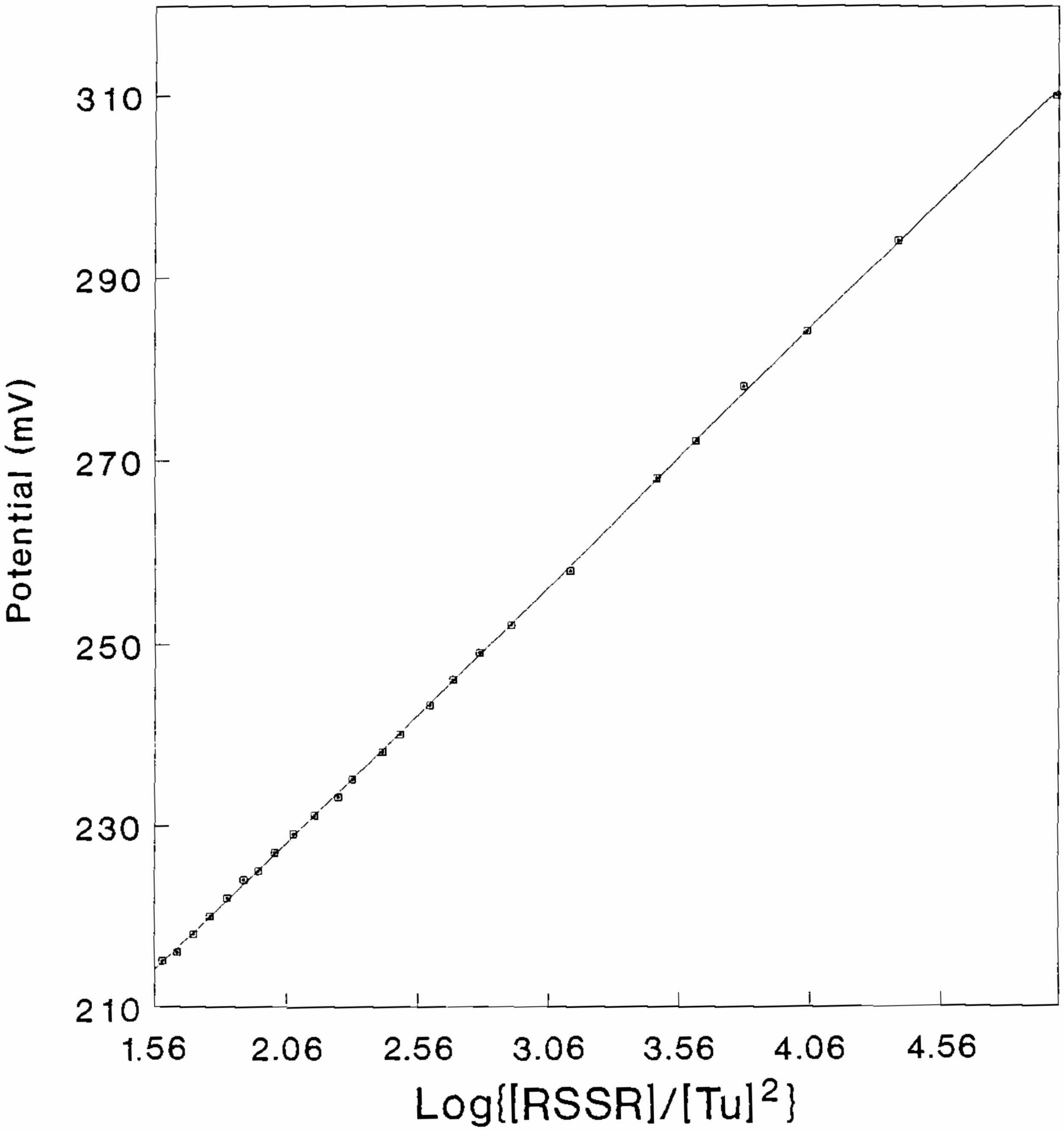
Total Volume of Thiourea added = 80cm$^3$.

**Table 2.1**

| Volume thiourea added (cm$^3$) | Conc.RSSR (Moles/dm$^3$) | Conc.Tu (Moles/dm$^3$) | Log $\frac{[RSSR]}{[Tu]^2}$ | Potential (mV) |
|---|---|---|---|---|
| 1 | 6.49E-3 | 2.58E-4 | 4.989 | 310 |
| 2 | 6.36E-3 | 5.06E-4 | 4.395 | 294 |
| 3 | 6.24E-3 | 7.45E-4 | 4.051 | 284 |
| 4 | 6.13E-3 | 9.75E-4 | 3.809 | 278 |
| 5 | 6.01E-3 | 1.20E-3 | 3.623 | 272 |
| 6 | 5.91E-3 | 1.41E-3 | 3.473 | 268 |
| 9 | 5.61E-3 | 2.01E-3 | 3.143 | 258 |
| 12 | 5.34E-3 | 2.55E-3 | 2.915 | 252 |
| 14 | 5.17E-3 | 2.88E-3 | 2.795 | 249 |
| 16 | 5.01E-3 | 3.19E-3 | 2.692 | 246 |
| 18 | 4.86E-3 | 3.48E-3 | 2.603 | 243 |
| 21 | 4.66E-3 | 3.89E-3 | 2.488 | 240 |
| 23 | 4.53E-3 | 4.15E-3 | 2.421 | 238 |
| 27 | 4.30E-3 | 4.62E-2 | 2.305 | 235 |
| 29 | 4.19E-3 | 4.83E-3 | 2.254 | 233 |
| 33 | 3.99E-3 | 5.23E-3 | 2.163 | 231 |
| 37 | 3.80E-3 | 5.60E-3 | 2.084 | 229 |
| 41 | 3.64E-3 | 5.93E-3 | 2.014 | 227 |
| 45 | 3.48E-3 | 6.23E-3 | 1.952 | 225 |
| 49 | 3.34E-3 | 6.51E-3 | 1.896 | 224 |
| 54 | 3.18E-3 | 6.83E-3 | 1.833 | 222 |
| 60 | 3.01E-3 | 7.18E-3 | 1.766 | 220 |
| 66 | 2.85E-3 | 7.49E-3 | 1.706 | 218 |
| 73 | 2.69E-3 | 7.81E-3 | 1.644 | 216 |
| 80 | 2.54E-3 | 8.09E-3 | 1.589 | 215 |

Figure 2.3 illustrates the relationship between the log{[RSSR/[Tu]$^2$} and the potential. The relationship can be seen to be linear as predicted by equation (5). Each experimental run yielded the following linear equations;

**Figure 2.3** Graph of Potential (mV) Versus $\mathrm{Log}_{10}\frac{[\mathrm{RSSR}]}{[\mathrm{Tu}]^2}$



$$Y = 27.51X + 175.18$$
$$Y = 28.12X + 170.09$$
$$Y = 27.47X + 165.11$$
$$Y = 28.65X + 166.13$$

It can be seen that the formal potential varies between 165mV and 175mV from the experimental results obtained. The slopes of the graphs can be seen to vary between 27.51mV and 28.65mV. The theoretical slope should be 29.28mV at 22°C. The variation in the results could be attributed to the gradual decomposition of formamidine disulphide to cyanamide and elemental sulphur. Since thiourea appears as $[\text{Thiourea}]^2$ in the Nernst equation, changes in the thiourea concentration due to formamidine disulphide decomposition would give rise to errors. After a couple of hours of standing, a yellow precipitate of elemental sulphur appeared in the beakers. It is therefore important that the experiments be carried out as quickly as possible. The average formal potential versus S.C.E is therefore found to be

$$E^{o\prime} = 169.1\text{mV} \quad , \text{std.deviation} = 4.57\text{mV}.$$

All redox potentials were measured with a platinum electrode relative to the saturated calomel electrode (S.C.E). To compare this result to the normal hydrogen electrode (N.H.E), the value of 242mV had to be added to this giving a formal potential of 411.1mV relative to the normal hydrogen electrode. The fact that the slopes of the graphs are close to 29mV confirms that there are two electrons involved in the oxidation process. The oxidation/reduction potential of the thiourea/formamidine disulphide system has been measured and the results confirm that equation (4)

$$E = E^{o\prime} + \frac{RT}{2F} \ln \frac{[RSSR]}{[Thiourea]^2}$$

applies to this reversible system.

## 2.5 EFFECT OF COPPER(II) ON THE ESTIMATION OF THE FORMAL POTENTIAL OF THE THIOUREA-FORMAMIDINE DISULPHIDE COUPLE

Copper(II) is a species which is common to a thiourea leach system since it is found in the ore. It is thought to form a number of complexes with thiourea and at the same time improve leaching. It was therefore necessary to investigate its effects on the redox couple of formamidine disulphide and thiourea. The same concentration of copper(II) was added to both thiourea and formamidine disulphide solutions and the resulting solutions were mixed as in section 2.3.3.

### 2.5.1 Experimental details

A 0.063M thiourea solution containing 0.5g/dm$^3$ copper(II) was made up in a 250cm$^3$ grade"A" volumetric flask with 0.01M $H_2SO_4$. A 0.0132M formamidine disulphide solution containing 0.5g/dm$^3$ copper(II) was also made up with 0.01M $H_2SO_4$ to 250cm$^3$. 150cm$^3$ of the copper-thiourea solution were added to 50cm$^3$ of the formamidine disulphide solution and the potential was noted after each 1cm$^3$ addition.

## 2.6 Results and discussion

**Table 2.2**

| Volume of Cu-Tu Soln. added ($cm^3$) | Potential (mV) | Volume of Cu-Tu Soln. added ($cm^3$) | Potential (mV) |
|---|---|---|---|
| 1 | 308 | 44 | 319 |
| 2 | 314 | 46 | 319 |
| 3 | 318 | 48 | 318 |
| 4 | 320 | 50 | 318 |
| 5 | 322 | 52 | 317 |
| 6 | 323 | 54 | 317 |
| 8 | 324 | 56 | 317 |
| 10 | 325 | 58 | 316 |
| 12 | 325 | 60 | 316 |
| 14 | 325 | 64 | 315 |
| 16 | 325 | 68 | 315 |
| 18 | 325 | 70 | 314 |
| 20 | 324 | 74 | 314 |
| 22 | 324 | 78 | 313 |
| 24 | 323 | 80 | 313 |
| 26 | 323 | 84 | 312 |
| 28 | 323 | 88 | 312 |
| 30 | 322 | 92 | 311 |
| 32 | 322 | 96 | 311 |
| 34 | 321 | 100 | 310 |
| 36 | 321 | 110 | 309 |
| 38 | 320 | 120 | 308 |
| 40 | 320 | 130 | 307 |
| 42 | 319 | 150 | 306 |

Table 2.2 illustrates the change in potential with the volume of the thiourea-copper solution added. It can be seen that the potential rises from 308mV to 325mV up to the $18cm^3$ addition of thiourea. The potential then drops very slowly to 306mV at $150cm^3$ of added thiourea. Instead of seeing a steady decrease in the potential, there is a small rise followed by a steady drop in potential and therefore it can be concluded that copper(II) is having an effect on the redox couple. Thiourea forms stable complexes with

copper but the complexation step is preceded by a redox reaction between copper(II) and thiourea [6]

$$2Cu(II) + 2Tu \longrightarrow 2Cu(I) + RSSR + 2H^+ \quad ....(6)$$

The monovalent copper ions in turn form complexes with thiourea [7,8]. Hanic and Durkanska [9] attempted to determine the structure of the $[Cu_2(Tu)_6]SO_4.H_2O$ complex whose formation was confirmed by Dupuis and Ghali [10]. If this is the case, the results of the experiment could be attributed to the formation of formamidine disulphide and the $[Cu_2(Tu)_6]SO_4.H_2O$ complex. The potential increases because the ratio of $[RSSR]/[Tu]^2$ increases and then slowly decreases as the solution becomes more dilute. If copper(II) reacts with thiourea to form RSSR and the resulting copper(I) ions react with the thiourea to form the copper-thiourea complex, it should therefore be possible to predict the resulting potential upon addition of copper(II) to a solution of thiourea. The $\log\{[RSSR]/[Tu]^2\}$ can be calculated after each copper addition based on the following stoichiometry if the reactions are fast.

$$2Cu(II) + 2Tu \longrightarrow RSSR + 2Cu(I) + 2H^+ \quad .....(6)$$

$$2Cu(I) + 6Tu \longrightarrow [Cu_2(Tu)_6]^{2+} \quad .....(7)$$

## 2.7 THE EFFECT OF COPPER(II) ADDITION TO THIOUREA

The following experiment therefore involved adding a copper(II) sulphate solution to a thiourea solution and noting the potential after each addition of the copper sulphate solution.

### 2.7.1 Experimental details

250cm$^3$ of a 0.1M thiourea solution was made up in 0.01M $H_2SO_4$. 250cm$^3$ of a 0.01M copper sulphate solution was made up in 0.01M $H_2SO_4$. 50cm$^3$ of the thiourea solution was pipetted into a 200cm$^3$ pyrex beaker. The electrodes were immersed in the solution which was stirred continuously with a magnetic stirrer. 50cm$^3$ of the copper sulphate solution was added in 1cm$^3$ steps from a burette and the potential was noted after each addition. The new concentrations of thiourea and formamidine disulphide were calculated based on the above stoichiometry in equations (6) and (7) taking into account the fact that copper(I) consumes thiourea by forming the copper-thiourea complex. The theoretical potential was calculated based on the concentrations of thiourea and formamidine disulphide, room temperature was 21.5°C and the formal potential for the thiourea/formamidine disulphide couple was 169.1mV. The theoretical potential was then compared to the actual observed potential and a graph was drawn of observed potential versus $\log\{[RSSR]/[Tu]^2\}$ as before.

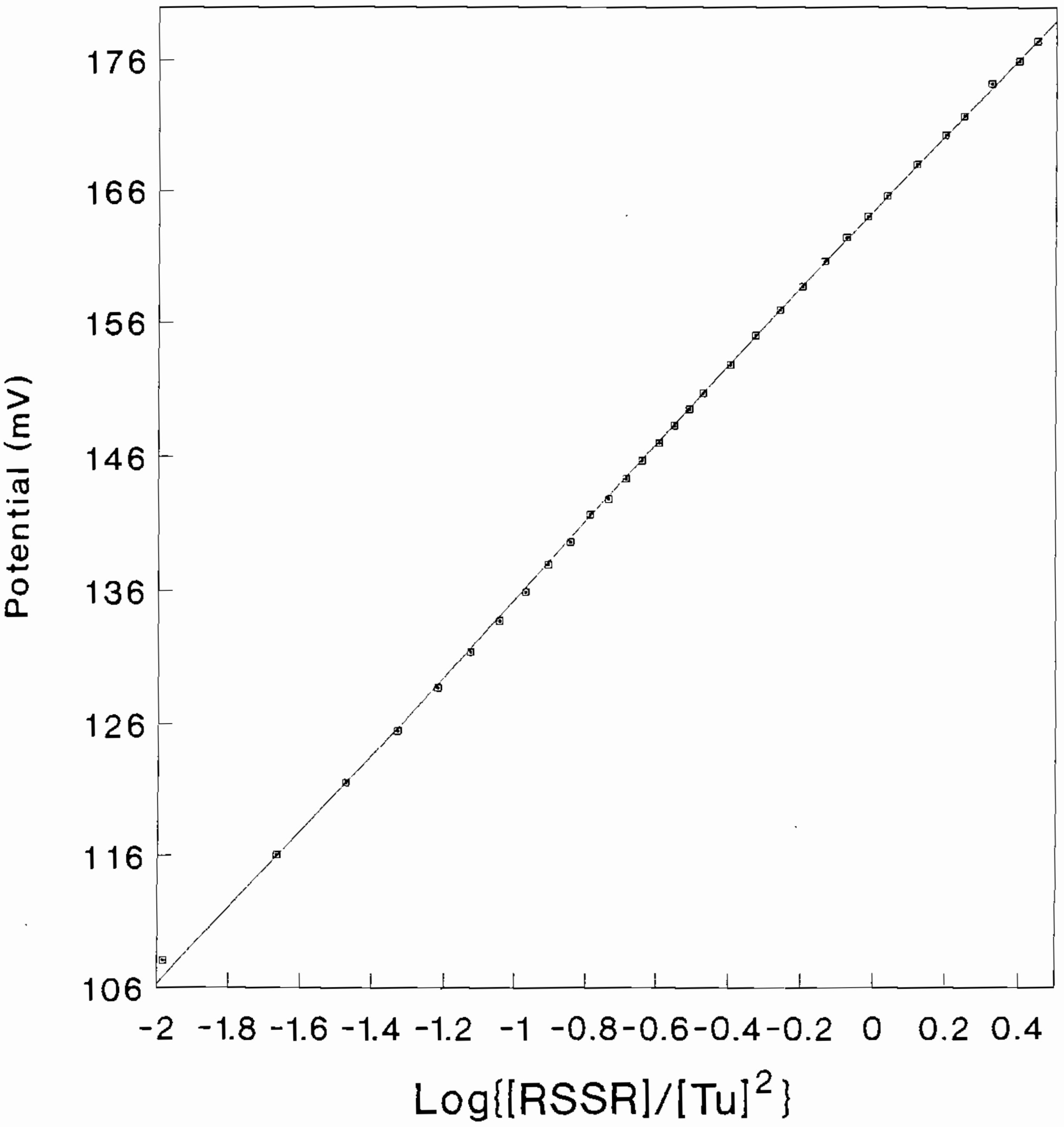
**Table 2.3**

| Volume Cu(II) added ($cm^3$) | Conc.Tu ($Mol/dm^3$) | Conc.RSSR ($Mol/dm^3$) | Log $\frac{[RSSR]}{[Tu]^2}$ | Observed Pot.(mV) | Theoretical Pot.(mV) |
|---|---|---|---|---|---|
| 1 | 9.74E-2 | 9.85E-5 | -1.984 | 108 | 111 |
| 2 | 9.48E-2 | 1.93E-4 | -1.667 | 116 | 120 |
| 3 | 9.22E-2 | 2.84E-4 | -1.476 | 122 | 126 |
| 4 | 8.98E-2 | 3.72E-4 | -1.366 | 125 | 130 |
| 5 | 8.74E-2 | 4.57E-4 | -1.223 | 129 | 133 |
| 6 | 8.51E-2 | 5.38E-4 | -1.129 | 131 | 136 |
| 7 | 8.29E-2 | 6.17E-4 | -1.047 | 134 | 138 |
| 8 | 8.08E-2 | 6.93E-4 | -0.974 | 136 | 141 |
| 9 | 7.88E-2 | 7.67E-4 | -0.908 | 138 | 142 |
| 10 | 7.68E-2 | 8.38E-4 | -0.847 | 140 | 144 |
| 12 | 7.30E-2 | 9.73E-4 | -0.739 | 143 | 147 |
| 14 | 6.95E-2 | 1.10E-3 | -0.643 | 146 | 150 |
| 16 | 6.62E-2 | 1.22E-3 | -0.555 | 148 | 153 |
| 18 | 6.30E-2 | 1.33E-3 | -0.475 | 151 | 155 |
| 20 | 6.01E-2 | 1.44E-3 | -0.400 | 153 | 157 |
| 22 | 5.73E-2 | 1.54E-3 | -0.329 | 155 | 159 |
| 24 | 5.47E-2 | 1.63E-3 | -0.263 | 157 | 161 |
| 26 | 5.22E-2 | 1.72E-3 | -0.199 | 159 | 163 |
| 28 | 4.98E-2 | 1.80E-3 | -0.138 | 161 | 165 |
| 34 | 4.34E-2 | 2.03E-3 | 3.42E-2 | 166 | 170 |
| 37 | 4.05E-2 | 2.14E-3 | 0.1154 | 168 | 172 |
| 40 | 3.78E-2 | 2.23E-3 | 0.1942 | 170 | 175 |
| 42 | 3.61E-2 | 2.29E-3 | 0.2457 | 172 | 176 |
| 45 | 3.37E-2 | 2.38E-3 | 0.3218 | 174 | 178 |
| 50 | 2.99E-2 | 2.51E-3 | 0.4461 | 177 | 182 |

## 2.8 Results and discussion

Table 2.3 illustrates the concentrations of the two components and the theoretical and observed potentials after each $1cm^3$ addition of 0.01M copper sulphate. As can be seen, the potential increases due to loss of thiourea and formation of formamidine disulphide as would be expected from the Nernst equation. In fact it can be seen that the theoretical potential is about 4.6mV above the observed potential in each case. For the experiments carried out to determine the value of the formal potential, the standard

**Figure 2.4** Graph of Potential (mV) Versus $\mathrm{Log}_{10}\frac{[\mathrm{RSSR}]}{[\mathrm{Tu}]^2}$



deviation was found to be 4.6mV. The results could therefore suggest that the formal potential is in fact lower than 169mV. The results however show good agreement with the previously reported potential. Figure 2.4 illustrates the graph of potential versus log{[RSSR]/[Tu]$^2$} and shows good linearity with a correlation coefficient of 0.9994. The slope is 29mV which supports the two electron involvement in the oxidation step i.e. n=2 in the Nernst equation. It can also be seen that the intercept of the Y-axis i.e. the formal potential for the thiourea/formamidine disulphide system is 165mV. The results of the experiment support the theory that copper(II) does in fact oxidise thiourea to formamidine disulphide according to equation (6).

The results also suggest the oxidation reaction in equation (6) is very rapid and that the formation of the complex $[Cu_2(Tu)_6]SO_4.H_2O$ is also a very rapid reaction under these conditions. The solubility of the copper-thiourea complex is very low as was found in the work carried out in chapter 5.

## **2.9 EFFECT OF IRON(III) ADDITION TO A THIOUREA-FORMAMIDINE DISULPHIDE SOLUTION**

Having predicted the effect of copper(II) on the potential of the thiourea/formamidine disulphide system, it was decided to look at the potential when an iron(III) solution was added to thiourea. Since iron(III) is expected to react very slowly with thiourea [10], an experiment was carried out in which a volume of iron(III) was added to a solution containing a known concentration of both thiourea and formamidine disulphide. The potential was then followed with time.

### 2.9.1 Experimental details

A 0.027M thiourea solution was made up along with a 0.0134M formamidine disulphide solution in 0.01M $H_2SO_4$. 50cm$^3$ of the thiourea solution were added to 50cm$^3$ of the formamidine disulphide solution. The initial redox potential was noted. 50cm$^3$ of a 1.013g/dm$^3$ iron(III) solution was added and the redox potential was measured over a 5 hour period using the platinum/saturated calomel electrode combination.

## 2.10 Results and discussion

The initial potential before the addition of iron(III) was 209mV which rose immediately to 321mV after the addition of iron(III).

**Table 2.4**

| Time (Minutes) | Potential (mV) |
|---|---|
| 0 | 321.0 |
| 5 | 322.8 |
| 10 | 323.9 |
| 15 | 324.6 |
| 23 | 325.6 |
| 25 | 325.7 |
| 35 | 326.8 |
| 40 | 327.2 |
| 45 | 327.7 |
| 50 | 328.6 |
| 55 | 329.0 |
| 60 | 329.3 |
| 120 | 331.9 |
| 240 | 336.0 |
| 277 | 336.8 |

**Figure 2.5** Graph of Potential (mV) Versus Time (Minutes) after the addition of Iron(III) to a Thiourea-Formamidine Disulphide solution.

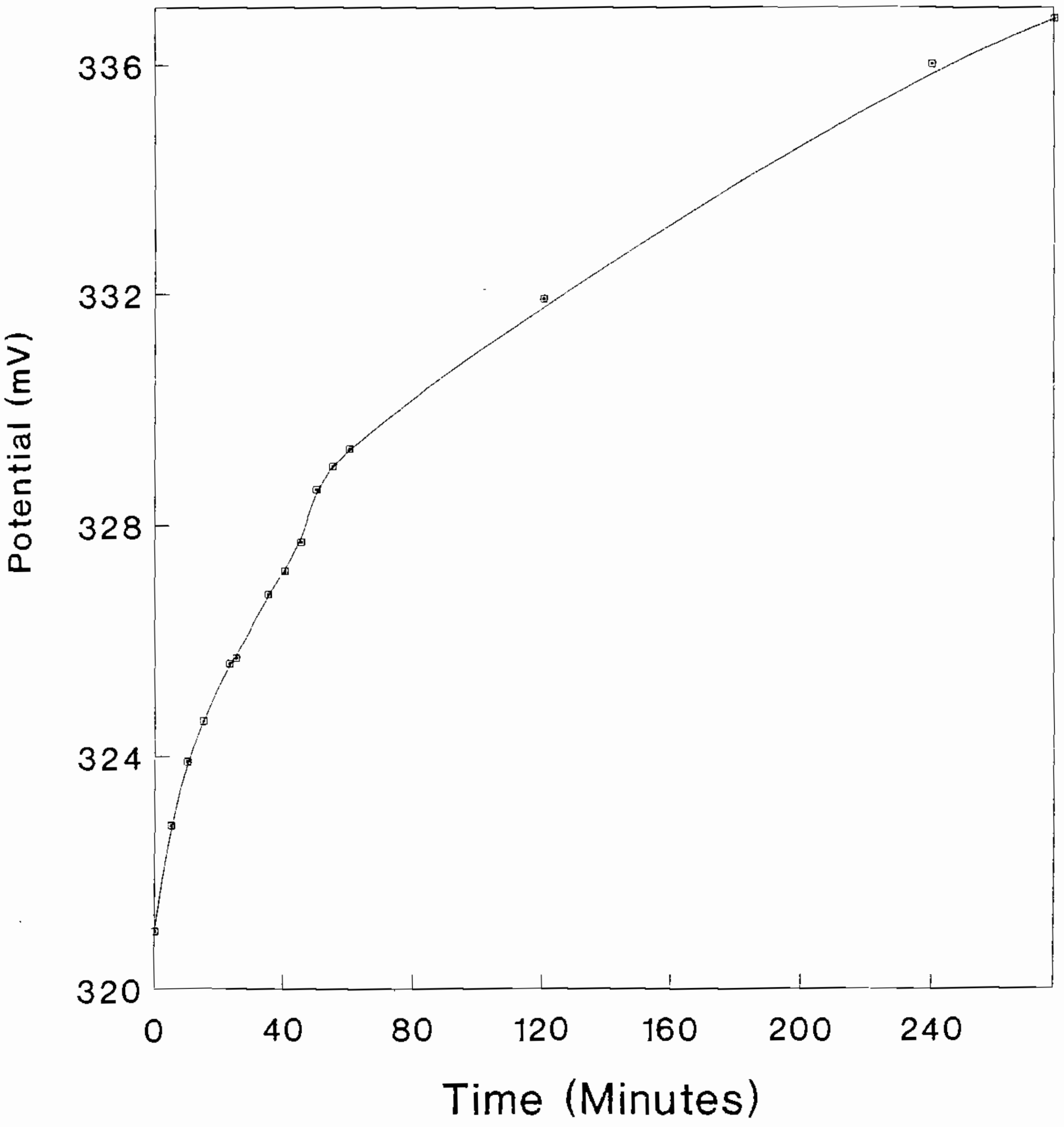


Figure 2.5 illustrates the variation of redox potential with time after the addition of 1g/$dm^3$ iron(III) solution. It can be seen that the potential jumps by 112mV from 209mV to 321mV on introduction of the iron(III) solution. After the introduction of the iron, the potential rises very slowly with time supporting the suggestion that iron reacts very slowly with thiourea unlike copper(II) which reacts very quickly in comparison. The increase in potential could be due to the formation of the complex $[Fe(III)SO_4.(CS(NH_2)_2)]$ causing a gradual decrease in thiourea concentration. The sudden rise in potential could however be due to the rapid formation of formamidine disulphide by an oxidation reaction or perhaps due to the presence of an $Fe^{3+}/Fe^{2+}$ couple along with the thiourea/formamidine disulphide couple. A mixture of both couples could be present and the electrodes may feel a potential due to the combined effect of each couple. Further work on the reaction between iron(III) and thiourea would be required to explain the results of the experiment however.

## 2.11 Conclusion

The implications of these results is that theoretically, it should be possible to follow the conversion of thiourea to formamidine disulphide in a leaching system by measurement of the redox potential and a knowledge of the initial concentration of thiourea, assuming there is no reagent loss due to formamidine disulphide decomposition. The presence of copper in a leach system simply oxidises thiourea to formamidine disulphide according to equation (6) and the resulting copper(I) ion forms the $[Cu_2(Tu)_6]SO_4.H_2O$ complex with thiourea. Iron(III) is an active oxidant for gold and is commonly introduced as an oxidant if the ore does not contain any native oxidants itself. Because iron(III) reacts very slowly with thiourea, its presence in solution can interfere with the potential due to the presence of thiourea and formamidine disulphide alone. Further work however, would be required on this subject. In the absence of iron however, the formal potential for the thiourea/formamidine disulphide reversible couple was found to be 411mV versus the normal hydrogen electrode in agreement with that predicted by Preisler and Berger [1] of 420mV Vs N.H.E. The standard deviation was found to be 5mV. The slopes of the graphs were found to be 28mV supporting the theory that the oxidation of thiourea involves 2 electrons according to the equation

$$2CS(NH_2)_2 \rightleftharpoons NHNH_2CSSCNH_2NH + 2H^+ + 2e^-.$$

## REFERENCES CHAPTER 2

1. Preisler, P.W., and Berger, L., "Oxidation-reduction potentials of thiol-dithio systems: thiourea-formamidine disulphide", J. Am. Chem. Soc., 69: 322-325, (1947).

2. Reddy, S.J., and Krishnan, V.R., "Electrochemical oxidation of thiourea", J. Electro-Anal. Chem. 27(3): 473-476, (1970).

3. Gorbachev, S.V., Atanasyanty, A.G., and Senatorov, Yu. M., "Mechanism of the electro-oxidation of thiourea", zh. Fiz. Khim., 46(9): 2429-2431, (Chem.Abstr.,77:159475y), (1974).

4. Walter, J.L, Ryan, J.A., and Lane, T.J., "A study of thiourea and substituted thiourea analogs by the Bjerrum titration method",J.Am.Chem.Soc.,78:5560-5562, (1956).

5. Aldrich Catalogue of Fine Chemicals 1990-1991, p656.

6. Ratajczak, H.M., et al, Electrochim. Acta., 20, 427 (1975).

7. Lane, T.J., et al., Anal.Chem., 29, 481 (1957).

8. Onstott, L.E. and Laitinen, H.A., J. Am. Chem. Soc., 72, p4724, (1950).

9. Hanic, F., and Durkanska, E., Inorg. Chim. Acta., 293-298, (June 1969).

10. Dupuis, C., and Ghali, E., Proc. Symp. on precious and rare metals, Albequerque, N.M., U.S.A., April (1988).

11. Maslowska, J.J., Mixed complexes of iron(III), Zess. Nauk. Politechn. Lodz, Chim., vol.20. pp.5-114, (1969).

# CHAPTER 3

# LEACHING

## 3.1 Introduction

The process by which gold is extracted from an ore, by conversion into a soluble form is termed "leaching". Gold forms many complexes with various leaching agents such as cyanide, thiosulphate, iodine, bromine, chlorine and thiourea as was discussed in chapter 1. The following experiments were concerned with the use of thiourea under acidic conditions as a leaching agent for gold. The aim of the experiments in this section was to determine the optimum redox potential for the leaching of gold under fixed conditions and to investigate procedures for extracting the dissolved gold from the leach liquor. The extraction methods used were activated carbon adsorption and cementation using steel shavings.

## 3.2 GOLD ASSAYS

In order to calculate the amount of gold extracted during leaching experiments, it was necessary to quantitatively determine the amount of gold in the leach solution, the ore and the carbon or steel shavings where applicable. A mass balance could therefore be obtained and the level of gold in each component of the leach slurry could be followed with time.

### 3.2.1 Assay of ore

Fire assay has been the main method of determining gold in ores, however, the method is not sensitive enough for the practical assay of many low grade ores or small laboratory samples. Atomic absorption spectroscopy (AAS) is at present the most common technique employed for metal analysis in all types of mining and metallurgy samples. The method is convenient and selective for the determination of metals in solution and was the method used in this project. The method is both fast and accurate and no interference by other metals was detected. Gold does not react with oxygen, sulphur, dry halogens and is not attacked by either hydrochloric or nitric acid, however, gold is soluble in a mixture of HCl and $HNO_3$. The mixture called "aqua regia" contains one part of $HNO_3$ to three parts concentrated HCl. Its enhanced dissolving power is attributed to the powerful oxidising power of the nitrate ion in strong acid accompanied with the complexing ability of the chloride ion. Since the level of gold in the digestion solution of aqua regia was below the sensitivity of the atomic absorption spectrometer, a preconcentration step was required after digestion. In aqua regia, gold exists as the $AuCl_4^-$ species with an oxidation state of +3 and hence a liquid anion exchanger had to be used. The solvent extraction step improved detection limits because the concentration of gold increased upon extraction into a smaller sample volume and also provided a sensitivity increase [1,2]. The organic solvent chosen was 2,6 dimethyl-4-heptanone (diisobutylketone) (DIBK). It is relatively involatile (b.Pt=168°C), has favourable flame characteristics and is only slightly soluble in highly acidic solutions (approximately 0.05% W/V). The $AuCl4^-$ species was extracted into the organic layer by the liquid anion exchanger tricaprylylmethyl ammonium chloride (Aliquat 336) with the alkyl group being mainly the octyl and decyl chain hydrocarbons. This organic chelating agent has a high solubility in diisobutyl ketone thus making the solvent and extractant suitable for the solvent extraction step.

The ore had to be roasted prior to exposure to aqua regia for a number of reasons; to oxidise sulphides to sulphates, to decompose the oxide $Au_2O_3$ to $Au^0$ and $O_2$ and to render metallic gold susceptible to attack by aqua regia. Mullins [3] determined the optimum preroasting temperature to be greater than 1000°C achieved by roasting the ore over a bunsen burner. A preroasting time of 1 hour was also found to be sufficient.

### 3.2.2 Reagents

The following reagents were used for the analysis of gold in the leach solutions, the ore, carbon and steel shavings. Aqua regia was prepared 1 hour prior to use by mixing 3 volumes of concentrated HCl (Riedel-De-Haen) with 1 volume of concentrated nitric acid (Riedel-De-Haen). A 1% W/V solution of tricaprylylmethyl ammonium chloride (Aliquat 336) in DIBK was made up by dissolving 5g of Aliquat 336 in DIBK and making up to 500 $cm^3$. 2,6 dimethyl-4-heptanone (DIBK) was supplied by Aldrich Chemicals as was Aliquat 336. A 10 ppm gold chloride solution was made up by dilution of a 1000 ppm gold chloride standard solution "SPECTROSOL", from BDH Chemicals, with deionised water.

### 3.2.3 Instrumentation

Both samples and standards were analysed with a Shimadzu AA670 Atomic Absorption/Flame Emission Spectrophotometer. The instrument conditions were as follows:

Wavelength = 242.8nm
Hollow cathode lamp current = 9mA
Burner height = 6.0mm
Slit width = 0.5nm
Flame type = Acetylene/Air
Oxidant flow rate = 8 $dm^3$/min
Fuel flow rate = 1 $dm^3$/min.
Deuterium lamp ON

### 3.2.4 Experimental details

The following work was carried out in a fume hood with extreme care.

Approximately 20g of ore were weighed accurately in a high temperature evaporating dish. The ore was roasted over a bunsen flame with occasional stirring for a period of 1 hour. After cooling, the roasted sample was transferred quantitatively to a 600$cm^3$ pyrex beaker. 150 $cm^3$ of aqua regia were added and the resulting solution was boiled with stirring on a magnetic hot plate for 1 hour. The level of the solution was maintained at the 125$cm^3$ mark for 45 minutes after which no more aqua regia was added. The resulting solution was filtered using a Buchner funnel apparatus with 3 glass fibre filter papers. The filter cake was washed with 15$cm^3$ of hot aqua regia. The filtrate was transferred to a 250$cm^3$ volumetric flask and was made up to the mark with deionised water.

A series of acid-matched standard solutions were made up from the 10 ppm gold chloride standard solution in order to construct a normal calibration curve.Standards of 0.1, 0.2, 0.3, 0.4 and 0.5 ppm gold solutions were made up by adding the appropriate volume of the 10 ppm gold standard solution to a 100 $cm^3$ volumetric flask to which was added 50$cm^3$ of aqua regia. The solutions were made up to the mark with deionised, distilled water.

### 3.2.5 Gold analysis

25cm$^3$ of the ore filtrate solution and standards were pipetted into 100cm$^3$ separating funnels to which was added 5cm$^3$ of the 1% W/V Aliquat 336 solution in DIBK. The funnel was shaken vigorously for three minutes after which time the layers were allowed to separate. When the layers had separated, the top organic layer was retained for analysis. A larger volume of 20cm$^3$ of the 1% Aliquat 336 in DIBK was taken for the blank solution.

## 3.3 Analysis of leach

The method used to analyse gold in the thiourea leach system was that described by Groenwald et al [4] and modified by Mullins [3]. In the thiourea leach system, gold exists in solution as the bis-thiourea complex $[Au(I)(NH_2CSNH_2)_2]^+$. The level of gold in the leach solutions is so low that it is below the detection limit of the atomic absorption spectrophotometer and again a preconcentration step had to be used. In order for the gold to be extracted into the organic layer it must exist as an anionic species instead of a cationic species as it is in the case of the gold-thiourea complex. The gold therefore has to be oxidised to the +3 state in the presence of excess chloride ion so that it will exist as the $AuCl_4^-$ species. All of the thiourea in solution has to be destroyed to prevent the reformation of the gold-thiourea complex. Aqua regia addition to the leach samples was used for both purposes.

### 3.3.1 Reagents

The assay was performed using the reagents described in section 3.2.2.

### 3.3.2 Instrumentation

The instrumentation employed was as described in section 3.2.3.

### 3.3.3 Experimental details

25cm$^3$ of the filtered leach solution were pipetted into 100cm$^3$ pyrex beakers. The solutions were heated to just before boiling on a hot plate. Aqua regia was added dropwise to each solution with a Pasteur pipette until effervescence ceased in the solution. A cloudiness in the solution was an indication of insufficient addition of aqua regia. After cooling. the solutions were transferred carefully to 100cm$^3$ separating funnels. 5cm$^3$ of a 1% W/V Aliquat 336 in DIBK was added to each funnel. The funnel was shaken vigorously for 3 minutes. Any pressure which built up was released by inverting the funnel and slowly opening the tap. The organic layer was retained for analysis. Aqueous standards of 0.1, 0.2, 0.3, 0.4 and 0.5 ppm gold were prepared as in section 3.2.4. 25cm$^3$ of each solution was shaken with 5cm$^3$ of the 1% W/V Aliquat 336 in DIBK solution. The top organic layers were retained for analysis.

## 3.4 Analysis of carbon for gold

Gold in the leach solutions is adsorbed as the gold-thiourea complex. Early practice in the mining industry was to load the activated carbon and sell it to smelters as a gold concentrate. In order to recover gold from carbon, the carbon has to be ashed, the ash is then dissolved in aqua regia and preconcentrated as before.

### 3.4.1 Reagents

The reagents used were as described in section 3.2.2.

### 3.4.2 Instrumentation

The instrumentation employed was as described in section 3.2.3.

### 3.4.3 Experimental details

Activated carbon in the leach slurry was recovered by passing the leach slurry through a fine copper mesh. The fine ore particles were washed off the carbon with deionised water. The carbon granules were transferred to a crucible. The crucible was roasted over a bunsen until complete ashing of the carbon had taken place. This took approximately 1 hour. After cooling, the ash sample was transferred to a 100cm$^3$ pyrex beaker. The crucible was rinsed out repeatedly with boiling aqua regia until the volume in the pyrex beaker was at the 50cm$^3$ level. The solution was allowed to boil on a hot plate for 1 hour. The level in the beaker was maintained at 50cm$^3$ by addition of further amounts of aqua regia. After cooling, the solutions were gravity filtered into 100 cm$^3$ grade "A" volumetric flasks using a glass fibre filter paper. The solution was made up to the mark with distilled deionised water. A 25cm$^3$ sample of each solution was pipetted into a 100cm$^3$ separating funnel. 5cm$^3$ of a 1% W/V Aliquat 336 in DIBK solution were added and shaken for 3 minutes. After separation, the top organic layer was retained for analysis. Gold standards of 0.1, 0.2, 0.3, 0.4 and 0.5 ppm were made up as before.

## 3.5 Analysis of steel shavings for gold

In order to recover the cemented gold from the steel shavings, it was necessary to oxidise the gold from the +1 to the +3 state in the presence of excess chloride. Aqua regia was used for this purpose.

### 3.5.1 Reagents

The assay was performed using the reagents described in section 3.2.2.

### 3.5.2 Instrumentation

The instrumentation employed was as described in section 3.2.3.

### 3.5.3 Experimental details

Steel shavings in the leach slurry were recovered using a magnetic follower. The fine ore particles were rinsed off the magnetic follower with deionised water taking care not to lose any of the steel sample. The steel shavings were transferred to a $100cm^3$ beaker which contained $50cm^3$ of aqua regia. The solution was boiled for 1 hour keeping the aqua regia level at the $50cm^3$ mark. After cooling, the solution was gravity filtered into a $100cm^3$ grade "A" volumetric flask through a glass fibre filter paper. The solution was made up to the mark with deionised water. A $25cm^3$ sample of the solution was taken and preconcentrated as before.

### 3.5.4 Leaching methods

The leaching system used consisted of the use of both conical flasks containing the slurry shaken on a flask shaker and open beakers containing the slurry stirred by a magnetic stirrer. Both systems were applied where appropriate. The ore was supplied with its associated minewater in the form of a slurry. The percentage solids and the gold content of the ore were measured frequently throughout the tests since all of the calculations were based on the values of these parameters.

The experiments carried out were concerned with the measurement of the level of gold in the solid ore, in solution and on the carbon adsorbent over a particular time period under specified conditions. It has been well established that optimum economic extraction of gold depends on a careful compromise between the thiourea concentration, pH, redox potential and the time of leaching. The results of this work however do not necessarily apply to all other ore types since ore composition varies from place to place. The aim of the experiments however was to determine optimum operating conditions for the ore used under specified levels of carbon and thiourea and to compare extraction by activated carbon with extraction by steel shavings. The pH of the ore slurries was adjusted by the dropwise addition of concentrated sulphuric acid (Riedel-De-Haen). The pH was measured with a glass pH electrode (Amagruss Electrodes Ireland Ltd., Model EC-1610-11) connected to a CD 640 digital pH meter (WPA Linton Cambridge U.K). The redox potential of the solution was measured using a platinum/saturated calomel electrode combination connected to a Hewlett-Packard 3468A multimeter. Sulphur dioxide was added in the form of sodium metabisulphite (BDH Chemicals). Thiourea (SKW-Trotsberg) was added as a solid in the appropriate quantities. Samples of the ore, leach solution and carbon were taken over specific time intervals by decantation of a slurry sample followed by filtration. The ore and filtered leach were analysed for gold by the application of the appropriate assay techniques.

## 3.6 PROBLEMS ASSOCIATED WITH THE ANALYSIS OF SMALL QUANTITIES OF GOLD IN ORES

The level of gold in the ore used was at a trace level. Because the gold is at such a low level, experimental error inevitably plays a major role in the analysis. All gold analyses carried out in this work involved the use of a preconcentration step, both samples and standards had to be preconcentrated in order to raise the level of gold above the sensitivity of the atomic absorption spectrometer. The many steps involved in the treatment of the gold analytes prior to preconcentration also increase the possibility of experimental error. As the number of steps increases, the associated error increases. The errors associated with the techniques can be seen from the large standard deviations associated with the results of the ore analysis i.e. as much as 10%.

The work involved the use of a real ore sample. The distribution of the gold throughout the ore sample is unknown and variations in samples may occur. Rapid stirring of the ore slurry was required to achieve uniform distribution of the ore particles. Settling of the ore during the sampling could contribute to the experimental error. The level of gold in the ore had to be regularly checked along with the % solids composition since all of the results obtained were based on these parameters. Because the ore is composed of such a complex matrix, it is possible that some of the components of this matrix could interfere with the analyses. In order to achieve reliable results from this type of work, it is therefore important to carry out experiments in replicate. There has to be a limit to the number of replicates however, since the analyses are long and involve a number of different steps. It is difficult to quantify the magnitude of the errors associated with this type of work, however, the standard deviation does give an indication of the error.

## 3.7 THE EFFECT OF REDOX POTENTIAL ON LEACHING EFFICIENCY

Optimum economic extraction of gold depends on a careful compromise between redox potential, pH, time of leaching and thiourea concentration. It has already been shown in chapter 2 that the redox potential of the thiourea leach system depends on the concentrations of both thiourea and formamidine disulphide according to the Nernst equation. Work by Bilston, Brooy and Woodcock [6] suggests that the major effect of redox potential on gold extraction was to increase the initial gold dissolution rate as the redox potential increased. Increasing the redox potential increases the proportion of thiourea in the leach liquor converted to formamidine disulphide which itself is claimed to be an active oxidant for gold [7]. Formamidine disulphide is less stable than thiourea decomposing to cyanamide, sulphur and thiourea and so therefore an increase in redox potential favours the oxidative degradation of formamidine disulphide which results in thiourea consumption. Groenewald [7] (1976) observed an increase in the rate of dissolution of metallic gold by increasing the concentration of hydrogen peroxide providing there was sufficient thiourea present. Chen, Lung and Wan (1980) [8] observed an increase in gold extraction with increase in ferric ion addition. Pyper and Hendrix [9] (1981) and Songina et al [10] (1971) who used ferric ion and hydrogen peroxide respectively as oxidants both observed increases in gold extraction with increase in oxidant addition but there was however a decrease above a certain addition. The fall in extraction was attributed to a decrease in free thiourea being present. It has been suggested that at higher redox potentials, passivation of the precious metal surface occurs. Groenewald [11] observed passivation of metallic gold at about 255mV versus S.C.E. Groenewald (1977) [12]; Plaksin and Kozhukhowa (1941) [13] and Panchenko et al (1975) [14] have suggested that thiourea products themselves probably give rise to some passivation of gold.

Mullins (1989) carried out work on two types of ore from the Avoca site in county Wicklow. The two types of ore were (i) high pyrites which was low in ferric ion and (ii) low pyrites which was high in ferric ion. It was found that using low pyrite ore and without any oxidant added to the ore, 65% of the gold was extracted after a 6 hour period using an initial thiourea concentration of $3g/dm^3$. It was therefore concluded that the ore itself released oxidants into the leach solutions. It was found that increasing the concentration of iron(III) to 27 mMolar, increased the initial leaching kinetics. The rate of dissolution was very quick within the first hour after which time the rate dropped off dramatically.

Schulze [15] reported that if formamidine disulphide was present in the leach solution, $SO_2$ would not reduce any other oxidants thus acting as a specific reducing agent i.e. it selectively reduces formamidine disulphide to thiourea. The ability of $SO_2$ to selectively reduce formamidine disulphide to thiourea could possibly be developed as a means of process control for the thiourea leachate system. The aim of the following experiment was to pretreat the ore with different quantities of $SO_2$ before addition of a fixed amount of thiourea and measure the amount of gold in the leach over a particular time period.

The type of ore used was low pyrite ore from the Avoca site with its associated minewater. The maximum particle size was 75μm. The $SO_2$ was added in the form of a salt, sodium metabisulphite.

### 3.7.1 Experimental details

The slurry used contained 11.06%W/W solids. Two 449.5g of the slurry were weighed in two 600cm$^3$ pyrex beakers. 0.5g of sodium metabisulphite was added to each beaker. Both beakers were placed on magnetic stirrers and allowed to stir at room temperature for 30 minutes. After the time had elapsed, 0.4g quantities of thiourea (SKW-Trotsberg) were weighed accurately and added to both beakers. The pH's of both solutions were adjusted to 2 by dropwise addition of concentrated $H_2SO_4$. After 30 minutes of leaching, approximately 35cm$^3$ of the slurry was decanted from each beaker and filtered using a Buchner funnel apparatus. 25cm$^3$ of the filtered leach solution was pipetted into a 100cm$^3$ pyrex beaker, sealed and retained for analysis. 35cm$^3$ of the leach was sampled subsequently after 1, 2, 3, 4, 5 and 6 hours since thiourea addition. The redox potential of the slurry was also measured after each hour using a platinum/saturated calomel electrode connected to a multimeter. All leach samples were analysed for gold as described in section 3.3. The average gold leached was calculated in each case and plotted against time and redox potential. The experiment was repeated without the use of sodium metabisulphite.

## 3.8 Results and discussion

The ore used contained gold at a level of 2.67 ppm with a standard deviation of 0.14 ppm. The slurry contained solids at a level of 11.06% w/w with a standard deviation of 0.15%.

**Table 3.1**

| | 0g/dm$^3$ $Na_2S_2O_5$ | | 1.25g/dm$^3$ $Na_2S_2O_5$ | | 1.88g/dm$^3$ $Na_2S_2O_5$ | | 3.75g/dm$^3$ $Na_2S_2O_5$ | | 8g/dm$^3$ $Na_2S_2O_5$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| Time (Hrs) | Redox Pot. (mV) | % Au | Redox Pot. (mV) | % Au | Redox Pot. (mV) | % Au | Redox Pot. (mV) | % Au | Redox Pot. (mV) | % Au |
| 1 | 407 | 26 | 356 | 47 | 293 | 63 | 226 | 56 | 207 | 38 |
| 2 | 405 | 29 | 355 | 48 | 298 | 62 | 237 | 69 | 194 | 36 |
| 3 | 396 | 28 | 353 | 49 | 300 | 59 | 257 | 63 | 192 | 51 |
| 4 | 369 | 29 | 347 | 53 | 301 | 59 | 263 | 61 | 192 | 44 |
| 5 | 382 | 34 | 342 | 50 | 300 | 61 | 265 | 75 | 188 | 39 |
| 6 | 376 | 30 | 340 | 47 | 299 | 67 | 266 | 67 | 184 | 59 |

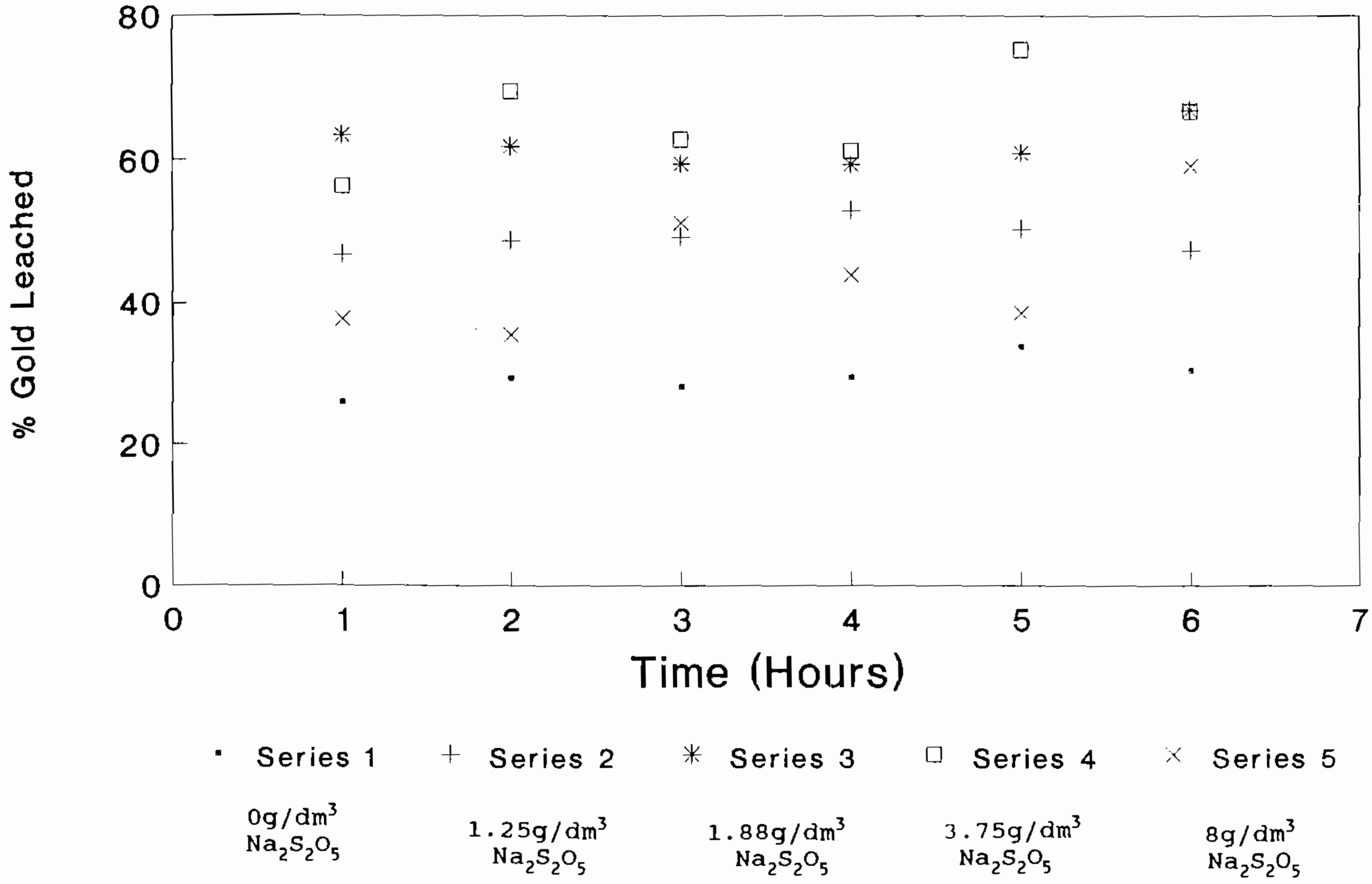
**Table 3.2**

| $Na_2S_2O_5$ Concentration (g/dm$^3$) | Redox Potential After 1 Hour (mV) |
|---|---|
| 0 | 405 |
| 1.25 | 356 |
| 1.88 | 293 |
| 3.75 | 226 |
| 8.00 | 207 |

All experiments were carried out at pH=2. The initial thiourea level was 1g/dm$^3$ or 0.013 moles/dm$^3$. Table 3.1 illustrates the solution redox potential in mV and gold concentration in the leach expressed as a percentage of the total gold over a period of 1 to 6 hours. It can be seen that the solution redox potential decreased with time by between 20 and 30mV for the leach solutions containing 0, 1.25 and 8g/dm$^3$ $Na_2S_2O_5$. This suggests that the concentration of RSSR is decreasing with time perhaps due to decomposition to thiourea i.e. the ratio of RSSR to thiourea is decreasing. In the experiments using 1.88 and 3.75 g/dm$^3$ $Na_2S_2O_5$, it was observed that the redox potential increased with time perhaps due to the formation of RSSR by oxidation of thiourea. The redox potential remained at around 190 mV for the solution containing 8g/dm$^3$ $Na_2S_2O_5$ suggesting the presence of a high concentration of thiourea and a low concentration of RSSR. The results suggest that gold dissolution is possible without the addition of any oxidant. It could therefore be concluded that the ore itself introduces oxidants into the system or results in the formation of formamidine disulphide which itself acts as an active oxidant for gold. This result is in agreement with Groenewald [7] and Mullins [3].

Figure 3.1 illustrates the % gold in the leach at each time period. At all levels of $Na_2S_2O_5$, it can be seen that most of the gold that can possibly be leached under those conditions is leached within the first hour and only shows a slight increase over the 6 hour period. Work carried out by Charley [16] suggested that most of the ultimate extraction for a leaching stage is completed in the first fifteen to thirty minutes of residence time although the values of the parameters such as thiourea concentration, redox potential and pH were not specified. Hiskey [17] found that 80% of the gold was extracted in the first 15 minutes of the leaching of a residue produced from the autoclave leaching of copper smelter flue dusts and

**Figure 3.1** % Gold leached Versus Time (Hours) at different levels of $Na_2S_2O_5$.



that little, if any, additional gold was extracted after 30 minutes using 1M thiourea and 0.5M Fe(III) as oxidant. The results therefore suggest that using 1g/dm$^3$ thiourea for this particular ore at a pH of 2, that a 1 hour residence time results in most of the ultimate extraction that would be extracted over a 6 hour period. The short residence time would therefore have beneficial economic implications.

Figure 3.2 illustrates the average % gold leached at different redox potentials which were controlled by the pretreatment of the ore with $Na_2S_2O_5$. The results suggest that at low redox potentials of around 200mV, 44% of the gold in the ore can be ultimately extracted. At around 245 mV, 65% of the gold can be extracted. As the redox potential increases to 295 mV, there is a reduction in the amount of gold extracted to 62%, at 350 mV 49% and at 390 mV 28% extraction. It is therefore apparent that there exists an optimum redox potential at which the maximum amount of gold can be extracted under conditions of 1g/dm$^3$ thiourea(0.013M), pH=2 and no added oxidant. Any deviation on either side of this operating point would result in a decrease in leaching efficiency. At this point there is an optimum level of complexing agent (thiourea) to oxidant (formamidine disulphide). At this optimum potential of around 250mV, the ratio of formamidine disulphide to thiourea is around 0.4. This is in agreement with Schulze [15] who suggested that the ratio be maintained at around 0.5 to obtain a high gold dissolution rate. To the left of this operating point the reduction in leaching efficiency could be attributed to too much thiourea and an insufficient level of oxidant. To the right of this point there is too much oxidant and insufficient thiourea to result in adequate complexation of the gold. Despite the findings of Deschenes and Ghali [18], the use of $SO_2$ does in fact have an effect on leaching efficiency by providing optimum levels of both thiourea and formamidine disulphide by addition of the appropriate quantity of $SO_2$. It has also

**Figure 3.2** % Gold leached Versus Redox Potential (mV).

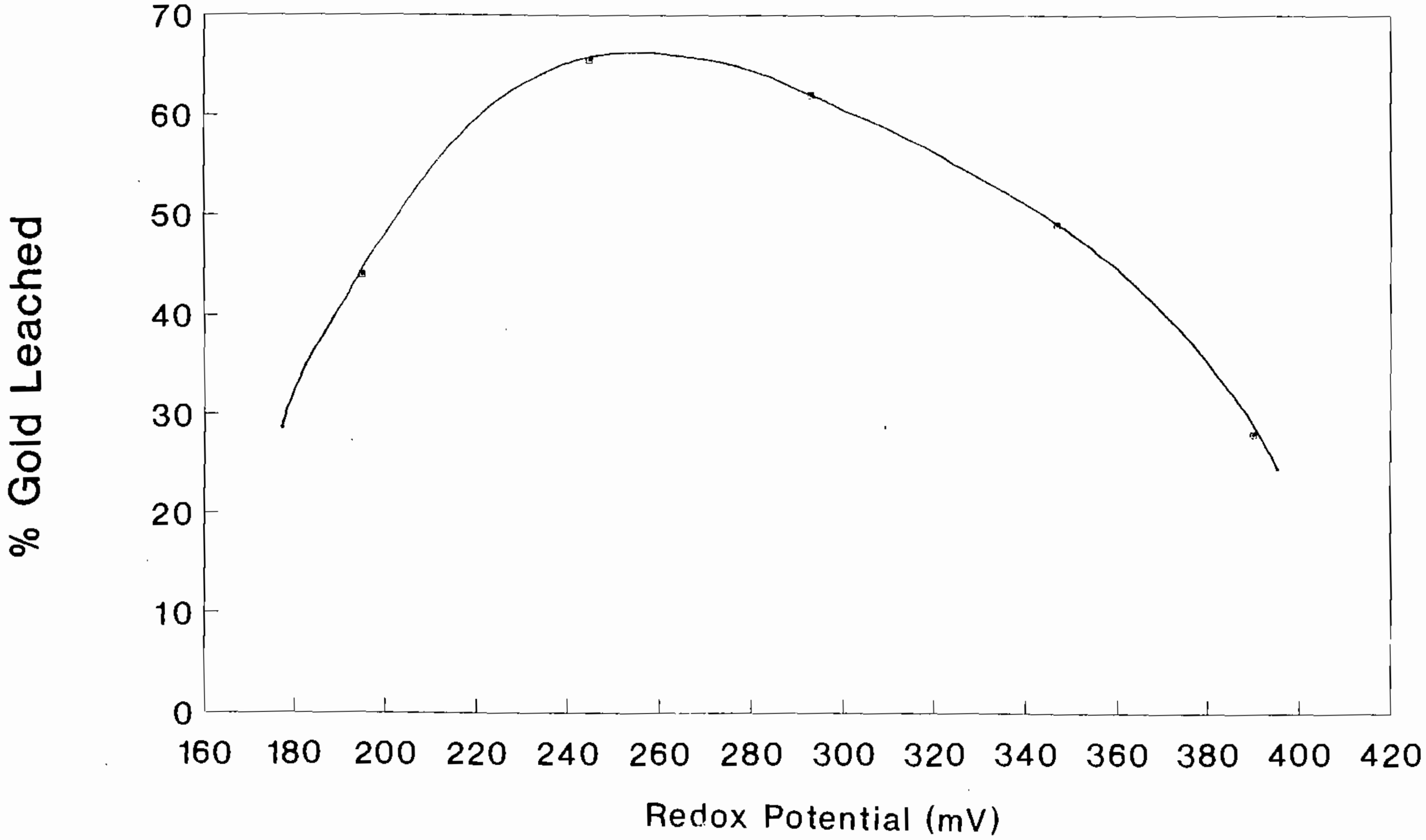
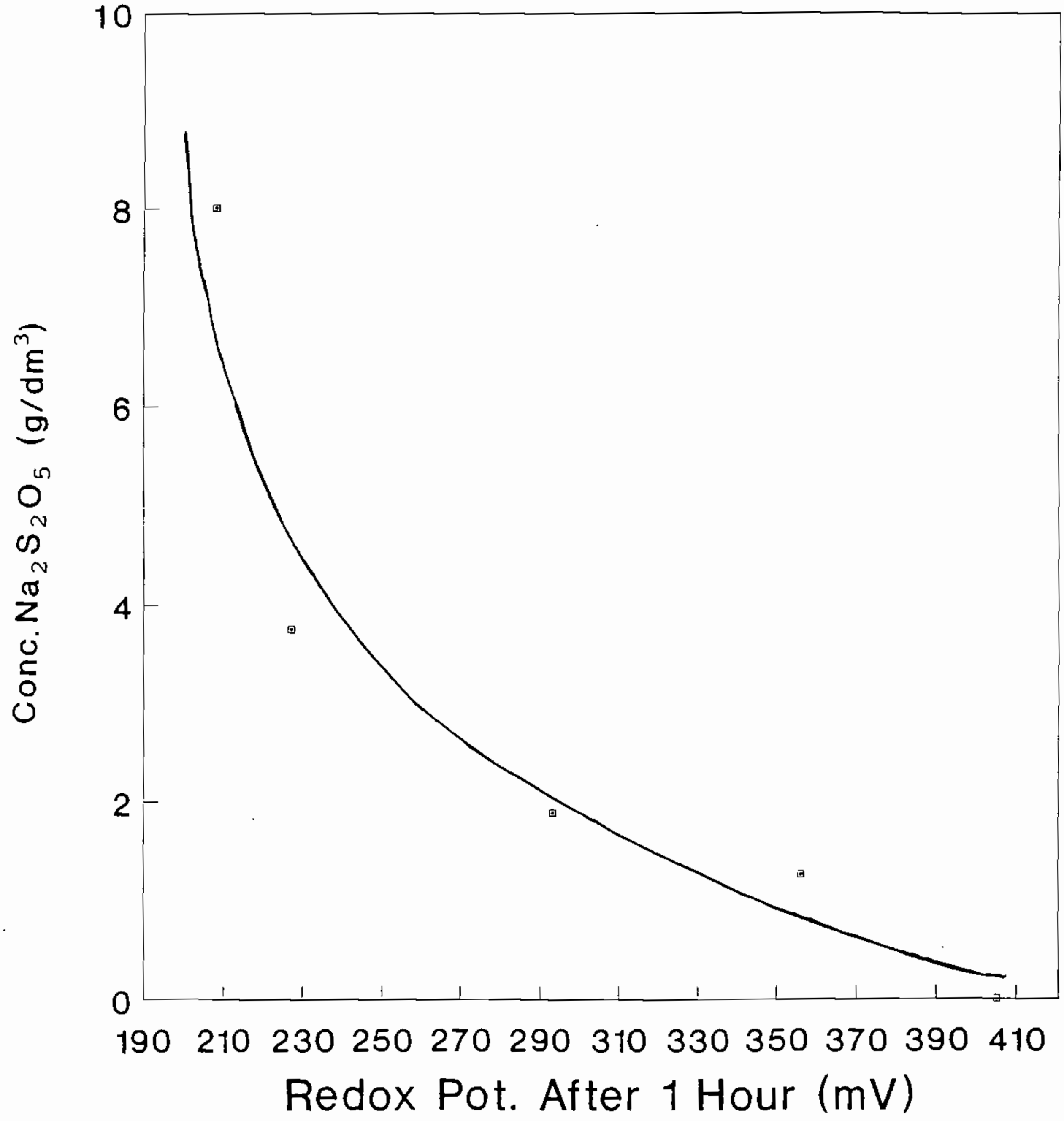


**Figure 3.3** $Na_2S_2O_5$ Concentration (g/dm$^3$) Versus Redox Potential of Ore Slurry After 1 Hour (mV).



been suggested that at high redox potentials, decomposition of formamidine disulphide to passivating sulphur results in poorer extraction. Increases in redox potential favour oxidative degradation of formamidine disulphide.

Table 3.2 and figure 3.3 illustrate the effect of different concentrations of $Na_2S_2O_5$ on the redox potential of the system at pH=2 and thiourea at a level of 1g/dm$^3$. It can be seen that with no $Na_2S_2O_5$ present, the redox potential of the slurry reaches around 400mV due to oxidation of thiourea to formamidine disulphide by oxidants in the ore itself. The redox potential almost decreases linearly up to 230mV by addition of $Na_2S_2O_5$. In order to lower the potential, by 20mV, a further, much greater addition of $Na_2S_2O_5$ is required.

Since the redox potential varies only by about 20mV in all experiments over a 6 hour period, the use of $Na_2S_2O_5$ as a reducing agent in process control could be applied to the thiourea system. The development of a control system based on $Na_2S_2O_5$ would therefore be of considerable benefit to the optimisation of gold dissolution.

## 3.9 EFFECT OF CARBON ADDITION TO LEACH

Having established that most of the gold is extracted after the first hour of leaching at a pH of 2 using 1g/dm$^3$ thiourea, it was decided to look at the effect of the addition of activated carbon to the leach after 1 hour and measure the level of gold in the carbon, ore and leach over a 6 hour period.

### 3.9.1 Reagents

The reagents used were those described in section 3.2.2.

### 3.9.2 Experimental details

224.7g of slurry were added to six 250cm$^3$ conical flasks. 0.75g of $Na_2S_2O_5$ was added to each solution and allowed to shake at speed 6 on a Stuart scientific shaker for 30 minutes. 0.2g of thiourea was weighed and added to each flask after 30 minutes. After 40 minutes, the contents of flask 1 were filtered and the leach and ore were analysed for gold. After 1 hour, the contents of flask 2 were filtered and the ore and leach were analysed for gold. At this time, 1g of "EUROCARB" activated carbon was added to each of the remaining flasks. After 1 hour contact with carbon, the contents of flask 3 were filtered through a copper mesh and the carbon recovered and analysed for gold. The leach slurry was filtered and the leach and ore were analysed for gold. This was repeated for flasks 4, 5 and 6 after 2, 4 and 4.5 hours contact with carbon. The redox potential remained at around 230mV throughout the experiment.

## 3.10 Results and discussion

### Table 3.3

100% Gold = 2.67 ppm.

| Time (Hrs) | Gold Conc. in leach (% Total) | Gold Conc. in ore (% Total) | Gold Conc. in carbon (% Total) | Total Gold |
|---|---|---|---|---|
| 0.6 | 47.0 | 55.6 | - | 102.7 |
| 1 | 50.6 | 50.9 | - | 101.6 |
| 2 | 40.2 | 40.1 | 33.2 | 113.4 |
| 3 | 34.2 | 28.1 | 46.4 | 108.7 |
| 5 | - | 6.3 | 60.3 | - |
| 5.5 | 43.2 | - | 67.2 | 110.4 |

(Note: - Not Detected)

Table 3.3 illustrates the concentrations of gold expressed as a % of the total gold i.e. 2.67 ppm in the ore, the leach and the carbon. As can be seen from the total gold column, the total gold appears to be greater than 100% in all cases. The standard deviation for the gold analysis of the ore was 0.14 ppm however and errors of this magnitude would be expected. There are clear trends however as can be seen from figures 3.4, 3.5 and 3.6. Figure 3.4 illustrates the concentration of gold in the leach with time. Again it can be seen that almost 50% of the gold was extracted in the first hour of leaching. After 1 hour, carbon was added at a level of 5g/dm$^3$ and the concentration of gold in the leach therefore decreases to 40% and 34% after 2 and 3 hours respectively. Figure 3.5 illustrates the gold concentration on the carbon with time and it can be seen that there is a steady increase in the loading of the carbon up to 67% after 5.5 hours which represents 4.5 hours contact time.

**Figure 3.4** Gold Concentration in leach (% Total Gold) Versus Time (Hours).

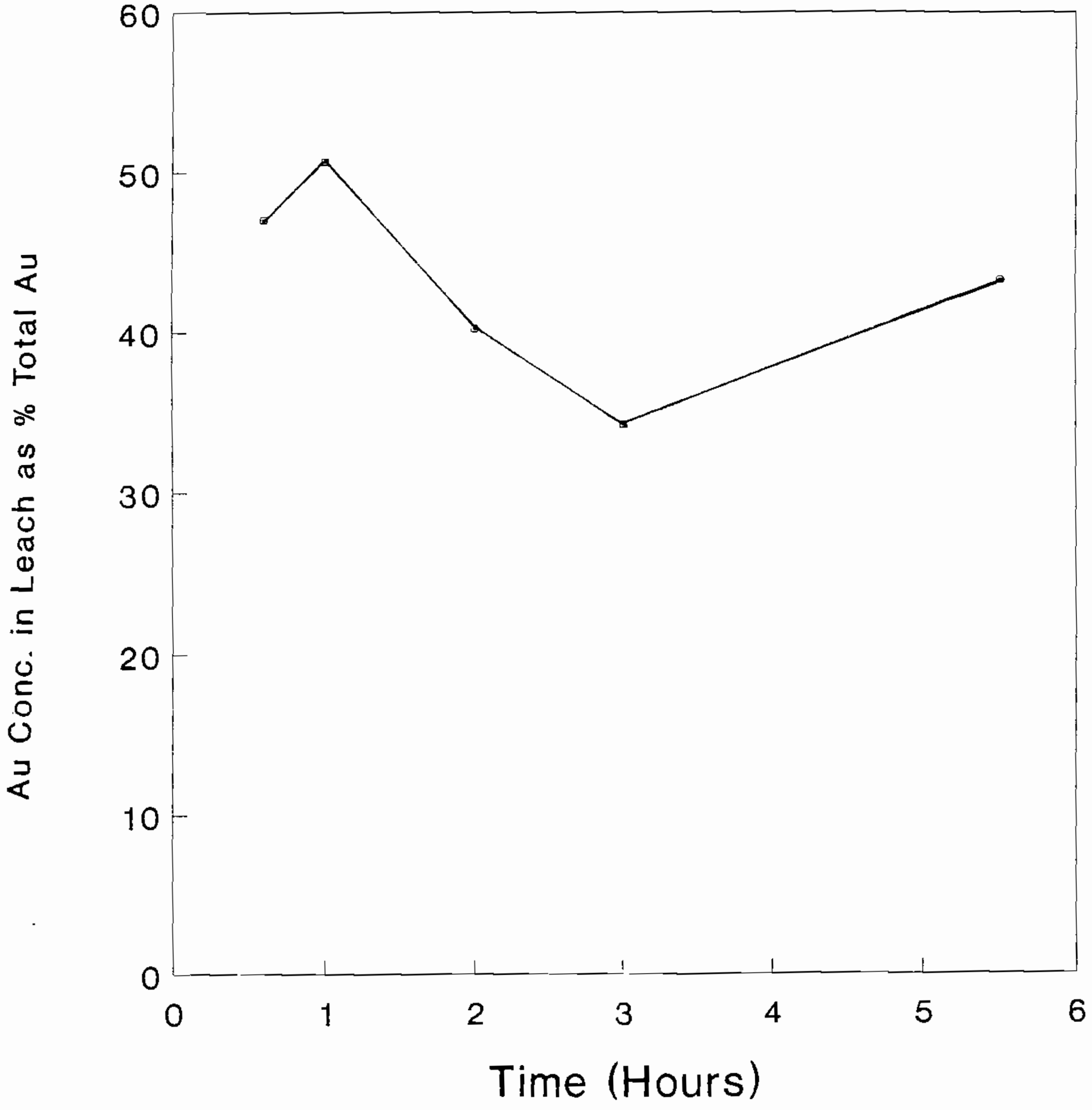


**Figure 3.5** Gold Concentration on Carbon (% Total Gold) Versus Time (Hours).

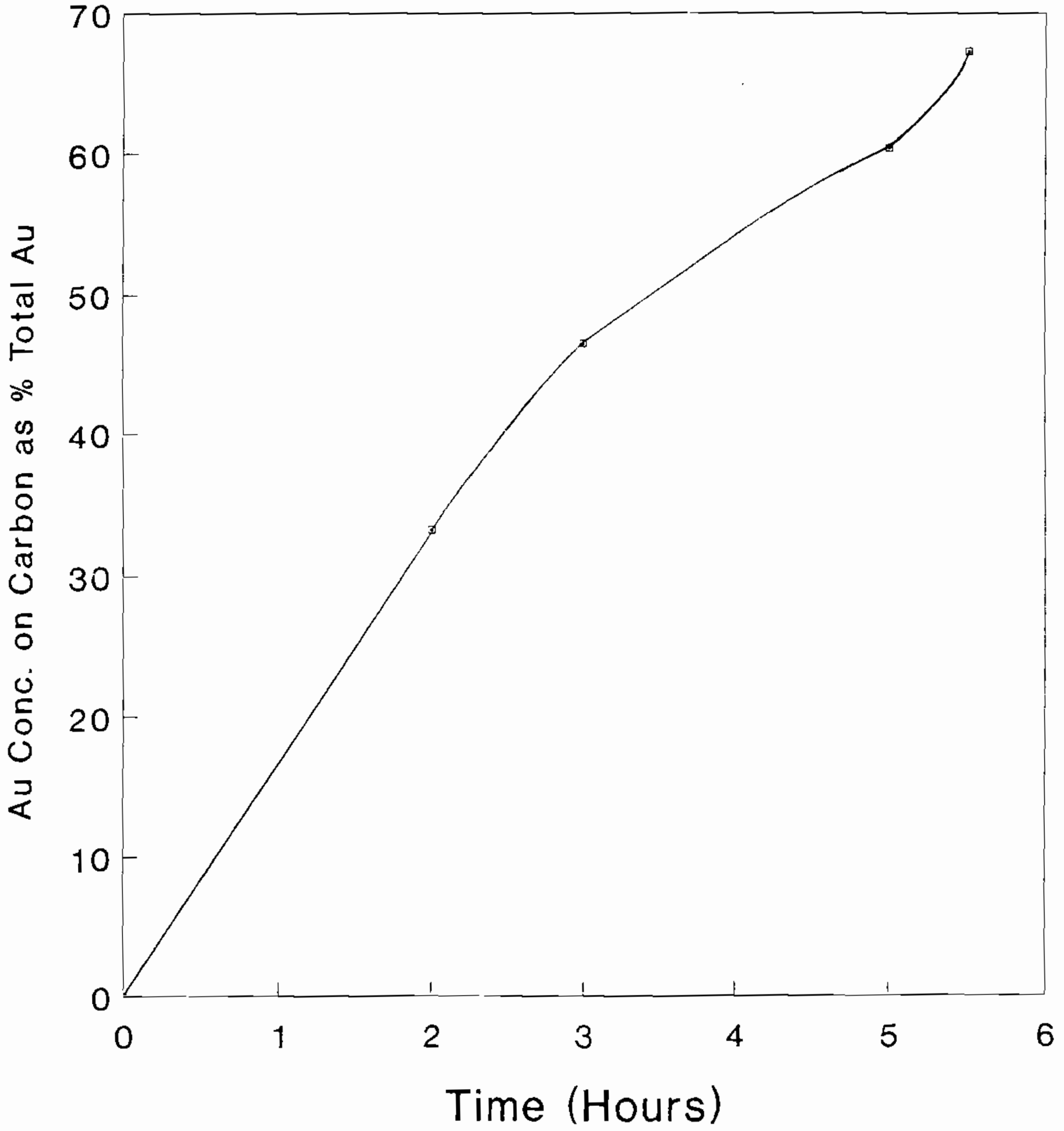
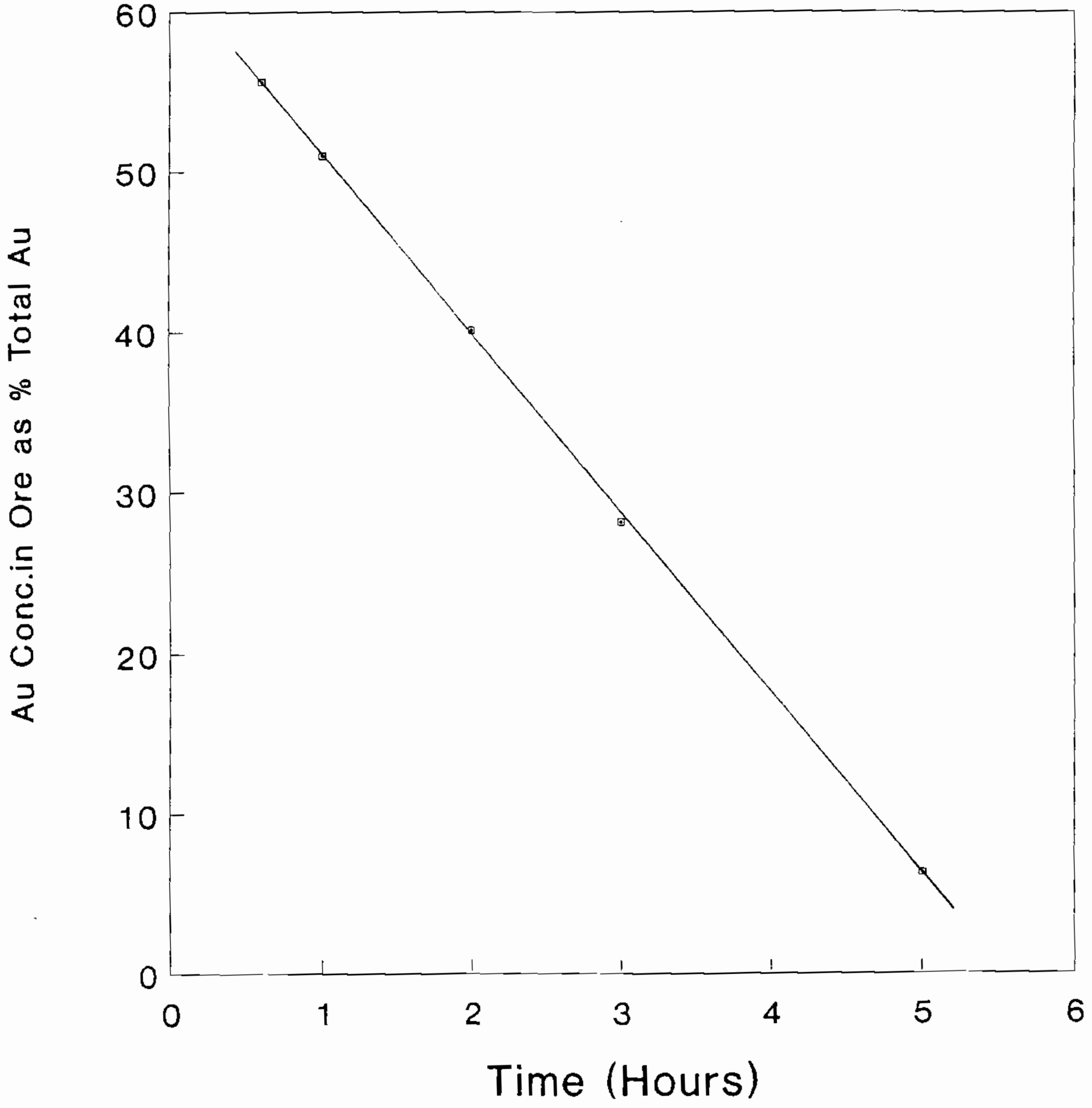


**Figure 3.6** Gold Concentration in Ore (% Total Gold) Versus Time (Hours).



It is interesting to note that in figure 3.6, it can be seen that the gold concentration drops to 6% after 5 hours and yet the concentration of gold in the leach remains high at 57%. The results of the previous experiment suggested that there was very little change in the ultimate extraction of gold over 6 hours compared to that extracted in 1 hour. It could therefore be suggested that the addition of carbon, apart from recovering the gold, improves the leaching efficiency of the system. Although from figure 3.4, the concentration of gold drops at 2 and 3 hours in the leach due to adsorption, it increases again at 5 hours. Therefore as the carbon extracts gold from the leach, more gold is leached from the ore. Perhaps the carbon is causing a shift in the equilibrium between gold in the ore and gold in the leach by taking up gold from the leach itself.

Although in the previous experiment it was found that the maximum dissolution of gold was 66% at a redox potential of around 250mV, in this case it can be seen that the level of gold in the ore is reduced to 6% after 5.5 hours representing a theoretical extraction of 94% due to the presence of carbon. Therefore it could be said that using thiourea at as low a level as $1g/dm^3$(0.013M), a very high extraction can be achieved by adding carbon after 1 hour. Although the concentration in the leach remains at around 50%, the concentration in the ore has decreased to 6% after 5.5 hours. Most of the gold now is either in the leach or the carbon. This simulation of the carbon-in-pulp process shows that gold can be extracted efficiently even using low levels of both thiourea and carbon resulting in reduced costs.

## 3.11 EFFECT OF CARBON ADDITION TO LEACH OVER 26 HOURS

Having observed the effect of the addition of activated carbon to the leach over a 4.5 hour period, its effect was investigated over a 26 hour period. In order to minimise experimental error, a batch of the leach slurry was allowed to leach under the same previous conditions and after 1 hour, this was divided into 2 conical flasks so that each solution was identical.

### 3.11.1 Experimental details

909.35g of the ore slurry were weighed in a 1 litre pyrex beaker. 3.75g/dm$^3$ $Na_2S_2O_5$ was added and the open beaker was allowed to stir on a magnetic stirrer for 30 minutes. Thiourea was then added at a concentration of 1g/dm$^3$ and the slurry was allowed to leach for 1 hour. After 1 hour, two 226g quantities A and B of the ore slurry were transferred accurately into two 250cm$^3$ conical flasks which contained 1g of carbon. The remaining leach slurry was filtered.The ore was analysed as before taking three 25cm$^3$ samples of the resulting solution for the solvent extraction step. Three 25cm$^3$ samples of the filtrate were also taken and analysed for gold as before. The average gold content was calculated in each case.

The two conical flasks containing the ore slurry were left to leach for 26 hours by placing them on Stuart scientific shaker at speed 6. After 26 hours, each slurry was filtered on a Buchner funnel apparatus. The ore samples were analysed for gold as before. Two 25cm$^3$ samples of the filtered leach were taken and analysed for gold as before. The carbon was obtained by filtering the ore slurry through a copper mesh prior to filtration of the actual slurry. Each carbon sample was ashed and analysed for gold as described in section 3.4 taking two 25cm$^3$ samples from each resulting solution. The average gold content was calculated in each case.

## 3.12 Results and discussion

**Table 3.4**

Total gold = 2.67 ppm

| Gold Conc.in leach After 1 Hour as % of total gold | Gold Conc.in Ore After 1 Hour as % of total gold | Total gold (%) |
|---|---|---|
| 51 | 40 | 91 |

| | Sample A | Sample B |
|---|---|---|
| Gold Conc.in leach After 26 Hrs as % of Total gold | 13 | 10 |
| Gold Conc.in Carbon After 26 Hrs as % of Total gold | 66 | 70 |
| Gold Conc.in Ore After 26 Hrs as % of Total gold | 17 | 25 |
| Total gold | 96 | 105 |

Table 3.4 illustrates the % gold in each component of the slurry throughout the experiment. As it can be seen, the mass balance for gold is quite good suggesting good reliability of the results. Again it can be seen that 50% of the gold is extracted in the first hour of leaching at a redox potential of 231mV. This again

leaching at a redox potential of 231mV. This again highlights the importance of the redox potential in the leaching process. After 26 hours of leaching, the gold concentration in the leach has been reduced to between 13 and 10%. The carbon has also been loaded with 66 to 70% of the gold from the ore which is almost the same result as was obtained in the previous experiment as seen from table 3.3 where the carbon has been loaded with 67% of the gold after 5.5 hours. This result would suggest that there is no improvement in the loading of the carbon under these conditions compared to a 6 hour period. In fact it can be seen that the level of gold in the ore was between 17 and 25% after 26 hours which is greater than that of 6% after 5.5 hours in the previous experiment. This could be due to adsorption of the gold-thiourea complex in the leach onto the ore itself. This adsorbed gold would then interfere with the ore analysis. Passivation of the gold surface by redox products may also explain the same level of carbon loading achieved in this experiment as with the previous experiment. The fouling of the gold surface has been reported by Groenewald (1975) [11] and also by Panchenko [14], Plaksin and Kozhukhowa [13] and again by Groenewald in 1977 [12]. It was suggested by Groenewald that this occurs above 255mV. The initial redox potential of the slurry in this experiment was 231mV, however, an increase in potential was observed after 26 hours due to thiourea degradation to formamidine disulphide. The final potential was 289mV. It therefore appears that there is no real improvement in carbon loading compared to a 6 hour period and remaining gold may only be recovered by addition of fresh batches of carbon.

## 3.13 THE USE OF CARBON AND STEEL SHAVINGS FOR GOLD RECOVERY

The following experiments involved the use of a new type of ore which was already pretreated with $Na_2S_2O_5$. The gold content of the ore was found to be 1.54 ppm with a standard deviation of 0.18 ppm. It has already been shown in chapter 1 that recovery of gold with activated carbon is not the only recovery method available. Cementation of the gold-thiourea complex has been previously reported [5,19-27]. Gold can be recovered by electrowinning [28-31] and by the use of ion exchange resins [31-34]. The following experiments involved the investigation of the recovery of gold by cementation onto steel shavings and a comparison of the method to activated carbon recovery.

### 3.13.1 Experimental details

The ore slurry used had a solids content of 12.21% w/w and a gold content of 1.54 ppm with a standard deviation of 0.18 ppm. 911.3g of the slurry were weighed in a 1 litre pyrex beaker. 0.8g of thiourea was weighed accurately and added to the slurry which was allowed to leach for 1 hour on a magnetic stirrer. After 1 hour, three 227.8g samples of slurry were transferred accurately to three $250cm^3$ conical flasks to which was added 1g of activated carbon. The remaining slurry was filtered and the solid ore and filtered leach were analysed for gold as before. The 3 samples were allowed to leach for 6 hours and the carbon, leach and ore were analysed for gold as before. The experiment was repeated using fine steel shavings and larger steel shavings at the same concentration of $5g/dm^3$. The redox potential during each experiment was 286mV.

## 3.14 Results and discussion

**Table 3.5**

5g/dm$^3$ carbon, 1g/dm$^3$ thiourea.
100% gold = 1.54 ppm

| Gold Conc.in leach After 1 hour as % of total gold | Gold Conc.in Ore After 1 hour as % of total gold | Total gold (%) |
|---|---|---|
| 54 | 39 | 93 |

| | Sample A | Sample B | Sample C |
|---|---|---|---|
| Gold Conc. in leach After 6 hours as % of total gold | 0 | 0 | 0 |
| Gold Conc.in Carbon After 6 hours as % of total gold | 71 | 67 | 70 |
| Gold Conc.in Ore After 6 hours as % of total gold | 29 | 26 | 35 |
| Total gold | 100 | 93 | 105 |

**Table 3.6**

5g/dm$^3$ fine steel, 1g/dm$^3$ thiourea

| Gold Conc.in leach After 1 hour as % of total gold | Gold Conc.in Ore After 1 hour as % of total gold | Total gold (%) |
|---|---|---|
| 55 | 45 | 100 |

| | Sample A | Sample B | Sample C |
|---|---|---|---|
| Gold Conc.in leach After 6 hours as % of total gold | 0 | 0 | 0 |
| Gold Conc.on steel After 6 hours as % of total gold | 88 | 78 | 83 |
| Gold Conc.in Ore After 6 hours as % of total gold | 9 | 15 | 4 |
| Total gold | 97 | 93 | 87 |

**Table 3.7**

5g/dm$^3$ large steel shavings, 1g/dm$^3$ thiourea

| Gold Conc.in leach after 1 hour as % of total gold | Gold conc.in ore after 1 hour as % of total gold | Total gold (%) |
|---|---|---|
| 41 | 58 | 99 |

| | Sample A | Sample B | Sample C |
|---|---|---|---|
| Gold Conc.in leach after 6 hours as % of total gold | 0 | 0 | 0 |
| Gold Conc.on steel after 6 hours as % of total gold | 69 | 72 | 72 |
| Gold Conc.in ore after 6 hours as % of total gold | 32 | 34 | 36 |
| Total gold | 101 | 106 | 108 |

Tables 3.5, 3.6 and 3.7 illustrate the concentration of gold in the leach, ore and carbon or steel shavings after 1 and 6 hours of leaching. Again it can be seen that between 40 and 60% of the gold can be leached within the first hour in all three experiments. It can also be seen that the concentration of gold in the leach is zero after 6 hour contact with either steel shavings or activated carbon. This is not surprising since the level of gold is so small compared to that of the ore used in previous experiments. Using activated carbon, the gold recovery in 6 hours was found to be between 67 and 71%. Using fine steel shavings it was found to be between 78 and 88% and there is probably no statistical difference between the results bearing in mind that the calculations are based on a gold content in the ore of 1.54 ppm ± 12%. Using large steel shavings, the recovery was found to be between 69 and 72%. The greater recovery associated with the finer steel shavings may be attributed to the larger surface area available for cementation compared to the larger shavings. The most important fact, however, is that after 6 hours contact of the ore with either steel shavings or activated carbon, the concentration of gold in the leach is zero i.e. all the available gold in solution has been adsorbed or cemented. Using activated carbon, the concentration of gold in the ore after 6 hours was between 26 and 35%. Using fine steel shavings, it was between 4 and 15% and using coarse steel shavings it was between 32 and 36%. These results suggest that fine steel shavings would be more useful than either activated carbon or coarse steel shavings for the recovery of gold. Further work, however, would be required to confirm these results and further refinement of the analytical techniques would be of great benefit to this type of work.

It can therefore be concluded that by carrying out optimisation experiments on an ore by the addition of different amounts of $SO_2$, the redox potential at which the maximum amount of gold can be dissolved over a fixed period of time can be determined. The addition of this reagent would be economically beneficial to the leaching process and could merit the development of a process control system based on sulphur dioxide.

It appears that there is a slight benefit in choosing steel shavings over activated carbon for the recovery of gold from the ore. Steel shavings may also be preferred due to cost considerations, ease of recovery from the leach solution by magnetic separation and ease of recovering the cemented gold from the steel.

## RERENCES CHAPTER 3

1. Morrison, G.H. and Freisei, H., "Solvent extractions in Analytical Chemistry". John Wiley and Sons, New York, (1957).

2. Stony, J., "The solvent extraction of metal chelates". The MacMillan Co., New York, (1964).

3. K.Mullins, "Precious metal extraction", M.Sc.Thesis, Dublin Institute of Technology, (1989).

4. Groenewald, T., Jones, B.M., Analytical Chemistry, 43(12), (Oct.1971).

5. Wen, C.D., "Studies and prospects of gold extraction from carbon-bearing clayey gold ore by the thiourea process"; Proc.XIV Int. Min. Proc. Cong.,17-23:Oct 1982.

6. Bilston, D.W., La-Brooy, S.R., and Woodcock, J.T., "Gold and silver leaching from an oxidised gold ore with thiourea under controlled conditions". The Aus. I.M.M., Melbourne branch, symposium on "Extractive Metallurgy", pp.51-60, (November 1984).

7. Groenwald, T., "The dissolution of gold in acidic solutions of thiourea", Hydrometallurgy, 1,277 (1976).

8. Chen, C.K., Lung, T.N., and Wan, C.C., Hydrometallurgy, 5, 207-212 (1980).

9. Hendrix, J.L., Pyper, R.A., "Gold and Silver Leaching, Recovery and Economics", SME-AIME, 83, (1981).

10. Songina, O.A., Ospanov, Kh.K., Muldagalieva, I. Kh., and Salnikova, S.D., "Dissolution of gold using thiourea in hydrochloric acid medium", IZV. Akad. Nauk. Kaz. SSR, Ser. Khim., 21(3) : 9- (Chem. Abstr., 75: 91715z).(1971).

11. Groenewald, T., "Electrochemical studies on gold electrodes in acidic solutions of thiourea containing gold(I)-thiourea complex ion", J. Appl. Electrochem., 5(1):71-78, (1975).

12. Groenewald, T., "Potential applications of thiourea in the processing of gold", J.S.Afr. IMM., 77(II): 217-223, (1977).

13. Plaksin, I. and Kozukhowa, M., "Solubility of gold and silver in thiourea", Doklady akadomic Nark, SSR, 31, 671-674, Russ (1941).

14. Panchenko, A.F., Kakovskii, I.A., Shamis, L.A., and Khmel'Nitskaya, O.D., "Dissolution kinetics of gold, silver and their alloys in aqueous thiourea". Izv. Akad. Nauk. SSSR Met., 6:32-37 (Chem.Abstr., 84:138813h), (1975).

15. Schulze, R.G., Journal of metals, 36, 62-65 (June 1984).

16. Charley, W.R., "Hydrometallurgical extraction of precious metals using thiourea", Practical Hydromet. 7th Annual symposium on uranium and precious metals, ed. G.F. Chlumsky, SME-AIME, New York, (1984).

17. Hiskey, J.B., "Thiourea leaching of gold and silver-technology update and additional applications". Minerals and metallurgical processing (November 1984).

18. Deschenes, G. and Ghali, E. Hydrometallurgy, 20,179-202, (1988).

19. Hutchings, W., "Laboratory experiments on aluminium and zinc dusts as precipitates of gold in cyanidation practice"; Can. Min. J. 70:10: 74-79; (1949).

20. Van Lierde, A.Ollivier, P. and Lesoille, M., "Développement de nouveau procédé de traitement pour le minerai de Salsigne", Ind. Min., les tech. la, 399-410; (1982).

21. Laskorin, B.N. et Al., "The liquid extraction of complex compounds of gold and silver from alkaline solutions"; Dok.Ak.Nauk.SSSR, 39:1170-1172; (1968).

22. Tataru, S., "Précipitation par cémentation de l'or en solutions acides"; Rev.Roam.Chim., 1043-1049; (1968).

23. Tataru, S.,"Ion exchange processes for gold recovery", Rev.Roum. Chim.,19:4:717-725; (1974).

24. Kakovskii, I.A., Khmel'Nilskaya, O.D., Panchenko, A.F. et al., "Thiocarbamide solvent for gold and silver", Fiz.Kh.Os.Pe.Mi.Syr., 148-55; (1982).

25. Simpson, W.W., Peterson, L.,and Sandberg, R.G., "Gold and Silver recovery from thiourea leach solutions", Pac.Northwest metals and Min.Conf., Portland, Oregon; (April 1984).

26. Yen, W.T., and Wyslouzil, D.M., "Gold recovery from the thiourea leach system", AIME Santa Fe, Oct. 14-15; (1985).

27. Zadra, J.B., Engel, A.L., and Heinen, H.J., "Process for recovering gold and silver from activated carbon by leaching and electrolysis", U.S.B.M report 4843; (1952).

28. Jha, M.C., "Recovery of gold and silver from cyanide solutions: a comparitive study of various processes", 1st I.S.P.M.R., Reno, Nev.; (June 1984).

29. Paul, R.L., Filmer, A.O., and Nicol, M.J., "The recovery of gold from concentrated aurocyanide solutions", Hydromet.R.D. and plant practice, TMS, AIME, N.Y., 689-704; (1982).

30. Elges, C.H., Wroblewski, M.D., and Eisele, J.A., "Direct electrowinning of gold", Int. Symp. Electro. Chem.in Min.and Met.proc., AIME;10,501-512; (1984).

31. Hiskey, S.J., "Application of ion exchange resins in the cyanidation of gold and silver ores", U.S.B.M. report 4374; (1949).

32. Flemming, C.A., and Nicol, M.J., "Alternative processes to filtration; carbon-in-pulp and resin-in-pulp in the Metallurgical Industry", Hydromet, S.C.I., London,C2-16; (1981).

33. McGarvey, F.X., "Recovery of gold by ion exchange"; gold and silver recovery innovations, 2, R.I.Ltd., Beth., Penn.,1107-1111; (1981).

34. Gabra, G., "Leaching of gold from pyrite and chalcopyrite concentrates using acidified thiourea", 23rd Ann. CIM Conf.of Met., Quebec; (August 1984).

# CHAPTER 4

# FACTORIAL DESIGNED EXPERIMENTS

## 4.1 Introduction

Factorial designed experiments are carried out by researchers in all fields in order to study the individual and combined effects of experimental variables on a measured response. The pioneers for the use of statistical methods were Sir Ronald A. Fisher and Frank Yates [1]. Many of the early applications were in the agricultural and biological sciences and much of the terminology has come from this agricultural background. Fisher first used the analysis of variance as the primary method of statistical analysis in experimental design [2,3].

The experiments allow the experimenter to evaluate the combined effects of two or more variables when used simultaneously. An interaction effect is an effect attributable to the combination of variables above and beyond that which can be predicted from the variables considered singly. Since interaction effects can be evaluated, a more complete set of information can be obtained than that from a series of single factor experiments.

A scientific approach to planning the experiment must be considered if an experiment is to be performed most efficiently. When the problem involves data that are subject to experimental error, statistical methodology is the only objective approach to the analysis if meaningful conclusions are to be drawn from the data.

### 4.1.1 Experimental Design

The design of any experiment is very important because the results obtained to a large extent depend on the manner in which the data were collected. The two basic principles of experimental design are replication and randomisation.

Replication allows the experimenter to estimate experimental error. The estimate of error allows the experimenter to determine whether observed differences in data are statistically different. With only a single replicate, it is impossible to compute an estimate of experimental error. The estimate of experimental error becomes more reliable as the number of replicates, n, increases. Also if a sample mean (y) is used to estimate the effect of a factor on a particular response (e.g. the shelf-life of a food item), replication allows the experimenter to obtain a more precise estimate of this effect. For example, if the effects of two levels of radiation on the shelf life of a food item are to be investigated, the number of replicates being equal to one and the result of both observations $y_1$ and $y_2$ were 64 and 68 days respectively. In this case, satisfactory inferences about the effect of radiation could not be made as the difference could be due to experimental error. If however, the number of replicates was large and the experimental error sufficiently small, then it would be reasonably safe in saying that a change in the level of radiation received by the food item has a significant effect on its shelf-life. The reliability of conclusions therefore increases as the number of replicates increase. However, time and cost likewise increase so, in most cases, a reasonable compromise has to be reached.

The second important aspect of experimental design is randomisation i.e. the order in which the runs or trials of an experiment are performed are randomly determined. Randomisation validates the assumption that both observations and errors are independently distributed random variables. Randomisation also assists in eliminating the effects of extraneous factors which may bias the observations e.g. changes in temperature or humidity.

The design of factorial experiments is concerned with deciding the following:

(a) What factors should be included?

(b) How many levels of each factor should be included?

(c) How should the levels of the factors be spaced?

(d) What response variable should be selected, i.e. will it provide information about the problem under study?

(e) What steps should be taken to control experimental error?

(f) How many experimental units should be selected for each treatment combination?

The objective of this study was to investigate the effect of the main variables in a typical leach system on the amount of gold adsorbed onto activated carbon. The work of W. Janhunin [4] suggests that the abstraction of the gold-cyanide complex in basic solution onto activated carbon is strongly dependant on the concentration of calcium, iron, copper, ethanol, carbon and gold itself in the system.

In the thiourea system, the factors of interest were pH, time, type of carbon used, iron(III), copper(II) and thiourea concentration. The response chosen was the mg's of gold adsorbed per kilogram of carbon. A series of experiments were carried out to look at the effects of these factors on the response.

### 4.1.2 The General Factorial Experiment

In an experiment where there are "a" levels of factor A, "b" levels of factor B, "c" levels of factor C and so on, then, in general there will be abc...n observations where n = the number of replicates. The effect of a factor is defined to be the change in the response produced by a change in the level. This is called the main effect because it refers to the primary factors of interest in the experiment. If we have k factors each at two levels, $2^k$ observations are required. The $2^k$ design is particularly useful in the early stages of experimental work when there are many factors to be investigated. For a $2^k$ design, the complete model would contain $2^k-1$ effects. In each experiment a series of solutions was made up each containing the same amount of gold and also containing each combination of the factors of interest for the particular experiment.

Before carrying out any experiments on the effects of the various components of a typical leach system on the adsorption of gold, it was necessary to investigate the effects of these compounds on the method of measurement. The method of measurement to be used was Atomic Absorption Spectrophotometry which measures the amount of light absorbed by neutral unexcited atoms in the gaseous state. The use of the method can be affected by species which affect the production of neutral unexcited atoms in the flame. Some of the neutral atoms may combine with radicals in the flame gases to form new compounds e.g. metal hydroxides or monoxides. The formation of refractory compounds with the element of interest results in a decreased signal i.e. a chemical interference.

Changes in the nebulisation efficiency due to unexpected changes in viscosity, surface tension and density can also affect the signal. Light scattering also becomes a problem at high concentration.

To investigate whether or not the absorbance of a standard gold solution was affected by the sample matrix, a series of measurements were taken from 5ppm solutions of gold which contained various combinations of copper(II), iron(III) and thiourea at a pH of 1 and 2.

## 4.2 THE EFFECT OF pH, COPPER(II), IRON(III) AND THIOUREA CONCENTRATION ON THE ABSORBANCE OF A 5 ppm GOLD SOLUTION

The objective of the experiment was to investigate the effects of pH, copper(II) concentration, iron(III) concentration and thiourea concentration each at two levels on the absorbance of a 5 ppm gold solution. The levels of each factor were chosen as follows:

| **Factor** | **Level 1** | **Level 2** |
|---|---|---|
| pH | 1 | 2 |
| Cu(II) | 100 ppm | 500 ppm |
| Fe(III) | 500 ppm | 1500 ppm |
| Thiourea | 0.2g/dm$^3$ | 2g/dm$^3$ |

### 4.2.1 Reagents

1000 ppm gold chloride standard solution "SPECTROSOL" (BDH chemicals).
1000 ppm copper(II) solution from copper sulphate pentahydrate (Riedel-De-Haen).
10,000 ppm iron(III) solution from ferric sulphate (Riedel-De-Haen).
10g/dm$^3$ Thiourea solution from Thiourea (SKW-Trotsberg).
Deionised distilled water (Elgastat U.H.Q).

### 4.2.2 Instrumentation

All samples were analysed using a Shimadzu atomic absorption/flame emission spectrophotometer.

**Instrument Conditions**
Wavelength = 242.8 nm
Hollow cathode lamp current = 9mA
Burner height = 10 cm
Slit width = 0.5 nm
Flame type = Acetylene/Air
Fuel flow rate = 1.6 dm$^3$/min.
Deuterium lamp ON.

Glass pH electrode (Amagruss Electrodes Ireland Ltd.)
Model EC-1610-11

### 4.2.3 Experimental details

There were four factors each at two levels. Two replicates were taken and therefore there were 32 observations. The treatment combination levels were as follows:

| **Number** | **Cu(II)** | **Fe(III)** | **Thiourea** | **Ph** |
|---|---|---|---|---|
| 1 | 1 | 1 | 1 | 1 |
| 2 | 2 | 1 | 1 | 1 |
| 3 | 1 | 2 | 1 | 1 |
| 4 | 2 | 2 | 1 | 1 |
| 5 | 1 | 1 | 2 | 1 |
| 6 | 2 | 1 | 2 | 1 |
| 7 | 1 | 2 | 2 | 1 |
| 8 | 2 | 2 | 2 | 1 |
| 9 | 1 | 1 | 1 | 2 |
| 10 | 2 | 1 | 1 | 2 |
| 11 | 1 | 2 | 1 | 2 |
| 12 | 2 | 2 | 1 | 2 |
| 13 | 1 | 1 | 2 | 2 |
| 14 | 2 | 1 | 2 | 2 |
| 15 | 1 | 2 | 2 | 2 |
| 16 | 2 | 2 | 2 | 2 |

A 100 ppm gold solution was made up at both pH 1 and 2 by adding 25cm$^3$ of the 1000 ppm gold chloride standard solution to a 250cm$^3$ grade "A" volumetric flask and making up to the mark with a sulphuric acid solution at the correct pH. 5cm$^3$ of this solution was added to eight 100cm$^3$ grade "A" volumetric flasks. Solutions 1 to 4 were made up in duplicate. The appropriate volumes of copper(II), iron(III) and thiourea were added to each flask from the stock solution so as to give each combination of factors for numbers 1 to 4. Two 5 ppm gold chloride reference solutions were made up by taking 5cm$^3$ of the 100 ppm gold stock solution and making them up to the mark in a 100cm$^3$ grade "A" volumetric flask with distilled deionised water.

The absorbance of solutions 1 to 4 and also the 2 reference solutions were measured three times and the average signal was recorded. The absorbance of each solution was divided by that of the reference 5 ppm solution to give the "relative signal". This relative signal was computed in each case.

(NOTE: As there may be small changes in the condition of the flame each time the spectrometer is used, it is important to use the "relative signal" as the response factor. Comparing absorbance figures obtained on different occasions could mean large errors.)

The procedure was repeated for solution 5 to 8, 9 to 12 and 13 to 16. The data was analysed by the statistical software package MINITAB. Details of MINITAB along with an explanation of the terms found in the analysis of variance for each experiment i.e. DF, SS, MS, F and P can be found in appendix 1.

**Table 4.1** Relative signal at each factor combination

| ROW | Cu | Fe | Tu | pH | Signal |
|---|---|---|---|---|---|
| 1 | 1 | 1 | 1 | 1 | 1.024 |
| 2 | 1 | 1 | 1 | 1 | 1.022 |
| 3 | 2 | 1 | 1 | 1 | 1.022 |
| 4 | 2 | 1 | 1 | 1 | 1.028 |
| 5 | 1 | 2 | 1 | 1 | 1.026 |
| 6 | 1 | 2 | 1 | 1 | 1.030 |
| 7 | 2 | 2 | 1 | 1 | 1.013 |
| 8 | 2 | 2 | 1 | 1 | 1.019 |
| 9 | 1 | 1 | 2 | 1 | 1.050 |
| 10 | 1 | 1 | 2 | 1 | 1.035 |
| 11 | 2 | 1 | 2 | 1 | 0.774 |
| 12 | 2 | 1 | 2 | 1 | 0.777 |
| 13 | 1 | 2 | 2 | 1 | 1.056 |
| 14 | 1 | 2 | 2 | 1 | 1.041 |
| 15 | 2 | 2 | 2 | 1 | 1.022 |
| 16 | 2 | 2 | 2 | 1 | 1.022 |
| 17 | 1 | 1 | 1 | 2 | 1.006 |
| 18 | 1 | 1 | 1 | 2 | 1.020 |
| 19 | 2 | 1 | 1 | 2 | 1.064 |
| 20 | 2 | 1 | 1 | 2 | 1.017 |
| 21 | 1 | 2 | 1 | 2 | 1.019 |
| 22 | 1 | 2 | 1 | 2 | 1.057 |
| 23 | 2 | 2 | 1 | 2 | 1.025 |
| 24 | 2 | 2 | 1 | 2 | 1.055 |
| 25 | 1 | 1 | 2 | 2 | 1.026 |
| 26 | 1 | 1 | 2 | 2 | 1.030 |
| 27 | 2 | 1 | 2 | 2 | 0.901 |
| 28 | 2 | 1 | 2 | 2 | 0.901 |
| 29 | 1 | 2 | 2 | 2 | 1.047 |
| 30 | 1 | 2 | 2 | 2 | 1.042 |
| 31 | 2 | 2 | 2 | 2 | 1.040 |
| 32 | 2 | 2 | 2 | 2 | 1.042 |

**Table 4.2** Mean Relative Signal at each factor level

| Cu | N | Signal |
|---|---|---|
| 1 | 16 | 1.0332 |
| 2 | 16 | 0.9826 |

| Fe | N | Signal |
|---|---|---|
| 1 | 16 | 0.9811 |
| 2 | 16 | 1.0347 |

| Tu | N | Signal |
|---|---|---|
| 1 | 16 | 1.0279 |
| 2 | 16 | 0.9879 |

| pH | N | Signal |
|---|---|---|
| 1 | 16 | 0.9976 |
| 2 | 16 | 1.0182 |

| Cu | Fe | N | Signal |
|---|---|---|---|
| 1 | 1 | 8 | 1.0266 |
| 1 | 2 | 8 | 1.0397 |
| 2 | 1 | 8 | 0.9355 |
| 2 | 2 | 8 | 1.0297 |

| Tu | pH | N | Signal |
|---|---|---|---|
| 1 | 1 | 8 | 1.0230 |
| 1 | 2 | 8 | 1.0329 |
| 2 | 1 | 8 | 0.9721 |
| 2 | 2 | 8 | 1.0036 |

| Cu | Tu | N | Signal |
|---|---|---|---|
| 1 | 1 | 8 | 1.0255 |
| 1 | 2 | 8 | 1.0409 |
| 2 | 1 | 8 | 1.0304 |
| 2 | 2 | 8 | 0.9349 |

| Cu | pH | N | Signal |
|---|---|---|---|
| 1 | 1 | 8 | 1.0355 |
| 1 | 2 | 8 | 1.0309 |
| 2 | 1 | 8 | 0.9596 |
| 2 | 2 | 8 | 1.0056 |

| Fe | Tu | N | Signal |
|---|---|---|---|
| 1 | 1 | 8 | 1.0254 |
| 1 | 2 | 8 | 0.9367 |
| 2 | 1 | 8 | 1.0305 |
| 2 | 2 | 8 | 1.0390 |

| Fe | pH | N | Signal |
|---|---|---|---|
| 1 | 1 | 8 | 0.9665 |
| 1 | 2 | 8 | 0.9956 |
| 2 | 1 | 8 | 1.0286 |
| 2 | 2 | 8 | 1.0409 |

**Table 4.3** Analysis of Variance for Relative Signal

| Source | DF | SS | MS | F | P |
|---|---|---|---|---|---|
| Cu | 1 | 0.020453 | 0.020453 | 122.45 | 0.000 |
| Fe | 1 | 0.023059 | 0.023059 | 138.05 | 0.000 |
| Tu | 1 | 0.012840 | 0.012840 | 76.87 | 0.000 |
| pH | 1 | 0.003424 | 0.003424 | 20.50 | 0.000 |
| Cu*Fe | 1 | 0.013163 | 0.013163 | 78.80 | 0.000 |
| Cu*Tu | 1 | 0.024587 | 0.024587 | 147.20 | 0.000 |
| Cu*pH | 1 | 0.005126 | 0.005126 | 30.69 | 0.000 |
| Fe*Tu | 1 | 0.018867 | 0.018867 | 112.95 | 0.000 |
| Fe*pH | 1 | 0.000570 | 0.000570 | 3.41 | 0.083 |
| Tu*pH | 1 | 0.000935 | 0.000935 | 5.60 | 0.031 |
| Cu*Fe*Tu | 1 | 0.020352 | 0.020352 | 121.84 | 0.000 |
| Cu*Fe*pH | 1 | 0.002064 | 0.002064 | 12.36 | 0.003 |
| Cu*Tu*pH | 1 | 0.001907 | 0.001907 | 11.41 | 0.004 |
| Fe*Tu*pH | 1 | 0.001938 | 0.001938 | 11.60 | 0.004 |
| Cu*Fe*Tu*pH | 1 | 0.001391 | 0.001391 | 8.33 | 0.011 |
| Error | 16 | 0.002673 | 0.000167 | | |
| Total | 31 | 0.153345 | 0.004947 | | |

## 4.3 Results and discussion

The levels of each factor chosen were those of a typical leach system. The levels were also of the order of those used in subsequent experiments. The column marked "Signal" in tables 4.1 and 4.2 refer to the "Relative Signal".

The average signal, considering all observations is 1.008 i.e 0.8 % above the absorbance of a reference 5ppm solution. Table 4.1 illustrates the relative signal at levels 1 and 2 of each factor. From this table, it can be seen by inspection that the most outstanding results are those from rows 11, 12 and 27, 28. In both these cases the relative signals are 78% and 90% of that of the reference solution respectively. It can be seen that both copper and thiourea are at level 2 and iron is at level 1. A white precipitate was formed in these solutions after standing for a few hours. This was thought to be the copper-thiourea complex. If the relative signal in these cases are compared with that of rows 15, 16 and 31, 32 i.e both copper and thiourea are still high, it can be seen that the relative signal is very close to the mean. Perhaps the iron(III) has oxidised the thiourea present to formamidine disulphide and reduced the thiourea level as to make it impossible to form the complex. It is also possible that there is competition between copper(II) and iron(III) to form thiourea complexes and the iron(III) complex is probably more soluble. The loss in absorbance could be attributed to occlusion of the gold-thiourea complex in the precipitate. The loss could also be due to a reduction in the nebulisation efficiency due to the presence of the precipitate in the solution.

From Table 4.2, the mean relative signal can be seen at levels 1 and 2. The results suggest that changing the level of copper(II) from 100 ppm to 500 ppm reduces the relative signal by about 5%. Increasing the level of iron(III) from 500 ppm to 1500 ppm increases the relative signal by 5%. Increasing the level of thiourea from 0.2g/dm$^3$ to 2g/dm$^3$ reduces the average signal by about 4%. The least significant effect appears to be that of pH. By changing the pH from 1 to 2, the mean relative signal only changes by about 2%. It can be seen that n=16 in each case and as n increases, the reliability of the conclusions increases accordingly. Also from this table, the mean relative signal can be seen at levels 1 and 2 of each two-factor combination. The same trends can also be seen i.e. increasing the level of copper(II) in each case reduces the relative signal. The average random error associated with the absorbance of the reference solution would be expected to be around 0.3% taking into account the fact that the 5cm$^3$ pipette and 100cm$^3$ volumetric would have a cumulative random error of 0.3%.

Table 4.3 illustrates the analysis of variance for the response. It can be seen that the most important effect is that of the interaction effect between copper(II) and thiourea. The F-Value for this is 147. A change in the level of copper(II) accompanied by a change in the thiourea level has the most significant effect on the relative signal.

The next most statistically significant effect is that of iron(III). As can be seen from the means in Table 4.2, increasing the iron(III) level changes the response by 5%. The next most significant effect is that of copper(II) followed by the interaction effect of copper(II), iron(III) and thiourea i.e. F=121.84. It can also be seen from Table 4.3 that a change in the pH from 1 to 2 does not have a very significant effect on the signal in comparison with the other three factors. The single factor F-Value for pH is only 20.5, the lowest of them all. The higher order interactions, especially those involving pH are not as significant as interactions excluding pH. The P-Values are less than the 99.9% probability level.

The practical significance of these findings is important considering the subsequent experiments that were carried out in this study. Subsequent experiments involved the calculation of the amount of gold adsorbed onto a sample of activated carbon by assuming that the initial concentration of gold in each sample was 10 ppm. By measuring the level of gold after exposure to activated carbon by AAS, the amount of gold adsorbed can be calculated by difference. If however, solutions which contain both copper(II) and thiourea at high levels are used, the calculated amount of gold adsorbed would be incorrect assuming the absorbance of a 10 ppm solution was correct. It was decided therefore to measure the gold signal in these solutions before and after exposure to the carbon and calculate the gold adsorbed by the difference in the two measurements.

Although iron(III) increases the relative signal, the fact that copper reduces the signal somewhat compensates for this effect. A more serious scenario would exist if both factors increased or decreased the signal. Without considering rows 11,12 and 27,28, the mean signal is 1.035 i.e. 3.5% above the reference solution. It must also be realised that the accumulative errors associated with the use of glassware and changes in the stability of the flame also give rise to errors. The gold standard solution is quoted as being 1000 ± 5ppm. In making up a 100 ppm gold stock solution and adding 5cm$^3$ of this to a 100cm$^3$ volumetric flask, the worst possible error associated with the final concentration could be 0.97%.

## 4.4 THE EFFECT OF IRON(III), COPPER(II), pH, TIME AND THIOUREA CONCENTRATION ON THE ADSORPTION OF GOLD ONTO ACTIVATED CARBON

The aim of this experiment was to determine which factors had the most significant effect on the adsorption of the gold-thiourea complex onto activated carbon. The factors chosen were those which would be typically found in a thiourea leach system. The levels chosen were those which would be expected to be present in a typical ore during leaching. By choosing the most important parameters of the leaching system at their respective levels, an attempt is made to simulate the environment in which the gold-thiourea complex competes for sites on the activated carbon and hence determine the effects of the factors which influence adsorption. The factors were chosen at the following levels:

| **Factor** | **Level 1** | **Level 2** |
|---|---|---|
| Iron(III) | 500 ppm | 1500 ppm |
| Copper(II) | 100 ppm | 500 ppm |
| pH | 1 | 2 |
| Thiourea | 0.2g/dm$^3$ | 2g/dm$^3$ |
| Time | 30 Mins. | 120 Mins. |

### 4.4.1 Reagents

1000 ppm Gold chloride standard solution "SPECTROSOL" (BDH Chemicals).

1000 ppm Copper(II) solution from copper sulphate pentahydrate (Riedel-De-Haen).

10,000 ppm Iron(III) solution from ferric sulphate (Riedel-De-Haen).

10g/dm$^3$ Thiourea solution from thiourea (SKW-Trotsberg).

Sulphuric acid (Riedel-De-Haen).

Sodium hydroxide (Riedel-De-Haen).

### 4.4.2 Instrumentation

All standards and samples were measured using a Shimadzu AA670 Atomic Absorption/Flame Emission spectrophotometer. The instrument conditions were as described in section 4.2.2.

There are five factors each at two levels. Therefore with n=2, there will be $2^6$=64 observations. The treatment combination levels are therefore as follows:

| **Number** | **Fe(III)** | **Cu(II)** | **pH** | **Thiourea** | **Time** |
|---|---|---|---|---|---|
| 1 | 1 | 1 | 1 | 1 | 1 |
| 2 | 2 | 1 | 1 | 1 | 1 |
| 3 | 1 | 2 | 1 | 1 | 1 |
| 4 | 2 | 2 | 1 | 1 | 1 |
| . | . | . | . | . | . |
| . | . | . | . | . | . |
| . | . | . | . | . | . |
| . | . | . | . | . | . |
| . | . | . | . | . | . |
| 30 | 2 | 1 | 2 | 2 | 2 |
| 31 | 1 | 2 | 2 | 2 | 2 |
| 32 | 2 | 2 | 2 | 2 | 2 |

### 4.4.3 Experimental details

Each stock solution was made up at both pH 1 and 2 using sulphuric acid. The appropriate volume was taken from each stock solution and transferred to a 100cm$^3$ grade "A" volumetric flask which contained 10cm$^3$ of the 100 ppm gold chloride stock solution. Each solution was made up to the mark with the appropriate $H_2SO_4$ solution. Each solution was transferred to a 250 cm$^3$ conical flask. 0.2g of activated carbon (Eurocarb 1.4-2.00mm) was weighed out accurately and added to each conical flask. The flasks were sealed and put on a Stuart Scientific shaker. The shaker was set at speed 7 and the flasks were left to shake for the appropriate time combination.

After the time had elapsed, the solutions were filtered and the level of gold remaining in solution was measured using atomic absorption spectrophotometry.

(NOTE: It is important to filter each solution as fine particles of carbon possibly produced by abrasion can block the delivery tube of the spectrometer and affect the flow rate and hence the absorbance.)

The response (i.e. the mg's of gold adsorbed per kilogram of activated carbon) was calculated for all solutions by the following equation:

$$\text{mg gold adsorbed per kg of carbon} = \frac{([Au]_0 - [Au]_t)(1000)}{10\ (M_c)}$$

$[Au]_0$ = Initial concentration of gold (ppm)
$[Au]_t$ = Final concentration of gold (ppm)
$M_c$ = Mass of carbon (g)

( Note that $[Au]_0$ was equal to 10 ppm in all cases except for those solutions which contained both copper(II) and thiourea at level two in which case the initial signal was measured.)

The results were analysed by the statistical software package MINITAB.

## 4.5 Results and discussion

The column labelled "Gold" in tables 4.4, 4.5 and 4.6 refers to the response i.e. the mg's of gold adsorbed per kg of carbon. Table 4.4 illustrates the results of each observation. Table 4.5 illustrates the mean gold adsorbed at both factor levels 1 and 2. The number of observations for each factor is equal to 32. Table 4.6 illustrates the

**Table 4.4** Gold Adsorbed at each factor combination

| ROW | Fe | Cu | pH | Tu | Time | Gold |
|---|---|---|---|---|---|---|
| 1 | 1 | 1 | 1 | 1 | 1 | 1.20200 |
| 2 | 1 | 1 | 1 | 1 | 1 | 1.15600 |
| 3 | 2 | 1 | 1 | 1 | 1 | 1.01400 |
| 4 | 2 | 1 | 1 | 1 | 1 | 1.15300 |
| 5 | 1 | 2 | 1 | 1 | 1 | 1.11800 |
| 6 | 1 | 2 | 1 | 1 | 1 | 1.19300 |
| 7 | 2 | 2 | 1 | 1 | 1 | 0.99010 |
| 8 | 2 | 2 | 1 | 1 | 1 | 1.01000 |
| 9 | 1 | 1 | 2 | 1 | 1 | 0.98350 |
| 10 | 1 | 1 | 2 | 1 | 1 | 1.08200 |
| 11 | 2 | 1 | 2 | 1 | 1 | 1.08400 |
| 12 | 2 | 1 | 2 | 1 | 1 | 1.08300 |
| 13 | 1 | 2 | 2 | 1 | 1 | 1.03800 |
| 14 | 1 | 2 | 2 | 1 | 1 | 1.11800 |
| 15 | 2 | 2 | 2 | 1 | 1 | 1.07400 |
| 16 | 2 | 2 | 2 | 1 | 1 | 1.09700 |
| 17 | 1 | 1 | 1 | 2 | 1 | 0.06773 |
| 18 | 1 | 1 | 1 | 2 | 1 | 0.06783 |
| 19 | 2 | 1 | 1 | 2 | 1 | 0.07420 |
| 20 | 2 | 1 | 1 | 2 | 1 | 0.07642 |
| 21 | 1 | 2 | 1 | 2 | 1 | 0.14260 |
| 22 | 1 | 2 | 1 | 2 | 1 | 0.03063 |
| 23 | 2 | 2 | 1 | 2 | 1 | 0.15590 |
| 24 | 2 | 2 | 1 | 2 | 1 | 0.21850 |
| 25 | 1 | 1 | 2 | 2 | 1 | 0.33860 |
| 26 | 1 | 1 | 2 | 2 | 1 | 0.35580 |
| 27 | 2 | 1 | 2 | 2 | 1 | 0.26020 |
| 28 | 2 | 1 | 2 | 2 | 1 | 0.18490 |
| 29 | 1 | 2 | 2 | 2 | 1 | 0.13000 |
| 30 | 1 | 2 | 2 | 2 | 1 | 0.20310 |
| 31 | 2 | 2 | 2 | 2 | 1 | 0.12690 |
| 32 | 2 | 2 | 2 | 2 | 1 | 0.13470 |
| 33 | 1 | 1 | 1 | 1 | 2 | 3.24700 |
| 34 | 1 | 1 | 1 | 1 | 2 | 3.38100 |
| 35 | 2 | 1 | 1 | 1 | 2 | 2.89200 |
| 36 | 2 | 1 | 1 | 1 | 2 | 3.13200 |
| 37 | 1 | 2 | 1 | 1 | 2 | 3.20500 |
| 38 | 1 | 2 | 1 | 1 | 2 | 3.18200 |
| 39 | 2 | 2 | 1 | 1 | 2 | 2.93600 |
| 40 | 2 | 2 | 1 | 1 | 2 | 2.85900 |

**Table 4.4** Continued...

| | | | | | | |
|---|---|---|---|---|---|---|
| 41 | 1 | 1 | 2 | 1 | 2 | 2.97000 |
| 42 | 1 | 1 | 2 | 1 | 2 | 3.02100 |
| 43 | 2 | 1 | 2 | 1 | 2 | 2.59900 |
| 44 | 2 | 1 | 2 | 1 | 2 | 2.56200 |
| 45 | 1 | 2 | 2 | 1 | 2 | 3.03500 |
| 46 | 1 | 2 | 2 | 1 | 2 | 2.78100 |
| 47 | 2 | 2 | 2 | 1 | 2 | 2.75900 |
| 48 | 2 | 2 | 2 | 1 | 2 | 2.48000 |
| 49 | 1 | 1 | 1 | 2 | 2 | 0.22220 |
| 50 | 1 | 1 | 1 | 2 | 2 | 0.34720 |
| 51 | 2 | 1 | 1 | 2 | 2 | 0.43940 |
| 52 | 2 | 1 | 1 | 2 | 2 | 0.41980 |
| 53 | 1 | 2 | 1 | 2 | 2 | 0.22360 |
| 54 | 1 | 2 | 1 | 2 | 2 | 0.34160 |
| 55 | 2 | 2 | 1 | 2 | 2 | 0.23230 |
| 56 | 2 | 2 | 1 | 2 | 2 | 0.33700 |
| 57 | 1 | 1 | 2 | 2 | 2 | 0.65970 |
| 58 | 1 | 1 | 2 | 2 | 2 | 0.58940 |
| 59 | 2 | 1 | 2 | 2 | 2 | 0.43080 |
| 60 | 2 | 1 | 2 | 2 | 2 | 0.52500 |
| 61 | 1 | 2 | 2 | 2 | 2 | 0.31260 |
| 62 | 1 | 2 | 2 | 2 | 2 | 0.42340 |
| 63 | 2 | 2 | 2 | 2 | 2 | 0.49320 |
| 64 | 2 | 2 | 2 | 2 | 2 | 0.49320 |

**Table 4.5** Mean Gold Adsorbed at each factor level

| Fe | N | Gold |
|---|---|---|
| 1 | 32 | 1.1928 |
| 2 | 32 | 1.1040 |

| Cu | N | Gold |
|---|---|---|
| 1 | 32 | 1.1756 |
| 2 | 32 | 1.1211 |

| pH | N | Gold |
|---|---|---|
| 1 | 32 | 1.1583 |
| 2 | 32 | 1.1384 |

| Tu | N | Gold |
|---|---|---|
| 1 | 32 | 2.0136 |
| 2 | 32 | 0.2831 |

| Time | N | Gold |
|---|---|---|
| 1 | 32 | 0.6239 |
| 2 | 32 | 1.6729 |

| Fe | Cu | N | Gold |
|---|---|---|---|
| 1 | 1 | 16 | 1.2307 |
| 1 | 2 | 16 | 1.1548 |
| 2 | 1 | 16 | 1.1206 |
| 2 | 2 | 16 | 1.0873 |

| Fe | pH | N | Gold |
|---|---|---|---|
| 1 | 1 | 16 | 1.1955 |
| 1 | 2 | 16 | 1.1901 |
| 2 | 1 | 16 | 1.1212 |
| 2 | 2 | 16 | 1.0867 |

| Fe | Tu | N | Gold |
|---|---|---|---|
| 1 | 1 | 16 | 2.1070 |
| 1 | 2 | 16 | 0.2785 |
| 2 | 1 | 16 | 1.9203 |
| 2 | 2 | 16 | 0.2877 |

| Fe | Time | N | Gold |
|---|---|---|---|
| 1 | 1 | 16 | 0.6392 |
| 1 | 2 | 16 | 1.7464 |
| 2 | 1 | 16 | 0.6086 |
| 2 | 2 | 16 | 1.5994 |

| Cu | pH | N | Gold |
|---|---|---|---|
| 1 | 1 | 16 | 1.1807 |
| 1 | 2 | 16 | 1.1706 |
| 2 | 1 | 16 | 1.1360 |
| 2 | 2 | 16 | 1.1062 |

| Cu | Tu | N | Gold |
|---|---|---|---|
| 1 | 1 | 16 | 2.0351 |
| 1 | 2 | 16 | 0.3162 |
| 2 | 1 | 16 | 1.9922 |
| 2 | 2 | 16 | 0.2500 |

| Cu | Time | N | Gold |
|---|---|---|---|
| 1 | 1 | 16 | 0.6364 |
| 1 | 2 | 16 | 1.7148 |
| 2 | 1 | 16 | 0.6113 |
| 2 | 2 | 16 | 1.6309 |

| pH | Tu | N | Gold |
|---|---|---|---|
| 1 | 1 | 16 | 2.1044 |
| 1 | 2 | 16 | 0.2123 |
| 2 | 1 | 16 | 1.9229 |
| 2 | 2 | 16 | 0.3538 |

| pH | Time | N | Gold |
|---|---|---|---|
| 1 | 1 | 16 | 0.6044 |
| 1 | 2 | 16 | 1.7123 |
| 2 | 1 | 16 | 0.6434 |
| 2 | 2 | 16 | 1.6334 |

| Tu | Time | N | Gold |
|---|---|---|---|
| 1 | 1 | 16 | 1.0872 |
| 1 | 2 | 16 | 2.9401 |
| 2 | 1 | 16 | 0.1605 |
| 2 | 2 | 16 | 0.4056 |

| Fe | Cu | pH | N | Gold |
|---|---|---|---|---|
| 1 | 1 | 1 | 8 | 1.2114 |
| 1 | 1 | 2 | 8 | 1.2500 |
| 1 | 2 | 1 | 8 | 1.1796 |
| 1 | 2 | 2 | 8 | 1.1301 |
| 2 | 1 | 1 | 8 | 1.1501 |
| 2 | 1 | 2 | 8 | 1.0911 |
| 2 | 2 | 1 | 8 | 1.0924 |
| 2 | 2 | 2 | 8 | 1.0822 |

**Table 4.5** Continued...

| Fe | Cu | Tu | N | Gold |
|---|---|---|---|---|
| 1 | 1 | 1 | 8 | 2.1303 |
| 1 | 1 | 2 | 8 | 0.3311 |
| 1 | 2 | 1 | 8 | 2.0838 |
| 1 | 2 | 2 | 8 | 0.2259 |
| 2 | 1 | 1 | 8 | 1.9399 |
| 2 | 1 | 2 | 8 | 0.3013 |
| 2 | 2 | 1 | 8 | 1.9006 |
| 2 | 2 | 2 | 8 | 0.2740 |

| Fe | Cu | Time | N | Gold |
|---|---|---|---|---|
| 1 | 1 | 1 | 8 | 0.6567 |
| 1 | 1 | 2 | 8 | 1.8047 |
| 1 | 2 | 1 | 8 | 0.6217 |
| 1 | 2 | 2 | 8 | 1.6880 |
| 2 | 1 | 1 | 8 | 0.6162 |
| 2 | 1 | 2 | 8 | 1.6250 |
| 2 | 2 | 1 | 8 | 0.6009 |
| 2 | 2 | 2 | 8 | 1.5737 |

| Fe | pH | Tu | N | Gold |
|---|---|---|---|---|
| 1 | 1 | 1 | 8 | 2.2105 |
| 1 | 1 | 2 | 8 | 0.1804 |
| 1 | 2 | 1 | 8 | 2.0036 |
| 1 | 2 | 2 | 8 | 0.3766 |
| 2 | 1 | 1 | 8 | 1.9983 |
| 2 | 1 | 2 | 8 | 0.2442 |
| 2 | 2 | 1 | 8 | 1.8422 |
| 2 | 2 | 2 | 8 | 0.3311 |

| Fe | pH | Time | N | Gold |
|---|---|---|---|---|
| 1 | 1 | 1 | 8 | 0.6222 |
| 1 | 1 | 2 | 8 | 1.7687 |
| 1 | 2 | 1 | 8 | 0.6561 |
| 1 | 2 | 2 | 8 | 1.7240 |
| 2 | 1 | 1 | 8 | 0.5865 |
| 2 | 1 | 2 | 8 | 1.6559 |
| 2 | 2 | 1 | 8 | 0.6306 |
| 2 | 2 | 2 | 8 | 1.5428 |

| Fe | Tu | Time | N | Gold |
|---|---|---|---|---|
| 1 | 1 | 1 | 8 | 1.1113 |
| 1 | 1 | 2 | 8 | 3.1028 |
| 1 | 2 | 1 | 8 | 0.1670 |
| 1 | 2 | 2 | 8 | 0.3900 |
| 2 | 1 | 1 | 8 | 1.0631 |
| 2 | 1 | 2 | 8 | 2.7774 |
| 2 | 2 | 1 | 8 | 0.1540 |
| 2 | 2 | 2 | 8 | 0.4213 |

| Cu | pH | Tu | N | Gold |
|---|---|---|---|---|
| 1 | 1 | 1 | 8 | 2.1471 |
| 1 | 1 | 2 | 8 | 0.2143 |
| 1 | 2 | 1 | 8 | 1.9231 |
| 1 | 2 | 2 | 8 | 0.4180 |
| 2 | 1 | 1 | 8 | 2.0616 |
| 2 | 1 | 2 | 8 | 0.2103 |
| 2 | 2 | 1 | 8 | 1.9227 |
| 2 | 2 | 2 | 8 | 0.2896 |

| Cu | pH | Time | N | Gold |
|---|---|---|---|---|
| 1 | 1 | 1 | 8 | 0.6014 |
| 1 | 1 | 2 | 8 | 1.7601 |
| 1 | 2 | 1 | 8 | 0.6715 |
| 1 | 2 | 2 | 8 | 1.6696 |
| 2 | 1 | 1 | 8 | 0.6073 |
| 2 | 1 | 2 | 8 | 1.6646 |
| 2 | 2 | 1 | 8 | 0.6152 |
| 2 | 2 | 2 | 8 | 1.5972 |

| Cu | Tu | Time | N | Gold |
|---|---|---|---|---|
| 1 | 1 | 1 | 8 | 1.0947 |
| 1 | 1 | 2 | 8 | 2.9755 |
| 1 | 2 | 1 | 8 | 0.1782 |
| 1 | 2 | 2 | 8 | 0.4542 |
| 2 | 1 | 1 | 8 | 1.0798 |
| 2 | 1 | 2 | 8 | 2.9046 |
| 2 | 2 | 1 | 8 | 0.1428 |
| 2 | 2 | 2 | 8 | 0.3571 |

| pH | Tu | Time | N | Gold |
|---|---|---|---|---|
| 1 | 1 | 1 | 8 | 1.1045 |
| 1 | 1 | 2 | 8 | 3.1042 |
| 1 | 2 | 1 | 8 | 0.1042 |
| 1 | 2 | 2 | 8 | 0.3204 |
| 2 | 1 | 1 | 8 | 1.0699 |
| 2 | 1 | 2 | 8 | 2.7759 |
| 2 | 2 | 1 | 8 | 0.2168 |
| 2 | 2 | 2 | 8 | 0.4909 |

**Table 4.6** Analysis of Variance for Gold Adsorbed

| Source | DF | SS | MS | F | P |
|---|---|---|---|---|---|
| Fe | 1 | 0.1262 | 0.1262 | 21.99 | 0.000 |
| Cu | 1 | 0.0477 | 0.0477 | 8.30 | 0.007 |
| pH | 1 | 0.0064 | 0.0064 | 1.11 | 0.300 |
| Tu | 1 | 47.9179 | 47.9179 | 8E+03 | 0.000 |
| Time | 1 | 17.6062 | 17.6062 | 3E+03 | 0.000 |
| Fe*Cu | 1 | 0.0072 | 0.0072 | 1.26 | 0.270 |
| Fe*pH | 1 | 0.0034 | 0.0034 | 0.59 | 0.447 |
| Fe*Tu | 1 | 0.1535 | 0.1535 | 26.76 | 0.000 |
| Fe*Time | 1 | 0.0542 | 0.0542 | 9.44 | 0.004 |
| Cu*pH | 1 | 0.0015 | 0.0015 | 0.27 | 0.609 |
| Cu*Tu | 1 | 0.0022 | 0.0022 | 0.38 | 0.542 |
| Cu*Time | 1 | 0.0138 | 0.0138 | 2.41 | 0.130 |
| pH*Tu | 1 | 0.4173 | 0.4173 | 72.73 | 0.000 |
| pH*Time | 1 | 0.0556 | 0.0556 | 9.69 | 0.004 |
| Tu*Time | 1 | 10.3386 | 10.3386 | 2E+03 | 0.000 |
| Fe*Cu*pH | 1 | 0.0188 | 0.0188 | 3.27 | 0.080 |
| Fe*Cu*Tu | 1 | 0.0050 | 0.0050 | 0.86 | 0.360 |
| Fe*Cu*Time | 1 | 0.0021 | 0.0021 | 0.36 | 0.551 |
| Fe*pH*Tu | 1 | 0.0256 | 0.0256 | 4.47 | 0.042 |
| Fe*pH*Time | 1 | 0.0062 | 0.0062 | 1.08 | 0.307 |
| Fe*Tu*Time | 1 | 0.1035 | 0.1035 | 18.03 | 0.000 |
| Cu*pH*Tu | 1 | 0.0439 | 0.0439 | 7.65 | 0.009 |
| Cu*pH*Time | 1 | 0.0073 | 0.0073 | 1.27 | 0.268 |
| Cu*Tu*Time | 1 | 0.0000 | 0.0000 | 0.01 | 0.940 |
| pH*Tu*Time | 1 | 0.1237 | 0.1237 | 21.57 | 0.000 |
| Fe*Cu*pH*Tu | 1 | 0.0047 | 0.0047 | 0.81 | 0.374 |
| Fe*Cu*pH*Time | 1 | 0.0171 | 0.0171 | 2.98 | 0.094 |
| Fe*Cu*Tu*Time | 1 | 0.0052 | 0.0052 | 0.91 | 0.348 |
| Fe*pH*Tu*Time | 1 | 0.0166 | 0.0166 | 2.89 | 0.099 |
| Cu*pH*Tu*Time | 1 | 0.0048 | 0.0048 | 0.83 | 0.368 |
| Fe*Cu*pH*Tu*Time | 1 | 0.0062 | 0.0062 | 1.08 | 0.306 |
| Error | 32 | 0.1836 | 0.0057 | | |
| Total | 63 | 77.3260 | 1.2274 | | |

analysis of variance for the factors in the experiment. The factor which has the largest F-Value associated with it (and therefore the smallest P-Value) has the most significant effect on the amount of gold adsorbed.

( NOTE: Some of the P-Values have been rounded off to three decimal places by the computer even though they are not equal to zero.)

From Table 4.6 it can be seen that a change in the level of thiourea from 0.2g/dm$^3$ to 2g/dm$^3$ has the most significant effect on the amount of gold adsorbed (F=8E+3). Only 14% of that adsorbed at level 1 is adsorbed at level 2. This may be due to the fact that activated carbon has a very high capacity for thiourea and therefore the gold-thiourea complex finds it difficult to compete with thiourea for sites on the carbon.

The next most significant effect is that of time (F=3E+3). By changing the contact time from 30 minutes to 120 minutes, the amount of gold adsorbed increases by a factor of 2.7. This increase is expected simply because the contact time with the carbon has increased and hence the level of gold in solution decreases. Since the rate of adsorption is first order [5], the level of gold in solution will decrease exponentially according to the equation:

$$[Au]_t = [Au]_o e^{-kt}$$

An important point is that the significance of a change in the time level is not as significant as a change in the level of thiourea. Therefore, a decrease in the level of thiourea may have a greater significance economically than having to increase the contact time.

The next most significant effect is that of the interaction effect of time and thiourea (F=2E+3), however this may be expected since their individual effects are very significant. It can also be seen that higher order effects involving time and thiourea are significant.

By considering Table 4.5, it can be seen that by changing the pH, copper(II) and iron(III) level there is only a slight change in the amount of gold adsorbed. It becomes difficult to interpret the effects of copper(II), iron(III) and pH in the presence of factors which have a very significant effect i.e. the effects of thiourea and time have "masked" the effects of copper(II), iron(III) and pH.

The next most significant effect is that of pH and thiourea i.e. pH*thiourea (F=73), iron(III) and thiourea (Fe*thiourea, F=27) and iron(III) alone (F=22). Although increasing the pH from 1 to 2 has the effect of slightly decreasing the amount of gold adsorbed, there would in fact be a large economic saving in reagent use. Ten times less sulphuric acid would be required and this may offset the disadvantage of a decrease in the level of adsorption. By increasing the level of iron(III) from 500 ppm to 1500 ppm, there is a slight decrease in the amount of gold adsorbed. Iron is an active oxidant for gold however and so the loss in gold may be outweighed by the benefit of the presence of an oxidant for the dissolution of gold. Another disadvantage of the increase in the level of iron(III) is the loss of thiourea due to complex formation although the formation has been reported to be slow [6].

## 4.6 THE EFFECT OF IRON(III), COPPER(II), pH, TIME AND THIOUREA CONCENTRATION ON THE ADSORPTION OF GOLD ONTO MODIFIED PEAT

In order to use adsorbents for applications of an industrial scale, low cost processes for production of these adsorbents must be developed. Naturally occurring materials which are readily available can be used. Various agricultural products and by-products have been shown to possess ion exchange properties in the modified [7,8] and unmodified form [9]. Peat, which is a widely available and abundant natural substance resulting from the decay of plant material, under certain environmental conditions, has cation exchange properties. It has been shown that peat exhibits enhanced cation exchange properties after treatment with sulphuric acid [10,11,12,13]. Peat is easy to mine and is relatively inexpensive which makes its use for industrial applications attractive. The sulphuric acid treatment process which results in a product which is granular in nature is both inexpensive in its use of small amounts of acid and simple in the mere heating of the wet peat with acid. Sulphuric acid treated peat has been used to remove metal ions [14,15,16,17,13]. The preparation of the sulphuric acid treated peat has been described by Ansted and MacCarthy [18].

### 4.6.1 Reagents

Horticultural moss peat (Bord Na Mona).
Concentrated sulphuric acid (Riedel-De-Haen).

### 4.6.2 Experimental details

40g of horticultural moss peat were weighed in a 800cm$^3$ pyrex beaker. In a fume hood, 133cm$^3$ of concentrated sulphuric acid (i.e. 4cm$^3$ per 1.2g of dry peat ) were added slowly with care. This was heated to between 160 and 180°C on a hot plate for two hours with regular stirring. The product was allowed to cool and then washed with deionised water until the pH of the wash water was equal to that of the deionised water. The material was then dried in an oven at 110°C for 24 hours. The modified peat was then sieved and divided according to particle size. The particle size in the range 1.4-2.0mm was used for all subsequent experiments.

In this experiment, the same five factors were chosen. Modified peat, size range 1.4 to 2.0mm was used instead of "EUROCARB" activated carbon. The levels of each factor were chosen as follows:

| **Factor** | **Level 1** | **level 2** |
|---|---|---|
| Iron(III) | 500 ppm | 1500 ppm |
| Copper(II) | 100 ppm | 500 ppm |
| pH | 1 | 2 |
| Thiourea | 0.2 g/dm$^3$ | 1 g/dm$^3$ |
| Time | 30 Mins. | 120 Mins. |

Level 2 of thiourea was reduced from 2g/dm$^3$ to 1g/dm$^3$ because in the previous experiment, a white precipitate developed in solutions which had both copper(II) and thiourea at level 2. The level of copper in the precipitate was found to be, by analysis, 18.5% and so was thought to be the copper-thiourea complex $[Cu_2(Tu)_6]SO_4.H_2O$. The effects of copper(II), pH and iron(III) may also become clearer if the level of thiourea is reduced.

### 4.6.3 Experimental details

See section 4.4.3

## 4.7 Results and discussion

Table 4.8 illustrates the mean gold adsorbed per kilogram of carbon at each factor level. Table 4.9 illustrates the analysis of variance for the factors in the experiment from which it can be seen that a change in the time level is the most significant effect (F=3E+3). This was expected as in the case of section 4.2. The next most significant effect is that of thiourea (F=572). All the P-Values for the single factor effects are less than 0.001 i.e. 99.9% of the time, it can be said that a change in the level of each factor is significant. Again it can be seen that the interaction effect of time and thiourea is very significant, however this is as expected. The next most significant effects are those of time and pH (F=234) and copper and time (F=131) but again these effects involve time i.e. higher order interactions appear significant because the single factor effect is very significant.

The evidence from the means in Table 4.8 suggest that increasing the level of iron(III) from 500 ppm to 1500 ppm enhances the adsorption of gold onto modified peat whereas increasing the copper level from 100 ppm to 500 ppm inhibits the adsorption of gold. This effect with iron(III) can be seen from the data where n=16 i.e. the effect of iron(III) with each factor. If the gold adsorbed with iron(III) at level 1 is compared with the gold adsorbed at level 2 at the same level of the compared factor, it can be seen that there is a slight increase in the response and this information is reliable because n=16. As iron(III) is compared with 2 other factors, n=8 and the conclusions that can be drawn from the data becomes less reliable although the same trends are present. The inhibition effect of copper can be seen similarly. This effect is very marked when comparing copper(II) at levels 1 and 2 to pH at levels 1 and 2. At pH=2, there is a change in the response by 0.2 when the level of copper is increased from level 1 to level 2. This effect is not surprising since F=39, the largest F-Value in the 2-factor interaction column which does not involve thiourea and time. The effect of pH appears to be more significant than that in a change in the level of iron(III).

**Table 4.7** Gold Adsorbed at each factor combination

| ROW | Fe | Cu | Tu | Time | pH | Gold |
|---|---|---|---|---|---|---|
| 1 | 1 | 1 | 1 | 1 | 1 | 0.7124 |
| 2 | 1 | 1 | 1 | 1 | 1 | 0.7156 |
| 3 | 2 | 1 | 1 | 1 | 1 | 0.7760 |
| 4 | 2 | 1 | 1 | 1 | 1 | 0.7278 |
| 5 | 1 | 2 | 1 | 1 | 1 | 0.7144 |
| 6 | 1 | 2 | 1 | 1 | 1 | 0.6796 |
| 7 | 2 | 2 | 1 | 1 | 1 | 0.6538 |
| 8 | 2 | 2 | 1 | 1 | 1 | 0.7175 |
| 9 | 1 | 1 | 2 | 1 | 1 | 0.4592 |
| 10 | 1 | 1 | 2 | 1 | 1 | 0.5234 |
| 11 | 2 | 1 | 2 | 1 | 1 | 0.6807 |
| 12 | 2 | 1 | 2 | 1 | 1 | 0.6971 |
| 13 | 1 | 2 | 2 | 1 | 1 | 1.2440 |
| 14 | 1 | 2 | 2 | 1 | 1 | 1.2150 |
| 15 | 2 | 2 | 2 | 1 | 1 | 0.5848 |
| 16 | 2 | 2 | 2 | 1 | 1 | 0.6041 |
| 17 | 1 | 1 | 1 | 2 | 1 | 1.5630 |
| 18 | 1 | 1 | 1 | 2 | 1 | 1.6850 |
| 19 | 2 | 1 | 1 | 2 | 1 | 1.6450 |
| 20 | 2 | 1 | 1 | 2 | 1 | 1.6420 |
| 21 | 1 | 2 | 1 | 2 | 1 | 1.4050 |
| 22 | 1 | 2 | 1 | 2 | 1 | 1.4300 |
| 23 | 2 | 2 | 1 | 2 | 1 | 1.4200 |
| 24 | 2 | 2 | 1 | 2 | 1 | 1.4620 |
| 25 | 1 | 1 | 2 | 2 | 1 | 0.8689 |
| 26 | 1 | 1 | 2 | 2 | 1 | 0.7460 |
| 27 | 2 | 1 | 2 | 2 | 1 | 1.1760 |
| 28 | 2 | 1 | 2 | 2 | 1 | 1.1670 |
| 29 | 1 | 2 | 2 | 2 | 1 | 0.6843 |
| 30 | 1 | 2 | 2 | 2 | 1 | 0.6329 |
| 31 | 2 | 2 | 2 | 2 | 1 | 0.9876 |
| 32 | 2 | 2 | 2 | 2 | 1 | 0.8968 |
| 33 | 1 | 1 | 1 | 1 | 2 | 0.5809 |
| 34 | 1 | 1 | 1 | 1 | 2 | 0.5751 |
| 35 | 2 | 1 | 1 | 1 | 2 | 0.6383 |
| 36 | 2 | 1 | 1 | 1 | 2 | 0.6612 |
| 37 | 1 | 2 | 1 | 1 | 2 | 0.4713 |
| 38 | 1 | 2 | 1 | 1 | 2 | 0.4526 |
| 39 | 2 | 2 | 1 | 1 | 2 | 0.5338 |
| 40 | 2 | 2 | 1 | 1 | 2 | 0.5170 |

**Table 4.7** Continued...

| | | | | | | |
|---|---|---|---|---|---|---|
| 41 | 1 | 1 | 2 | 1 | 2 | 0.3363 |
| 42 | 1 | 1 | 2 | 1 | 2 | 0.3465 |
| 43 | 2 | 1 | 2 | 1 | 2 | 0.4603 |
| 44 | 2 | 1 | 2 | 1 | 2 | 0.4849 |
| 45 | 1 | 2 | 2 | 1 | 2 | 0.4800 |
| 46 | 1 | 2 | 2 | 1 | 2 | 0.4590 |
| 47 | 2 | 2 | 2 | 1 | 2 | 0.3033 |
| 48 | 2 | 2 | 2 | 1 | 2 | 0.2897 |
| 49 | 1 | 1 | 1 | 2 | 2 | 1.6920 |
| 50 | 1 | 1 | 1 | 2 | 2 | 1.6640 |
| 51 | 2 | 1 | 1 | 2 | 2 | 1.6460 |
| 52 | 2 | 1 | 1 | 2 | 2 | 1.6490 |
| 53 | 1 | 2 | 1 | 2 | 2 | 1.4160 |
| 54 | 1 | 2 | 1 | 2 | 2 | 1.3350 |
| 55 | 2 | 2 | 1 | 2 | 2 | 1.3860 |
| 56 | 2 | 2 | 1 | 2 | 2 | 1.3670 |
| 57 | 1 | 1 | 2 | 2 | 2 | 1.2670 |
| 58 | 1 | 1 | 2 | 2 | 2 | 1.1580 |
| 59 | 2 | 1 | 2 | 2 | 2 | 1.2560 |
| 60 | 2 | 1 | 2 | 2 | 2 | 1.3940 |
| 61 | 1 | 2 | 2 | 2 | 2 | 0.8307 |
| 62 | 1 | 2 | 2 | 2 | 2 | 0.9061 |
| 63 | 2 | 2 | 2 | 2 | 2 | 0.9970 |
| 64 | 2 | 2 | 2 | 2 | 2 | 1.2070 |

**Table 4.8** Mean Gold Adsorbed at each factor level

| Fe | N | Gold |
|---|---|---|
| 1 | 32 | 0.91404 |
| 2 | 32 | 0.95715 |

| Cu | N | Gold |
|---|---|---|
| 1 | 32 | 0.98733 |
| 2 | 32 | 0.88385 |

| Tu | N | Gold |
|---|---|---|
| 1 | 32 | 1.0792 |
| 2 | 32 | 0.7920 |

| Time | N | Gold |
|---|---|---|
| 1 | 32 | 0.6030 |
| 2 | 32 | 1.2682 |

| pH | N | Gold |
|---|---|---|
| 1 | 32 | 0.97240 |
| 2 | 32 | 0.89878 |

| Fe | Cu | N | Gold |
|---|---|---|---|
| 1 | 1 | 16 | 0.9308 |
| 1 | 2 | 16 | 0.8972 |
| 2 | 1 | 16 | 1.0438 |
| 2 | 2 | 16 | 0.8705 |

| Fe | Tu | N | Gold |
|---|---|---|---|
| 1 | 1 | 16 | 1.0682 |
| 1 | 2 | 16 | 0.7598 |
| 2 | 1 | 16 | 1.0901 |
| 2 | 2 | 16 | 0.8241 |

| Fe | Time | N | Gold |
|---|---|---|---|
| 1 | 1 | 16 | 0.6228 |
| 1 | 2 | 16 | 1.2052 |
| 2 | 1 | 16 | 0.5831 |
| 2 | 2 | 16 | 1.3312 |

| Fe | pH | N | Gold |
|---|---|---|---|
| 1 | 1 | 16 | 0.95492 |
| 1 | 2 | 16 | 0.87316 |
| 2 | 1 | 16 | 0.98989 |
| 2 | 2 | 16 | 0.92441 |

| Cu | Tu | N | Gold |
|---|---|---|---|
| 1 | 1 | 16 | 1.1608 |
| 1 | 2 | 16 | 0.8138 |
| 2 | 1 | 16 | 0.9976 |
| 2 | 2 | 16 | 0.7701 |

| Cu | Time | N | Gold |
|---|---|---|---|
| 1 | 1 | 16 | 0.5860 |
| 1 | 2 | 16 | 1.3887 |
| 2 | 1 | 16 | 0.6200 |
| 2 | 2 | 16 | 1.1477 |

| Cu | pH | N | Gold |
|---|---|---|---|
| 1 | 1 | 16 | 0.98657 |
| 1 | 2 | 16 | 0.98809 |
| 2 | 1 | 16 | 0.95824 |
| 2 | 2 | 16 | 0.80947 |

| Tu | Time | N | Gold |
|---|---|---|---|
| 1 | 1 | 16 | 0.6330 |
| 1 | 2 | 16 | 1.5254 |
| 2 | 1 | 16 | 0.5730 |
| 2 | 2 | 16 | 1.0110 |

| Tu | pH | N | Gold |
|---|---|---|---|
| 1 | 1 | 16 | 1.1218 |
| 1 | 2 | 16 | 1.0366 |
| 2 | 1 | 16 | 0.8230 |
| 2 | 2 | 16 | 0.7610 |

| Time | pH | N | Gold |
|---|---|---|---|
| 1 | 1 | 16 | 0.7316 |
| 1 | 2 | 16 | 0.4744 |
| 2 | 1 | 16 | 1.2132 |
| 2 | 2 | 16 | 1.3232 |

| Fe | Cu | Tu | N | Gold |
|---|---|---|---|---|
| 1 | 1 | 1 | 8 | 1.1485 |
| 1 | 1 | 2 | 8 | 0.7132 |
| 1 | 2 | 1 | 8 | 0.9880 |
| 1 | 2 | 2 | 8 | 0.8065 |
| 2 | 1 | 1 | 8 | 1.1732 |
| 2 | 1 | 2 | 8 | 0.9145 |
| 2 | 2 | 1 | 8 | 1.0071 |
| 2 | 2 | 2 | 8 | 0.7338 |

**Table 4.8** Continued...

| Fe | Cu | Time | N | Gold |
|---|---|---|---|---|
| 1 | 1 | 1 | 8 | 0.5312 |
| 1 | 1 | 2 | 8 | 1.3305 |
| 1 | 2 | 1 | 8 | 0.7145 |
| 1 | 2 | 2 | 8 | 1.0800 |
| 2 | 1 | 1 | 8 | 0.6408 |
| 2 | 1 | 2 | 8 | 1.4469 |
| 2 | 2 | 1 | 8 | 0.5255 |
| 2 | 2 | 2 | 8 | 1.2154 |

| Fe | Cu | pH | N | Gold |
|---|---|---|---|---|
| 1 | 1 | 1 | 8 | 0.9092 |
| 1 | 1 | 2 | 8 | 0.9525 |
| 1 | 2 | 1 | 8 | 1.0006 |
| 1 | 2 | 2 | 8 | 0.7938 |
| 2 | 1 | 1 | 8 | 1.0640 |
| 2 | 1 | 2 | 8 | 1.0237 |
| 2 | 2 | 1 | 8 | 0.9158 |
| 2 | 2 | 2 | 8 | 0.8251 |

| Fe | Tu | Time | N | Gold |
|---|---|---|---|---|
| 1 | 1 | 1 | 8 | 0.6127 |
| 1 | 1 | 2 | 8 | 1.5237 |
| 1 | 2 | 1 | 8 | 0.6329 |
| 1 | 2 | 2 | 8 | 0.8867 |
| 2 | 1 | 1 | 8 | 0.6532 |
| 2 | 1 | 2 | 8 | 1.5271 |
| 2 | 2 | 1 | 8 | 0.5131 |
| 2 | 2 | 2 | 8 | 1.1352 |

| Fe | Tu | pH | N | Gold |
|---|---|---|---|---|
| 1 | 1 | 1 | 8 | 1.1131 |
| 1 | 1 | 2 | 8 | 1.0234 |
| 1 | 2 | 1 | 8 | 0.7967 |
| 1 | 2 | 2 | 8 | 0.7229 |
| 2 | 1 | 1 | 8 | 1.1305 |
| 2 | 1 | 2 | 8 | 1.0498 |
| 2 | 2 | 1 | 8 | 0.8493 |
| 2 | 2 | 2 | 8 | 0.7990 |

| Fe | Time | pH | N | Gold |
|---|---|---|---|---|
| 1 | 1 | 1 | 8 | 0.7829 |
| 1 | 1 | 2 | 8 | 0.4627 |
| 1 | 2 | 1 | 8 | 1.1269 |
| 1 | 2 | 2 | 8 | 1.2836 |
| 2 | 1 | 1 | 8 | 0.6802 |
| 2 | 1 | 2 | 8 | 0.4861 |
| 2 | 2 | 1 | 8 | 1.2996 |
| 2 | 2 | 2 | 8 | 1.3628 |

| Cu | Tu | Time | N | Gold |
|---|---|---|---|---|
| 1 | 1 | 1 | 8 | 0.6734 |
| 1 | 1 | 2 | 8 | 1.6482 |
| 1 | 2 | 1 | 8 | 0.4985 |
| 1 | 2 | 2 | 8 | 1.1291 |
| 2 | 1 | 1 | 8 | 0.5925 |
| 2 | 1 | 2 | 8 | 1.4026 |
| 2 | 2 | 1 | 8 | 0.6475 |
| 2 | 2 | 2 | 8 | 0.8928 |

| Cu | Tu | pH | N | Gold |
|---|---|---|---|---|
| 1 | 1 | 1 | 8 | 1.1833 |
| 1 | 1 | 2 | 8 | 1.1383 |
| 1 | 2 | 1 | 8 | 0.7898 |
| 1 | 2 | 2 | 8 | 0.8379 |
| 2 | 1 | 1 | 8 | 1.0603 |
| 2 | 1 | 2 | 8 | 0.9348 |
| 2 | 2 | 1 | 8 | 0.8562 |
| 2 | 2 | 2 | 8 | 0.6841 |

| Cu | Time | pH | N | Gold |
|---|---|---|---|---|
| 1 | 1 | 1 | 8 | 0.6615 |
| 1 | 1 | 2 | 8 | 0.5104 |
| 1 | 2 | 1 | 8 | 1.3116 |
| 1 | 2 | 2 | 8 | 1.4657 |
| 2 | 1 | 1 | 8 | 0.8016 |
| 2 | 1 | 2 | 8 | 0.4383 |
| 2 | 2 | 1 | 8 | 1.1148 |
| 2 | 2 | 2 | 8 | 1.1806 |

| Tu | Time | pH | N | Gold |
|---|---|---|---|---|
| 1 | 1 | 1 | 8 | 0.7121 |
| 1 | 1 | 2 | 8 | 0.5538 |
| 1 | 2 | 1 | 8 | 1.5315 |
| 1 | 2 | 2 | 8 | 1.5194 |
| 2 | 1 | 1 | 8 | 0.7510 |
| 2 | 1 | 2 | 8 | 0.3950 |
| 2 | 2 | 1 | 8 | 0.8949 |
| 2 | 2 | 2 | 8 | 1.1270 |

**Table 4.9** Analysis of Variance for Gold Adsorbed

| Source | DF | SS | MS | F | P |
|---|---|---|---|---|---|
| Fe | 1 | 0.0297 | 0.02973 | 12.90 | 0.001 |
| Cu | 1 | 0.1713 | 0.17132 | 74.33 | 0.000 |
| Tu | 1 | 1.3198 | 1.31983 | 572.63 | 0.000 |
| Time | 1 | 7.0801 | 7.08006 | 3E+03 | 0.000 |
| pH | 1 | 0.0867 | 0.08672 | 37.63 | 0.000 |
| Fe*Cu | 1 | 0.0782 | 0.07816 | 33.91 | 0.000 |
| Fe*Tu | 1 | 0.0072 | 0.00719 | 3.12 | 0.087 |
| Fe*Time | 1 | 0.1097 | 0.10969 | 47.59 | 0.000 |
| Fe*pH | 1 | 0.0011 | 0.00106 | 0.46 | 0.502 |
| Cu*Tu | 1 | 0.0572 | 0.05720 | 24.82 | 0.000 |
| Cu*Time | 1 | 0.3025 | 0.30246 | 131.23 | 0.000 |
| Cu*pH | 1 | 0.0904 | 0.09035 | 39.20 | 0.000 |
| Tu*Time | 1 | 0.8264 | 0.82644 | 358.57 | 0.000 |
| Tu*pH | 1 | 0.0022 | 0.00216 | 0.94 | 0.340 |
| Time*pH | 1 | 0.5392 | 0.53921 | 233.95 | 0.000 |
| Fe*Cu*Tu | 1 | 0.0721 | 0.07211 | 31.29 | 0.000 |
| Fe*Cu*Time | 1 | 0.1009 | 0.10089 | 43.77 | 0.000 |
| Fe*Cu*pH | 1 | 0.0398 | 0.03985 | 17.29 | 0.000 |
| Fe*Tu*Time | 1 | 0.1643 | 0.16428 | 71.27 | 0.000 |
| Fe*Tu*pH | 1 | 0.0002 | 0.00021 | 0.09 | 0.765 |
| Fe*Time*pH | 1 | 0.0482 | 0.04822 | 20.92 | 0.000 |
| Cu*Tu*Time | 1 | 0.0486 | 0.04864 | 21.10 | 0.000 |
| Cu*Tu*pH | 1 | 0.0195 | 0.01953 | 8.47 | 0.007 |
| Cu*Time*pH | 1 | 0.0153 | 0.01534 | 6.66 | 0.015 |
| Tu*Time*pH | 1 | 0.1952 | 0.19522 | 84.70 | 0.000 |
| Fe*Cu*Tu*Time | 1 | 0.0735 | 0.07350 | 31.89 | 0.000 |
| Fe*Cu*Tu*pH | 1 | 0.0274 | 0.02735 | 11.87 | 0.002 |
| Fe*Cu*Time*pH | 1 | 0.0072 | 0.00724 | 3.14 | 0.086 |
| Fe*Tu*Time*pH | 1 | 0.0166 | 0.01664 | 7.22 | 0.011 |
| Cu*Tu*Time*pH | 1 | 0.0163 | 0.01627 | 7.06 | 0.012 |
| Fe*Cu*Tu*Time*pH | 1 | 0.0061 | 0.00614 | 2.66 | 0.112 |
| Error | 32 | 0.0738 | 0.00230 | | |
| Total | 63 | 11.6268 | 0.18455 | | |

## 4.8 THE EFFECTS OF IRON(III), COPPER(II), TIME, pH AND CARBON TYPE ON THE ADSORPTION OF GOLD

The data from experiments 4.4 and 4.6 were combined to investigate the effects of copper(II), iron(III), pH, time and carbon type on the response. The levels of each factor were therefore as follows:

| **Factor** | **Level 1** | **level 2** |
|---|---|---|
| Iron(III) | 500 ppm | 1500 ppm |
| Copper(II) | 100 ppm | 500 ppm |
| pH | 1 | 2 |
| Time | 30 Mins. | 120 Mins. |
| Carbon type | EUROCARB | Modified Peat |

The factor thiourea could not be included because level 2 for thiourea was 2g/dm$^3$ and the only common level was level 1 i.e. 0.2g/dm$^3$.

## 4.9 Results and discussion

The results can be seen from the previous experiments.

From Table 4.12, the single factor with the highest F-Value is that of time (F=6E+3). The next most significant factor is that of carbon type, this fact is obvious from Tables 4.10 and 4.11 which suggests that modified peat adsorbs only 54% of that of activated carbon.

**Table 4.10** Gold Adsorbed at each factor combination

| ROW | Fe | Cu | pH | Time | Carbon | Gold |
|---|---|---|---|---|---|---|
| 1 | 1 | 1 | 1 | 1 | 1 | 1.2020 |
| 2 | 1 | 1 | 1 | 1 | 1 | 1.1560 |
| 3 | 2 | 1 | 1 | 1 | 1 | 1.0140 |
| 4 | 2 | 1 | 1 | 1 | 1 | 1.1530 |
| 5 | 1 | 2 | 1 | 1 | 1 | 1.1180 |
| 6 | 1 | 2 | 1 | 1 | 1 | 1.1930 |
| 7 | 2 | 2 | 1 | 1 | 1 | 0.9901 |
| 8 | 2 | 2 | 1 | 1 | 1 | 1.0100 |
| 9 | 1 | 1 | 2 | 1 | 1 | 0.9835 |
| 10 | 1 | 1 | 2 | 1 | 1 | 1.0820 |
| 11 | 2 | 1 | 2 | 1 | 1 | 1.0840 |
| 12 | 2 | 1 | 2 | 1 | 1 | 1.0830 |
| 13 | 1 | 2 | 2 | 1 | 1 | 1.0390 |
| 14 | 1 | 2 | 2 | 1 | 1 | 1.1180 |
| 15 | 2 | 2 | 2 | 1 | 1 | 1.0740 |
| 16 | 2 | 2 | 2 | 1 | 1 | 1.0970 |
| 17 | 1 | 1 | 1 | 2 | 1 | 3.2470 |
| 18 | 1 | 1 | 1 | 2 | 1 | 3.3810 |
| 19 | 2 | 1 | 1 | 2 | 1 | 2.8920 |
| 20 | 2 | 1 | 1 | 2 | 1 | 3.1320 |
| 21 | 1 | 2 | 1 | 2 | 1 | 3.2050 |
| 22 | 1 | 2 | 1 | 2 | 1 | 3.1820 |
| 23 | 2 | 2 | 1 | 2 | 1 | 2.9360 |
| 24 | 2 | 2 | 1 | 2 | 1 | 2.8590 |
| 25 | 1 | 1 | 2 | 2 | 1 | 2.9700 |
| 26 | 1 | 1 | 2 | 2 | 1 | 3.0210 |
| 27 | 2 | 1 | 2 | 2 | 1 | 2.5990 |
| 28 | 2 | 1 | 2 | 2 | 1 | 2.5620 |
| 29 | 1 | 2 | 2 | 2 | 1 | 3.0350 |
| 30 | 1 | 2 | 2 | 2 | 1 | 2.7810 |
| 31 | 2 | 2 | 2 | 2 | 1 | 2.7590 |
| 32 | 2 | 2 | 2 | 2 | 1 | 2.4800 |
| 33 | 1 | 1 | 1 | 1 | 2 | 0.7124 |
| 34 | 1 | 1 | 1 | 1 | 2 | 0.7156 |
| 35 | 2 | 1 | 1 | 1 | 2 | 0.7760 |
| 36 | 2 | 1 | 1 | 1 | 2 | 0.7278 |
| 37 | 1 | 2 | 1 | 1 | 2 | 0.7144 |
| 38 | 1 | 2 | 1 | 1 | 2 | 0.6796 |
| 39 | 2 | 2 | 1 | 1 | 2 | 0.6538 |
| 40 | 2 | 2 | 1 | 1 | 2 | 0.7175 |

**Table 4.10** Continued...

| | | | | | | |
|---|---|---|---|---|---|---|
| 41 | 1 | 1 | 2 | 1 | 2 | 0.5809 |
| 42 | 1 | 1 | 2 | 1 | 2 | 0.5751 |
| 43 | 2 | 1 | 2 | 1 | 2 | 0.6383 |
| 44 | 2 | 1 | 2 | 1 | 2 | 0.6612 |
| 45 | 1 | 2 | 2 | 1 | 2 | 0.4713 |
| 46 | 1 | 2 | 2 | 1 | 2 | 0.4526 |
| 47 | 2 | 2 | 2 | 1 | 2 | 0.5338 |
| 48 | 2 | 2 | 2 | 1 | 2 | 0.5170 |
| 49 | 1 | 1 | 1 | 2 | 2 | 1.5630 |
| 50 | 1 | 1 | 1 | 2 | 2 | 1.6850 |
| 51 | 2 | 1 | 1 | 2 | 2 | 1.6450 |
| 52 | 2 | 1 | 1 | 2 | 2 | 1.6420 |
| 53 | 1 | 2 | 1 | 2 | 2 | 1.4050 |
| 54 | 1 | 2 | 1 | 2 | 2 | 1.4300 |
| 55 | 2 | 2 | 1 | 2 | 2 | 1.4200 |
| 56 | 2 | 2 | 1 | 2 | 2 | 1.4620 |
| 57 | 1 | 1 | 2 | 2 | 2 | 1.6920 |
| 58 | 1 | 1 | 2 | 2 | 2 | 1.6640 |
| 59 | 2 | 1 | 2 | 2 | 2 | 1.6460 |
| 60 | 2 | 1 | 2 | 2 | 2 | 1.6490 |
| 61 | 1 | 2 | 2 | 2 | 2 | 1.4160 |
| 62 | 1 | 2 | 2 | 2 | 2 | 1.3350 |
| 63 | 2 | 2 | 2 | 2 | 2 | 1.3860 |
| 64 | 2 | 2 | 2 | 2 | 2 | 1.3670 |

**Table 4.11** Mean Gold Adsorbed at each factor level

| Cu | pH | N | Gold |
|---|---|---|---|
| 1 | 1 | 16 | 1.6652 |
| 1 | 2 | 16 | 1.5307 |
| 2 | 1 | 16 | 1.5610 |
| 2 | 2 | 16 | 1.4289 |

| Cu | Time | N | Gold |
|---|---|---|---|
| 1 | 1 | 16 | 0.8841 |
| 1 | 2 | 16 | 2.3119 |
| 2 | 1 | 16 | 0.8362 |
| 2 | 2 | 16 | 2.1536 |

| Cu | Carbon | N | Gold |
|---|---|---|---|
| 1 | 1 | 16 | 2.0351 |
| 1 | 2 | 16 | 1.1608 |
| 2 | 1 | 16 | 1.9923 |
| 2 | 2 | 16 | 0.9976 |

| pH | Time | N | Gold |
|---|---|---|---|
| 1 | 1 | 16 | 0.9083 |
| 1 | 2 | 16 | 2.3179 |
| 2 | 1 | 16 | 0.8119 |
| 2 | 2 | 16 | 2.1476 |

| pH | Carbon | N | Gold |
|---|---|---|---|
| 1 | 1 | 16 | 2.1044 |
| 1 | 2 | 16 | 1.1218 |
| 2 | 1 | 16 | 1.9230 |
| 2 | 2 | 16 | 1.0366 |

| Time | Carbon | N | Gold |
|---|---|---|---|
| 1 | 1 | 16 | 1.0873 |
| 1 | 2 | 16 | 0.6330 |
| 2 | 1 | 16 | 2.9401 |
| 2 | 2 | 16 | 1.5254 |

| Fe | Cu | pH | N | Gold |
|---|---|---|---|---|
| 1 | 1 | 1 | 8 | 1.7077 |
| 1 | 1 | 2 | 8 | 1.5711 |
| 1 | 2 | 1 | 8 | 1.6159 |
| 1 | 2 | 2 | 8 | 1.4560 |
| 2 | 1 | 1 | 8 | 1.6227 |
| 2 | 1 | 2 | 8 | 1.4903 |
| 2 | 2 | 1 | 8 | 1.5060 |
| 2 | 2 | 2 | 8 | 1.4017 |

| Fe | N | Gold |
|---|---|---|
| 1 | 32 | 1.5877 |
| 2 | 32 | 1.5052 |

| Cu | N | Gold |
|---|---|---|
| 1 | 32 | 1.5980 |
| 2 | 32 | 1.4949 |

| pH | N | Gold |
|---|---|---|
| 1 | 32 | 1.6131 |
| 2 | 32 | 1.4798 |

| Time | N | Gold |
|---|---|---|
| 1 | 32 | 0.8601 |
| 2 | 32 | 2.2327 |

| Carbon | N | Gold |
|---|---|---|
| 1 | 32 | 2.0137 |
| 2 | 32 | 1.0792 |

| Fe | Cu | N | Gold |
|---|---|---|---|
| 1 | 1 | 16 | 1.6394 |
| 1 | 2 | 16 | 1.5359 |
| 2 | 1 | 16 | 1.5565 |
| 2 | 2 | 16 | 1.4539 |

| Fe | pH | N | Gold |
|---|---|---|---|
| 1 | 1 | 16 | 1.6618 |
| 1 | 2 | 16 | 1.5135 |
| 2 | 1 | 16 | 1.5644 |
| 2 | 2 | 16 | 1.4460 |

| Fe | Time | N | Gold |
|---|---|---|---|
| 1 | 1 | 16 | 0.8621 |
| 1 | 2 | 16 | 2.3133 |
| 2 | 1 | 16 | 0.8582 |
| 2 | 2 | 16 | 2.1523 |

| Fe | Carbon | N | Gold |
|---|---|---|---|
| 1 | 1 | 16 | 2.1071 |
| 1 | 2 | 16 | 1.0682 |
| 2 | 1 | 16 | 1.9203 |
| 2 | 2 | 16 | 1.0901 |

**Table 4.11** Continued...

| Fe | Cu | Time | N | Gold |
|---|---|---|---|---|
| 1 | 1 | 1 | 8 | 0.8759 |
| 1 | 1 | 2 | 8 | 2.4029 |
| 1 | 2 | 1 | 8 | 0.8482 |
| 1 | 2 | 2 | 8 | 2.2236 |
| 2 | 1 | 1 | 8 | 0.8922 |
| 2 | 1 | 2 | 8 | 2.2209 |
| 2 | 2 | 1 | 8 | 0.8242 |
| 2 | 2 | 2 | 8 | 2.0836 |

| Fe | Cu | Carbon | N | Gold |
|---|---|---|---|---|
| 1 | 1 | 1 | 8 | 2.1303 |
| 1 | 1 | 2 | 8 | 1.1485 |
| 1 | 2 | 1 | 8 | 2.0839 |
| 1 | 2 | 2 | 8 | 0.9880 |
| 2 | 1 | 1 | 8 | 1.9399 |
| 2 | 1 | 2 | 8 | 1.1732 |
| 2 | 2 | 1 | 8 | 1.9006 |
| 2 | 2 | 2 | 8 | 1.0071 |

| Fe | pH | Time | N | Gold |
|---|---|---|---|---|
| 1 | 1 | 1 | 8 | 0.9364 |
| 1 | 1 | 2 | 8 | 2.3872 |
| 1 | 2 | 1 | 8 | 0.7878 |
| 1 | 2 | 2 | 8 | 2.2392 |
| 2 | 1 | 1 | 8 | 0.8803 |
| 2 | 1 | 2 | 8 | 2.2485 |
| 2 | 2 | 1 | 8 | 0.8360 |
| 2 | 2 | 2 | 8 | 2.0560 |

| Fe | pH | Carbon | N | Gold |
|---|---|---|---|---|
| 1 | 1 | 1 | 8 | 2.2105 |
| 1 | 1 | 2 | 8 | 1.1131 |
| 1 | 2 | 1 | 8 | 2.0037 |
| 1 | 2 | 2 | 8 | 1.0234 |
| 2 | 1 | 1 | 8 | 1.9983 |
| 2 | 1 | 2 | 8 | 1.1305 |
| 2 | 2 | 1 | 8 | 1.8422 |
| 2 | 2 | 2 | 8 | 1.0498 |

| Fe | Time | Carbon | N | Gold |
|---|---|---|---|---|
| 1 | 1 | 1 | 8 | 1.1114 |
| 1 | 1 | 2 | 8 | 0.6127 |
| 1 | 2 | 1 | 8 | 3.1028 |
| 1 | 2 | 2 | 8 | 1.5237 |
| 2 | 1 | 1 | 8 | 1.0631 |
| 2 | 1 | 2 | 8 | 0.6532 |
| 2 | 2 | 1 | 8 | 2.7774 |
| 2 | 2 | 2 | 8 | 1.5271 |

| Cu | pH | Time | N | Gold |
|---|---|---|---|---|
| 1 | 1 | 1 | 8 | 0.9321 |
| 1 | 1 | 2 | 8 | 2.3984 |
| 1 | 2 | 1 | 8 | 0.8360 |
| 1 | 2 | 2 | 8 | 2.2254 |
| 2 | 1 | 1 | 8 | 0.8845 |
| 2 | 1 | 2 | 8 | 2.2374 |
| 2 | 2 | 1 | 8 | 0.7878 |
| 2 | 2 | 2 | 8 | 2.0699 |

| Cu | pH | Carbon | N | Gold |
|---|---|---|---|---|
| 1 | 1 | 1 | 8 | 2.1471 |
| 1 | 1 | 2 | 8 | 1.1833 |
| 1 | 2 | 1 | 8 | 1.9231 |
| 1 | 2 | 2 | 8 | 1.1383 |
| 2 | 1 | 1 | 8 | 2.0616 |
| 2 | 1 | 2 | 8 | 1.0603 |
| 2 | 2 | 1 | 8 | 1.9229 |
| 2 | 2 | 2 | 8 | 0.9348 |

| Cu | Time | Carbon | N | Gold |
|---|---|---|---|---|
| 1 | 1 | 1 | 8 | 1.0947 |
| 1 | 1 | 2 | 8 | 0.6734 |
| 1 | 2 | 1 | 8 | 2.9755 |
| 1 | 2 | 2 | 8 | 1.6482 |
| 2 | 1 | 1 | 8 | 1.0799 |
| 2 | 1 | 2 | 8 | 0.5925 |
| 2 | 2 | 1 | 8 | 2.9046 |
| 2 | 2 | 2 | 8 | 1.4026 |

| pH | Time | Carbon | N | Gold |
|---|---|---|---|---|
| 1 | 1 | 1 | 8 | 1.1045 |
| 1 | 1 | 2 | 8 | 0.7121 |
| 1 | 2 | 1 | 8 | 3.1042 |
| 1 | 2 | 2 | 8 | 1.5315 |
| 2 | 1 | 1 | 8 | 1.0701 |
| 2 | 1 | 2 | 8 | 0.5538 |
| 2 | 2 | 1 | 8 | 2.7759 |
| 2 | 2 | 2 | 8 | 1.5194 |

**Table 4.12** Analysis of Variance for Gold Adsorbed

| Source | DF | SS | MS | F | P |
|---|---|---|---|---|---|
| Fe | 1 | 0.1088 | 0.1088 | 22.75 | 0.000 |
| Cu | 1 | 0.1699 | 0.1699 | 35.53 | 0.000 |
| pH | 1 | 0.2844 | 0.2844 | 59.48 | 0.000 |
| Time | 1 | 30.1457 | 30.1457 | 6E+03 | 0.000 |
| Carbon | 1 | 13.9720 | 13.9720 | 3E+03 | 0.000 |
| Fe*Cu | 1 | 0.0000 | 0.0000 | 0.00 | 0.981 |
| Fe*pH | 1 | 0.0036 | 0.0036 | 0.75 | 0.393 |
| Fe*Time | 1 | 0.0987 | 0.0987 | 20.64 | 0.000 |
| Fe*Carbon | 1 | 0.1743 | 0.1743 | 36.45 | 0.000 |
| Cu*pH | 1 | 0.0000 | 0.0000 | 0.00 | 0.944 |
| Cu*Time | 1 | 0.0487 | 0.0487 | 10.19 | 0.003 |
| Cu*Carbon | 1 | 0.0580 | 0.0580 | 12.13 | 0.001 |
| pH*Time | 1 | 0.0218 | 0.0218 | 4.56 | 0.040 |
| pH*Carbon | 1 | 0.0370 | 0.0370 | 7.74 | 0.009 |
| Time*Carbon | 1 | 3.6887 | 3.6887 | 771.33 | 0.000 |
| Fe*Cu*pH | 1 | 0.0026 | 0.0026 | 0.55 | 0.464 |
| Fe*Cu*Time | 1 | 0.0068 | 0.0068 | 1.42 | 0.243 |
| Fe*Cu*Carbon | 1 | 0.0002 | 0.0002 | 0.03 | 0.855 |
| Fe*pH*Time | 1 | 0.0222 | 0.0222 | 4.63 | 0.039 |
| Fe*pH*Carbon | 1 | 0.0017 | 0.0017 | 0.36 | 0.550 |
| Fe*Time*Carbon | 1 | 0.0576 | 0.0576 | 12.05 | 0.002 |
| Cu*pH*Time | 1 | 0.0000 | 0.0000 | 0.01 | 0.930 |
| Cu*pH*Carbon | 1 | 0.0275 | 0.0275 | 5.74 | 0.023 |
| Cu*Time*Carbon | 1 | 0.0118 | 0.0118 | 2.47 | 0.126 |
| pH*Time*Carbon | 1 | 0.1937 | 0.1937 | 40.51 | 0.000 |
| Fe*Cu*pH*Time | 1 | 0.0005 | 0.0005 | 0.11 | 0.745 |
| Fe*Cu*pH*Carbon | 1 | 0.0003 | 0.0003 | 0.06 | 0.807 |
| Fe*Cu*Time*Carbon | 1 | 0.0013 | 0.0013 | 0.27 | 0.608 |
| Fe*pH*Time*Carbon | 1 | 0.0034 | 0.0034 | 0.71 | 0.406 |
| Cu*pH*Time*Carbon | 1 | 0.0001 | 0.0001 | 0.02 | 0.888 |
| Fe*Cu*pH*Time*Carbon | 1 | 0.0009 | 0.0009 | 0.18 | 0.673 |
| Error | 32 | 0.1530 | 0.0048 |  |  |
| Total | 63 | 49.2953 | 0.7825 |  |  |

This would suggest that modified peat has a lower capacity for the gold-thiourea complex than does activated carbon. Another possible conclusion could be that the kinetics of adsorption onto modified peat are much slower i.e. the rate constant is smaller.

Although the capacity appears to be about 54% of that of activated carbon, the disadvantage of a lower capacity and brittleness may be far outweighed by its relatively cheap and straight forward means of manufacture. Modified peat is also easier to ash than activated carbon. The raw material, moss peat is also plentiful.

The next most significant single effect apart from time and carbon appears to be pH. The pH effect appeared significant in experiment 4.6 but not as significant in experiment 4.4. The effect of pH may therefore be appearing solely due to its effect on modified peat.

Again it can be seen that the combination effects involving both carbon and time appear to be significant however, this is expected since their individual effects are significant.

The effect of copper(II) appears to be significant. Experiment 4.4 and 4.6 appear to suggest that by increasing the level of copper, the amount of gold adsorbed decreases. Solubility tests on the copper-thiourea complex show that the complex is very insoluble. This could suggest that as the level of copper increases, the amount of the complex formed increases. The activated carbon and modified peat may act as ideal nucleation sites for crystal growth and hence in the presence of the complex, the capacity of the carbon is reduced due to surface coverage with the complex.

In order to investigate the effect of copper(II), iron(III) and thiourea, it was necessary to set up an experiment involving these three factors only. The advantage of this is that the effect of time and hence its combination effect would be totally eliminated thus enhancing the clarity of the effects of copper(II), iron(III) and thiourea.

## 4.10 THE EFFECT OF COPPER(II), IRON(III) AND THIOUREA ON THE ADSORPTION OF GOLD ONTO ACTIVATED CARBON

The aim of the experiment was to investigate the effects of copper(II), iron(III) and thiourea on the adsorption of gold without looking at the effects of time and pH. The factors were chosen at three levels. The design is now called a $3^3$ factorial designed experiment. The levels of copper(II) and iron(III) were equal at each level in order to quantify their relative effects. The factors were chosen at the following levels.

| **Factor** | **Level 1** | **Level 2** | **Level 3** |
|---|---|---|---|
| Thiourea | 0.05g/dm$^3$ | 0.2g/dm$^3$ | 1g/dm$^3$ |
| Copper(II) | 0 ppm | 100 ppm | 500 ppm |
| Iron(III) | 0 ppm | 100 ppm | 500 ppm |

The lowest level of thiourea was chosen so that the gold-thiourea complex would be formed in solution by reduction of Au(III) while maintaining an insignificant level of thiourea from the adsorption viewpoint.

### 4.10.1 Reagents

1000 ppm Gold chloride standard solution "SPECTROSOL" (BDH Chemicals).
1000 ppm copper(II) solution from copper sulphate pentahydrate (Riedel-De-Haen).
10,000 ppm iron(III) solution from ferric sulphate (Riedel-De-Haen).
10g/dm$^3$ thiourea solution from thiourea (SKW-Trotsberg).
Sulphuric acid (RiedelDe-Haen).

### 4.10.2 Instrumentation

All standards and samples were analysed using a Shimadzu AA670 Atomic Absorption/Flame Emission Spectrophotometer. The instrument conditions were those as in section 4.2.2.

### 4.10.3 Experimental details

All solutions were made up at a pH of 1 and the exposure time to the activated carbon was two hours.

## 4.11 Results and discussion

Table 4.13 illustrates the calculated response at each factor combination. Table 4.14 illustrates the mean response at each factor level. Table 4.15 illustrates the analysis of variance for the response.

**Table 4.13** Gold Adsorbed at each factor combination

| ROW | Fe | Cu | Tu | AuAds. |
|---|---|---|---|---|
| 1 | 1 | 1 | 1 | 3.7690 |
| 2 | 1 | 1 | 1 | 3.8010 |
| 3 | 2 | 1 | 1 | 3.5710 |
| 4 | 2 | 1 | 1 | 3.6150 |
| 5 | 3 | 1 | 1 | 3.5390 |
| 6 | 3 | 1 | 1 | 3.3770 |
| 7 | 1 | 2 | 1 | 3.1540 |
| 8 | 1 | 2 | 1 | 3.5780 |
| 9 | 2 | 2 | 1 | 3.5200 |
| 10 | 2 | 2 | 1 | 3.9510 |
| 11 | 3 | 2 | 1 | 3.2830 |
| 12 | 3 | 2 | 1 | 3.1910 |
| 13 | 1 | 3 | 1 | 3.1880 |
| 14 | 1 | 3 | 1 | 3.0230 |
| 15 | 2 | 3 | 1 | 3.7330 |
| 16 | 2 | 3 | 1 | 3.8130 |
| 17 | 3 | 3 | 1 | 3.3650 |
| 18 | 3 | 3 | 1 | 3.5310 |
| 19 | 1 | 1 | 2 | 2.9450 |
| 20 | 1 | 1 | 2 | 3.2010 |
| 21 | 2 | 1 | 2 | 3.0180 |
| 22 | 2 | 1 | 2 | 3.1910 |
| 23 | 3 | 1 | 2 | 3.0590 |
| 24 | 3 | 1 | 2 | 3.1680 |
| 25 | 1 | 2 | 2 | 1.8680 |
| 26 | 1 | 2 | 2 | 1.6300 |
| 27 | 2 | 2 | 2 | 2.2140 |
| 28 | 2 | 2 | 2 | 2.1280 |
| 29 | 3 | 2 | 2 | 2.5000 |
| 30 | 3 | 2 | 2 | 3.1420 |
| 31 | 1 | 3 | 2 | 0.3363 |
| 32 | 1 | 3 | 2 | 0.5459 |
| 33 | 2 | 3 | 2 | 0.8906 |
| 34 | 2 | 3 | 2 | 1.1830 |
| 35 | 3 | 3 | 2 | 3.1390 |
| 36 | 3 | 3 | 2 | 3.1690 |
| 37 | 1 | 1 | 3 | 3.5240 |
| 38 | 1 | 1 | 3 | 3.2670 |
| 39 | 2 | 1 | 3 | 3.3890 |
| 40 | 2 | 1 | 3 | 3.2140 |
| 41 | 3 | 1 | 3 | 2.5030 |
| 42 | 3 | 1 | 3 | 2.9150 |
| 43 | 1 | 2 | 3 | 0.0000 |
| 44 | 1 | 2 | 3 | 0.0000 |
| 45 | 2 | 2 | 3 | 0.7311 |
| 46 | 2 | 2 | 3 | 0.6380 |
| 47 | 3 | 2 | 3 | 0.7898 |
| 48 | 3 | 2 | 3 | 0.7997 |
| 49 | 1 | 3 | 3 | 0.0000 |
| 50 | 1 | 3 | 3 | 0.0000 |
| 51 | 2 | 3 | 3 | 0.0000 |
| 52 | 2 | 3 | 3 | 0.0000 |
| 53 | 3 | 3 | 3 | 0.5394 |
| 54 | 3 | 3 | 3 | 0.5650 |

**Table 4.14** Mean Gold Adsorbed at each factor level

| Fe | N | AuAds. |
|---|---|---|
| 1 | 18 | 2.1017 |
| 2 | 18 | 2.3778 |
| 3 | 18 | 2.5875 |

| Cu | N | AuAds. |
|---|---|---|
| 1 | 18 | 3.2814 |
| 2 | 18 | 2.0621 |
| 3 | 18 | 1.7234 |

| Tu | N | AuAds. |
|---|---|---|
| 1 | 18 | 3.5001 |
| 2 | 18 | 2.2960 |
| 3 | 18 | 1.2708 |

| Fe | Cu | N | AuAds. |
|---|---|---|---|
| 1 | 1 | 6 | 3.4178 |
| 1 | 2 | 6 | 1.7050 |
| 1 | 3 | 6 | 1.1822 |
| 2 | 1 | 6 | 3.3330 |
| 2 | 2 | 6 | 2.1970 |
| 2 | 3 | 6 | 1.6033 |
| 3 | 1 | 6 | 3.0935 |
| 3 | 2 | 6 | 2.2843 |
| 3 | 3 | 6 | 2.3847 |

| Fe | Tu | N | AuAds. |
|---|---|---|---|
| 1 | 1 | 6 | 3.4188 |
| 1 | 2 | 6 | 1.7544 |
| 1 | 3 | 6 | 1.1318 |
| 2 | 1 | 6 | 3.7005 |
| 2 | 2 | 6 | 2.1041 |
| 2 | 3 | 6 | 1.3287 |
| 3 | 1 | 6 | 3.3810 |
| 3 | 2 | 6 | 3.0295 |
| 3 | 3 | 6 | 1.3520 |

| Cu | Tu | N | AuAds. |
|---|---|---|---|
| 1 | 1 | 6 | 3.6120 |
| 1 | 2 | 6 | 3.0970 |
| 1 | 3 | 6 | 3.1353 |
| 2 | 1 | 6 | 3.4462 |
| 2 | 2 | 6 | 2.2470 |
| 2 | 3 | 6 | 0.4931 |
| 3 | 1 | 6 | 3.4422 |
| 3 | 2 | 6 | 1.5440 |
| 3 | 3 | 6 | 0.1841 |

| Fe | Cu | Tu | N | AuAds. |
|---|---|---|---|---|
| 1 | 1 | 1 | 2 | 3.7850 |
| 1 | 1 | 2 | 2 | 3.0730 |
| 1 | 1 | 3 | 2 | 3.3955 |
| 1 | 2 | 1 | 2 | 3.3660 |
| 1 | 2 | 2 | 2 | 1.7490 |
| 1 | 2 | 3 | 2 | 0.0000 |
| 1 | 3 | 1 | 2 | 3.1055 |
| 1 | 3 | 2 | 2 | 0.4411 |
| 1 | 3 | 3 | 2 | 0.0000 |
| 2 | 1 | 1 | 2 | 3.5930 |
| 2 | 1 | 2 | 2 | 3.1045 |
| 2 | 1 | 3 | 2 | 3.3015 |
| 2 | 2 | 1 | 2 | 3.7355 |
| 2 | 2 | 2 | 2 | 2.1710 |
| 2 | 2 | 3 | 2 | 0.6846 |
| 2 | 3 | 1 | 2 | 3.7730 |
| 2 | 3 | 2 | 2 | 1.0368 |
| 2 | 3 | 3 | 2 | 0.0000 |
| 3 | 1 | 1 | 2 | 3.4580 |
| 3 | 1 | 2 | 2 | 3.1135 |
| 3 | 1 | 3 | 2 | 2.7090 |
| 3 | 2 | 1 | 2 | 3.2370 |
| 3 | 2 | 2 | 2 | 2.8210 |
| 3 | 2 | 3 | 2 | 0.7947 |
| 3 | 3 | 1 | 2 | 3.4480 |
| 3 | 3 | 2 | 2 | 3.1540 |
| 3 | 3 | 3 | 2 | 0.5522 |

**Table 4.15** Analysis of Variance for Gold Adsorbed

| Source | DF | SS | MS | F | P |
|---|---|---|---|---|---|
| Fe | 2 | 2.1374 | 1.0687 | 39.69 | 0.000 |
| Cu | 2 | 24.1742 | 12.0871 | 448.87 | 0.000 |
| Tu | 2 | 44.8232 | 22.4116 | 832.28 | 0.000 |
| Fe*Cu | 4 | 3.8407 | 0.9602 | 35.66 | 0.000 |
| Fe*Tu | 4 | 3.6131 | 0.9033 | 33.54 | 0.000 |
| Cu*Tu | 4 | 14.7696 | 3.6924 | 137.12 | 0.000 |
| Fe*Cu*Tu | 8 | 2.2323 | 0.2790 | 10.36 | 0.000 |
| Error | 27 | 0.7271 | 0.0269 | | |
| Total | 53 | 96.3176 | 1.8173 | | |

Considering Table 4.14, it can be seen that increasing the level of iron(III) slightly enhances the amount of gold adsorbed per kilogram of carbon. Increasing the level of copper(II) has a more severe effect, it reduces the amount of gold adsorbed. Changing the copper(II) level from 0 ppm to 100 ppm reduces the amount of gold adsorbed by 37%. Increasing the amount of copper(II) by a factor of 5 has the effect of reducing the amount of gold adsorbed by 48%.

Thiourea again has the most significant effect thus suggesting that carbon has a very high capacity for thiourea, F=832 in table 4.15. From Table 4.14, it can be seen that when both copper(II) and thiourea are at level 3, the amount of gold adsorbed is zero except in the case where iron(III) is at level 3. This may support the suggestion that the copper-thiourea complex is severely inhibiting the adsorption process. Table 4.15 also supports this because the interaction effect of copper(II) and thiourea has the largest F-Value. This interaction effect is also greater than the single factor effect of iron(III).

## Conclusions

The results from all of the factorial designed experiments indicate certain trends thus indicating the usefulness and value of the method. The most significant conclusions that can be drawn from the results are as follows:

(1) Increasing the level of thiourea inhibits the adsorption of the gold-thiourea complex onto activated carbon.

(2) Activated carbon has a very high capacity for thiourea.

(3) Increasing the exposure time to carbon enhances the adsorption of the gold-thiourea complex.

(4) Modified peat adsorbs only 54% of the amount of gold adsorbed by activated carbon.

(5) Increasing the level of iron(III) slightly enhances the adsorption of the gold-thiourea complex.

(6) The presence of copper severely inhibits the adsorption of gold.

(7) High levels of both copper and thiourea severely inhibit the adsorption of gold.

Bearing these results in mind, careful control of the levels of the various chemicals present in a typical thiourea system is therefore very important to the chemistry and economics of the adsorption process. Careful control of the various parameters could therefore be executed in order to maximise gold recovery.

# REFERENCES CHAPTER 4

1. Fisher, R.A. and Frank Yates, "Statistical tables for biological, agricultural and medical research." 4th edition. Oliver and Boyd, Edinburgh, (1953).

2. Fisher, R.A., "Statistical methods for research workers". Oliver and Boyd, Edinburgh, (1958).

3. Fisher, R.A., "The design of experiments".8th edition. Hafner publishing company, New York, (1966).

4. W. Janhunin, G.Zucker, H.El-Shall and M.E El Dahshan, "Effect of some inorganic and organic chemicals on interaction of gold with activated carbon". Journal of Eng. Sci., Vol.13, No.1, pp 121-137, (1987).

5. McDougall, G.J. and Fleming, C.A., "Ion Exchange and Sorption Processes in Hydrometallurgy", Critical Reports on Applied Chemistry Volume 19, p.85-92, John Wiley and Sons, (1987).

6. Maslowska, J., "Mixed complexes of iron(III)". zess. Nauk. Politechn. Lodz, Chem., vol.20. pp. 5-114, (1969).

7. Freeland, G. N., Hoskinson, R. M., and Mayfield, R. J., "Adsorption of mercury from aqueous solutions by Polyethyleneimine-Modified Wool Fibers". Environ Sci. Technol., 8, 943 (1974).

8. Snyder, S. L., and Vigo, Tyrone L., "Removal of mercury from aqueous solutions by N-(2-aminoethyl) aminodeoxycellulose Cation". Environ. Sci. Technol., 8, 944 (1974).

9. Friedman, J., and Waiss, A. C., "Mercury uptake by selected agricultural Products and By-Products". Environ. Sci. Technol., 6, 457 (1972).

10. Riley, R., "Making Carbonaceous Zeolites". U.S Patent 2,170,065 (Nov.9,1935).

11. Liebknecht, O., "Carbonaceous zeolite and the production thereof." U.S Patent 2,191,060 (March 8 1965).

12. Smith, P., "Manufacture of absorbent and ion exchanging materials." U.S Patent 2,191,063 (Jan 10. 1935).

13. Goetz, P., "Process of making ion exchanging preparations and product thereof." U.S Patent 2,260,971 (Nov.20, 1937).

14. E.F. Smith, P. MacCarthy, T.C. Yu and H.B Mark, Jr., J. Water Poll. Control Fed. 49, 633 (1977).

15. E.F Smith, H. B. Mark, Jr. and P.MacCarthy, in Chemistry Of Wastewater Technology, A.J. Rubin, Ed., Ann Arbor Science, Ann Arbor, Chapter 21 Michigan, (1978).

16. A.P Kotkovskii, L.V. Kosonogova, N.N Volosovich and S.V Kashirina, "Production of Sulfonated Cation Exchangers from Coke and Peat semicoke, Pererab. Ispol' Torfa Sapropelei, 163(1971). [Chem abs.78,No. 60579r (1973)].

17. A.P Kotkovskii, L.V. Kosonogova and N.s Volosovich, "Polyfunctional Cation Exchangers from Peat and Peat semicoke", Vesti. Akad. Navuk. Belarus, SSR, Ser. Khim. Nauk. (3), 8(1973). [Chem. abs. 80, No. 72652p (1974)].

18. John P. Ansted, Patrick MacCarthy, "Removal of heavy metals from solution by chemically modified peat: Effects of pH, ionic strength and flow rate". Solvent Extraction and Ion Exchange, 2(7&8), 1105-1122 (1984).

# CHAPTER 5

# CAPACITY OF CARBON FOR SOME ORGANIC AND INORGANIC SPECIES

## 5.1 Introduction

The use of charcoal for purposes other than as a fuel and in metallurgy is very old. Its use in medicine is mentioned in an Egyptian papyrus from 1550 B.C. The ability of fluid molecules to adhere to the surfaces of solids, a phenomena known as adsorption, was first recognised by Sheele [1] in 1773. In 1785, Lowitz [2] recognised the ability of charcoal to decolourise solutions. The discovery by Figuers [1] in 1811 of the greater decolourising power of bone char led to its almost immediate adoption in the sugar refining industry, in fact, much of the early interest in the development of activated carbon was stimulated by a belief that a large potential market existed in the cane sugar industry.

During the 19th century, many studies were made to develop other decolourising carbons from other source materials. In 1822 Bussy [3] produced a carbon with between twenty to fifty times the decolourising power of bone char, this was done by heating blood with potash. In 1865, Hunter [4] reported on the gas adsorbing power of cocoa-nut char. That same year, Stenhouse [5] prepared a decolourising char by heating a mixture of flour, tar and magnesium carbonate. Winser and Swindells [6] also produced a char by heating paper mill waste with phosphates.

Although these activated carbons were produced relatively easily in the laboratory, their large scale industrial production posed many engineering difficulties due to the corrosive action of the activation conditions.

In 1915, as a consequence of gas warfare, the allied soldiers were provided with gas masks containing activated carbon. Although powdered activated carbon had been manufactured for some years, the powdered form was not suitable for gas masks and consequently granular grades had to be developed. The publicity given to activated carbon in World War I stimulated a search for new peacetime markets. At the end of the war, research found uses for granular carbon in various industrial operations. Processes were developed to recover gasoline from natural gas and to extract benzene from natural gas. Granular carbons were employed to purify various industrial gases. Sulphur compounds were removed from hydrogen and from acetylene and pyridine was removed from ammonia. Carbon dioxide for dry ice and carbonated beverages were decolourised.

Activated carbon was used in the production of penicillin during World War II by addition to an inoculated broth containing about 30 ppm penicillin. Elution of the carbon yielded a relatively concentrated penicillin solution. This adsorption-desorption process provided the only immediately available method for the large scale production of penicillin.

The ability of activated carbon to adsorb gold from chloride solutions was first reported in 1847 [7]. In 1880, Davis [8] patented a process in which wood charcoal was used for the recovery of gold from liquors resulting from chlorination leaching. In 1890, MacArthur and Forrest [9] discovered that cyanide was a good solvent for gold. Subsequently Johnson [10] patented the use of wood charcoal for the recovery of gold from cyanide leach solutions. Activated carbon is now used extensively on a commercial basis for the recovery of gold throughout the world.

### 5.1.1 Activated carbon

Activated carbon is the generic name for a family of highly porous carbon materials that are available in various forms. No member of the family can be characterised by a definite structural formula or by chemical analysis. Instead they are usually classified according to their adsorptive and catalytic properties. Activated carbon has been made from a variety of different sources such as coal, cereals, coconut shells, coffee beans, fruit pits, seaweed, peat, coke, petroleum coke, sawdust and wood to name but a few [11].

Activated carbon adsorbents contain a myriad of micropores the walls of which have surface areas that range from 400 to over 1800 square metres per gram in the various commercial brands. The method of manufacture of activated carbon is by carbonising the source material under appropriate conditions after which the resulting char is subjected to oxidation in a controlled environment. The carbonisation or pyrolysis step is usually carried out at temperatures below 600°C which results in dehydration and devolatilisation of the carbon atoms. The effectiveness of the carbonisation is enhanced when the source carbonaceous materials are impregnated with solutions of metallic chloride or potassium carbonate [1,12,13,14]. This step is usually carried out in the absence of air.

The process by which the carbonised product develops an extended surface area and a porous structure of molecular dimensions is referred to as activation. It is usually conducted at temperatures between 800 and 1100°C in the presence of a suitable oxidising agent such as steam, air or carbon dioxide. The kind of adsorptive powers developed within the carbon depend on the chemical nature and concentration of the oxidising gas, the temperature of the reaction, the extent to which the activation is conducted and the amount and kind of mineral ingredients in the char. When proper activation conditions are provided, the oxidation selectively erodes the surface so as to increase the surface area, develop greater porosity and leave the remaining atoms arranged in configurations that have specific affinities. Certain adsorptive powers develop only during late stages of activation whereas others show a consistent rate of increase throughout the activation process. It is thought that the active oxygen in the oxidising agent burns away the more reactive portions of the carbon skeleton in accordance with the reactions:

$$H_2O + C_x \text{----->} 1/2H_2 + CO + C_{x-1}$$

$$CO_2 + C_x \text{----->} 2CO + C_{x-1}$$

$$O_2 + C_x \text{----->} 2CO + C_{x-2}$$

$$O_2 + C_x \text{----->} CO_2 + C_{x-1}$$

Therefore as combustion proceeds, preferential etching occurs resulting in the development of a large internal surface area and the creation of a pore structure.

X-ray studies [15,16,17,18,19] have shown that many so-called amorphous substances have crystalline characteristics. An amorphous looking powder may be composed of crystals of sub-microscopic dimensions called crystallites. There is agreement that amorphous carbon consists of flat plates in which the carbon atoms are arranged in a hexagonal lattice, each atom being held by covalent linkages to three other carbon atoms. The crystallites are formed when two or more of these plates are stacked one above the other. The structure of thermally activated carbon is thought to be similar to that of graphite [20,21] however, there are differences. Many of the hexagonal carbon rings have undergone cleavage. They are randomly orientated and lack the directional relationship that is present in graphite. The separation between layers is also greater than that found in graphite. The size of the crystallites is influenced by the composition and structure of the raw material and on the temperature of carbonisation as can be seen from figure 5.1 [22]. It is thought that during the pyrolysis step, the original organic substance may be split into fragments which regroup to form the thermo-stable aromatic structure existing in the hexagon. It is also possible that the hexagonal lattice grows gradually at the expense of the original substance. It is presumed that the original hydrocarbons are attached by chemical bonds to the border atoms of the crystallites, therefore the surface is composed of oxygen-containing organic functional groups. The identity of these surface oxides is not well known but it has been suggested that the surface oxides shown in figure 5.2 [20] are present in thermally activated carbons. The proposed structure of activated carbon can be seen in figure 5.3 [21,22].

Granular carbons must have effective adsorptive capacity combined with great mechanical strength to withstand abrasion. Coconut shells were found to be ideal for the production of granular carbon. Very few other substances in their natural state are suitable for the manufacture of effective granular carbons, however, processes have been developed whereby some materials can be converted into forms from which effective granular carbons can be manufactured. In a typical process, coal is pulverised and mixed with sufficient binder to form a plastic mass which is briquetted or extruded at pressures ranging from 100 to 2000 lbs per square inch. The pellets or spaghetti-like rings are carbonised slowly to avoid rapid evolution of gas, after which the char is steam

**Figure 5.1** Influence of temperature on size of crystallites of Activated Carbon [22].

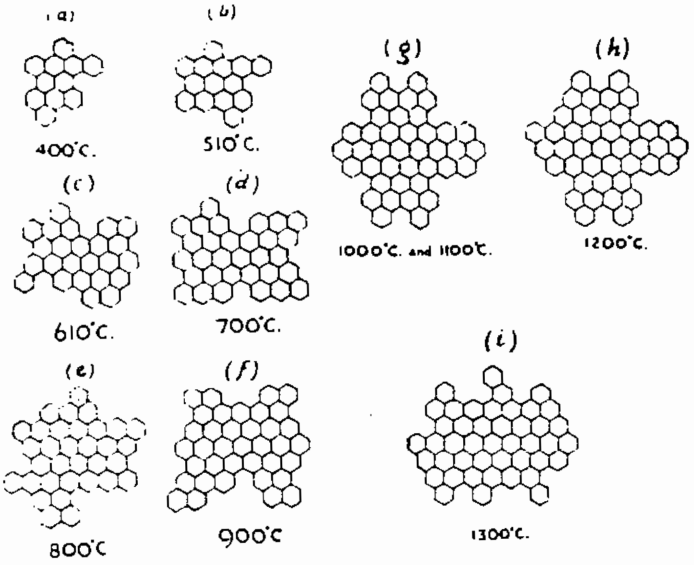
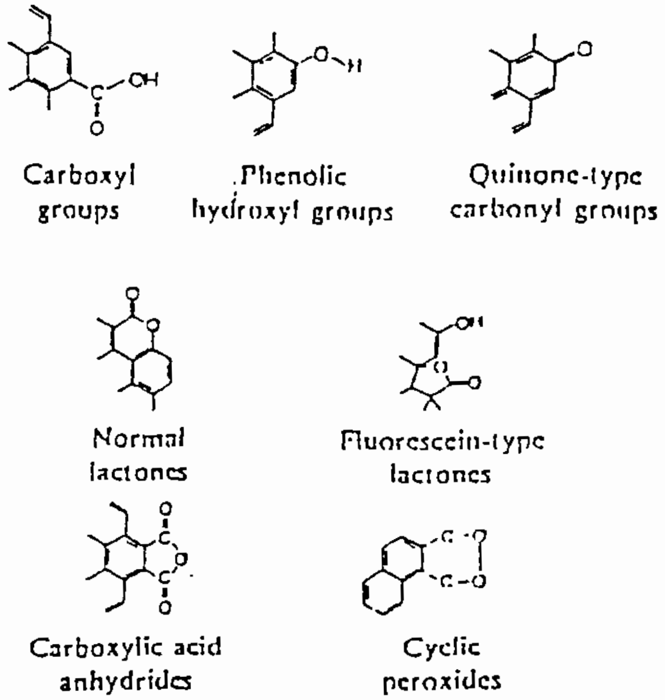


**Figure 5.2** Structure of some surface oxides that have been proposed as being present on the surface of Activated Carbon [20].



Carboxyl groups

Phenolic hydroxyl groups

Quinone-type carbonyl groups

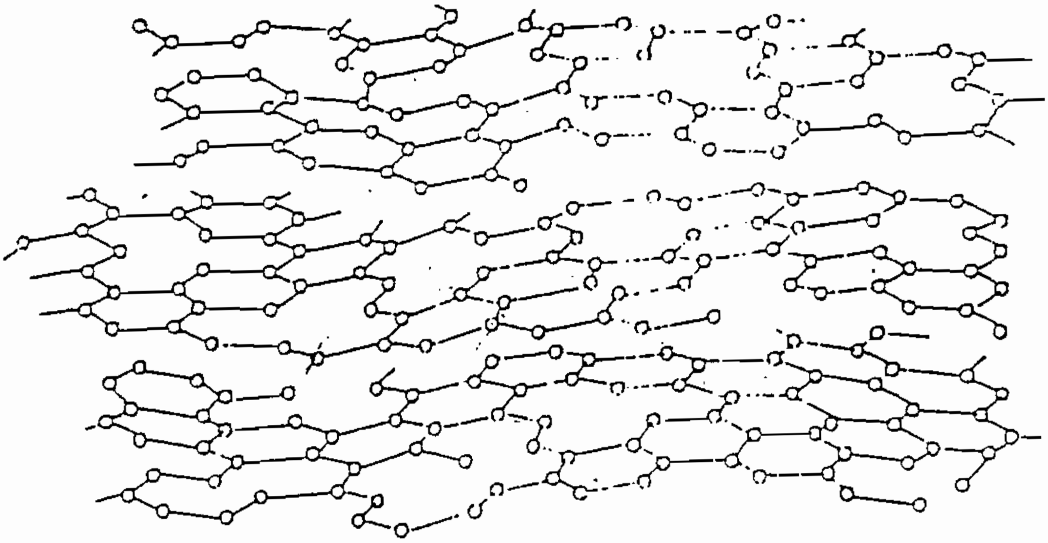
Normal lactones

Fluorescein-type lactones

Carboxylic acid anhydrides

Cyclic peroxides

**Figure 5.3** Schematic representations of the proposed structure of Activated Carbon. Oxygen-containing functional groups are located at the edges of broken ring systems [21,22].



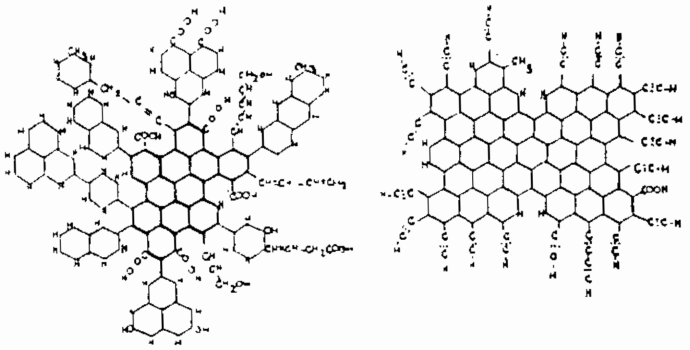
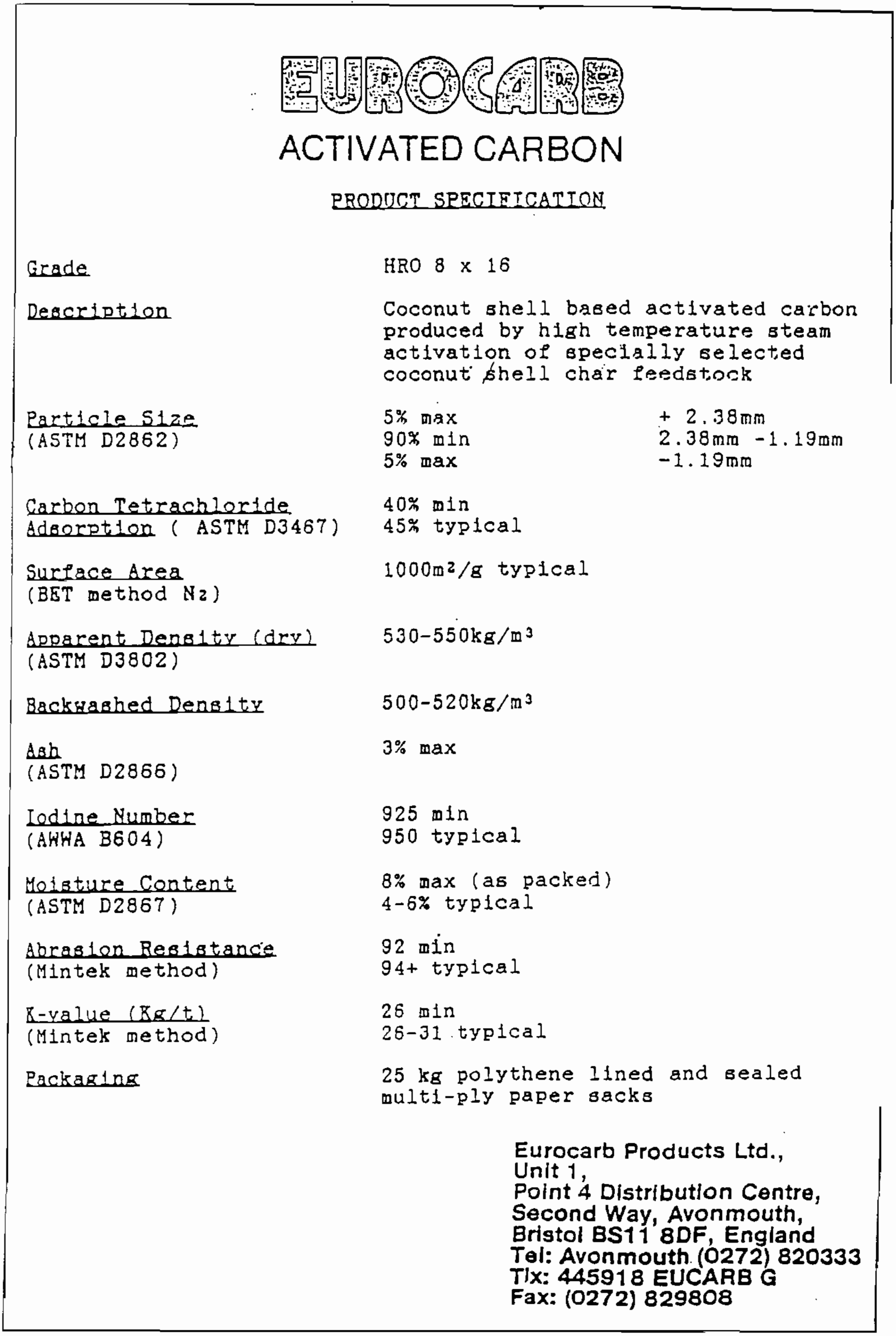


**Figure 5.4** Product specification for "EUROCARB" Activated Carbon.



EUROCARB

ACTIVATED CARBON

PRODUCT SPECIFICATION

| | | |
|---|---|---|
| Grade | HRO 8 x 16 | |
| Description | Coconut shell based activated carbon produced by high temperature steam activation of specially selected coconut shell char feedstock | |
| Particle Size<br>(ASTM D2862) | 5% max<br>90% min<br>5% max | + 2.38mm<br>2.38mm -1.19mm<br>-1.19mm |
| Carbon Tetrachloride Adsorption ( ASTM D3467) | 40% min<br>45% typical | |
| Surface Area<br>(BET method $N_2$) | 1000m$^2$/g typical | |
| Apparent Density (dry)<br>(ASTM D3802) | 530-550kg/m$^3$ | |
| Backwashed Density | 500-520kg/m$^3$ | |
| Ash<br>(ASTM D2866) | 3% max | |
| Iodine Number<br>(AWWA B604) | 925 min<br>950 typical | |
| Moisture Content<br>(ASTM D2867) | 8% max (as packed)<br>4-6% typical | |
| Abrasion Resistance<br>(Mintek method) | 92 min<br>94+ typical | |
| K-value (Kg/t)<br>(Mintek method) | 26 min<br>26-31 typical | |
| Packaging | 25 kg polythene lined and sealed multi-ply paper sacks | |

Eurocarb Products Ltd.,
Unit 1,
Point 4 Distribution Centre,
Second Way, Avonmouth,
Bristol BS11 8DF, England
Tel: Avonmouth (0272) 820333
Tlx: 445918 EUCARB G
Fax: (0272) 829808

activated. In the zinc chloride process, peat is added to a concentrated zinc chloride solution. When the mass becomes plastic, it is passed through an extrusion press, then dried and carbonised below 700°C. After an acid wash to remove the zinc, the dried granules are suitable for recovery of solvent vapours. For use in gas masks, it is given a supplementary steam activation.

The physical and chemical characteristics most often employed by manufacturers to characterise activated carbons are as follows:

| **Physical properties** | **Chemical properties** |
|---|---|
| Particle density | Surface area ($N_2$ B.E.T) |
| Bulk density | Iodine number |
| Pore volume | Carbon tetrachloride No. |
| Particle size | Benzene number |
| Ash content | |
| Moisture content | |
| Impact hardness | |

The type of carbon used for the experiments in this section was "EUROCARB" activated carbon and the product specification can be seen in figure 5.4.

## 5.2 Adsorption

Atoms and molecules are held together in a solid by cohesive forces that range from strong valence bonds to the relatively weak Van Der Waals forces of attraction. Molecules in the interior of a solid are completely surrounded and their attractive forces are satisfied on all sides but the attractive forces do not cease abruptly at the surface. Instead they extend outwards and can capture wandering fluid molecules. The accumulation of these fluid molecules at the surface is a phenomenon known as adsorption. The terms adsorbent and adsorbate describe the solid and its captured molecules respectively. In the case of activated carbon, adsorption is due primarily to its large internal surface area. When the solid is immersed in a fluid, the surface of the solid faces a corresponding surface of the fluid and the region enclosed by those two surfaces is an interface. It is within that interfacial region that adsorption occurs. The adsorption affinity that pulls molecules to the interface can be assisted or opposed by forces on the other side of the interface.

Molecules can adhere to surfaces in two ways. In physical adsorption there is a weak Van Der Waals interaction between the surface and the adsorbed molecule. The amount of energy released when a molecule is physisorbed is of the order of the enthalpy of condensation. A physisorbed molecule vibrates in its own shallow potential well and since the binding energy is low, the molecule remains on the surface for only a short period of time, retaining its chemical identity. Enthalpy changes of about 20 kJ/mole are typically observed and the processes are generally reversible.

In chemical adsorption, the molecules adhere to the surface as a result of the formation of a chemical bond, usually a covalent bond. The energy of attachment is usually of the order of 200kJ/mole. A molecule undergoing chemisorption may be cleaved to meet the demand of the unsatisfied valencies of the surface atoms and so may lose its chemical identity. Processes involving chemisorption are usually irreversible.

When a species is adsorbed on a surface, its translational freedom is reduced and so the process is accompanied by a decrease in entropy and since

$$\Delta G = \Delta H - T\Delta S$$

it follows that $\Delta H$ must be negative for $\Delta G$ to be negative and therefore chemisorption must be exothermic if it is to proceed spontaneously.

In activated carbon, the pores are wedge-shaped cavities and are generally classified in terms of their equivalent diameters.

| | |
|---|---|
| Macropores | 500-2000 Å |
| Transitional pores | 100- 500 Å |
| Micropores | 8-100 Å |

The pore size distribution and the structure of the pores depends on the source material. The macropores contribute very little to the total internal surface area. Transitional pores contribute about 5% of the surface area and the remainder (up to 95%) is due to the micropores.

The forces acting at the solid/liquid interface are complex and difficult to analyse however, it is thought that some of the factors influencing adsorption at the carbon/liquid interface are as follows:

a) Attraction of carbon for solute
b) Attraction of carbon for solvent
c) Solubilising power of solvent for solute
d) Association
e) Ionisation
f) Effect of solvent on orientation at interface
g) Competition for interface in presence of multiple solutes
h) Interaction of multiple solutes
i) Coadsorption
j) Molecular size of molecules in the system
k) Pore size distribution in the carbon
l) Particle size distribution of carbon
m) surface area of carbon
n) Concentration of constituents
o) Temperature
p) Activation energy

Since activated carbon is generally a non-polar material, it adsorbs organic compounds in preference to polar inorganic species. Adsorption of organic molecules is similar to that responsible for the salting out of organic materials dissolved in water by the addition of a simple inorganic salt.

Activated carbon is a very versatile substrate with various organic and inorganic compounds. It is suitable for gold recovery because of its mechanical strength which is very important in the carbon in pulp process where it is mixed directly with the leach slurry and must be able to withstand abrasion. Finely abraded carbon loaded with gold will be lost in the tailings. Typical carbon products employed in gold recovery have large internal surface areas usually between 900 and 1200 $m^2/g$ as measured by the nitrogen B.E.T method. The ability of activated carbon to adsorb various gold complexes follows the sequence:

$AuCl_4^- > Au(CN)_2^- > Au(SCN)_2^- > Au[CS(NH_2)_2]_2^+$ [23]

This would suggest that activated carbon would be more suitable for the recovery of gold from the cyanide medium rather than the acidic thiourea medium. It can also be seen that the gold thiourea complex is cationic rather than anionic and the order of adsorption may be a reflection of the ion exchange properties of the carbon. The reduction potential of most activated carbon products lies in the range +0.16 to -0.16V (Versus S.C.E). This potential is low enough for the reduction of the gold chloride complex, $AuCl_4^-$ ($E^o$=0.8V Vs S.C.E), the gold thiocyanate complex $Au(SCN)_2^-$ ($E^o$=0.74V Vs S.C.E) and the gold thiourea complex $Au(CS(NH_2)_2)_2^+$ ($E^o$=0.11 Vs S.C.E), to the metal, but not for the reduction of the aurocyanide complex ($E^o$=-0.79V Vs S.C.E), or the gold thiosulphate complex ($E^o$=-0.21V Vs S.C.E). Work is being carried out on the actual mechanism of adsorption of the gold-thiourea complex onto activated carbon.

### 5.2.1 The Langmuir Isotherm

When Van Der Waals adsorption occurs, the forces can extend from one layer of molecules to the other and it is therefore probable that the species adsorbed on the surface is several molecules thick especially at low temperatures and high pressures. By supposing that only a unimolecular layer of gas can be adsorbed, Langmuir (1916) was able to determine the dependance of the extent of adsorption on the pressure at a set temperature. This dependance is called the ADSORPTION ISOTHERM of the system.

When a molecule collides with the surface of a solid, it becomes trapped only if it is able to dissipate its energy into the thermal vibrations of the underlying lattice. If it is not trapped, it is reflected and returns to the gas phase. The proportion of collisions with the surface that lead to adsorption is called the sticking probability, S.

$$S = \frac{\text{rate of adsorption of molecules by the surface}}{\text{rate of collision of molecules with the surface}}$$

The sticking probability depends on how much of the surface is covered and so decreases as surface sites fill up. The extent of surface coverage is normally expressed in terms of the fractional coverage, θ, defined as

$$\theta = \frac{\text{number of adsorption sites filled}}{\text{number of adsorption sites available}}$$

The simplest isotherm is based on the view that every adsorption site is equivalent and the ability of the molecules to bind there is independent of whether or not the neighbouring sites are occupied. When an adsorbing surface is exposed to a gas, molecules of gas will strike the surface and adhere for an appreciable time while other gas molecules will tend to evaporate from the surface. When a state of adsorption equilibrium is attained, the rate of adsorption is equal to the rate of evaporation.

$$A_{(g)} + M_{(Surface)} \rightleftharpoons AM$$

At constant temperature, gas molecules strike the surface at a rate proportional to the concentration, C, of the gas and on the number of vacant sites on the surface, $N(1-\theta)$, where N is the total number of sites. Therefore the rate of adsorption i.e.

$$\frac{d\theta}{dt} = k_aCN(1-\theta)$$

The rate of desorption is proportional to the number of adsorbed species, $N\theta$, i.e.

$$\frac{d\theta}{dt} = k_dN\theta$$

Therefore at equilibrium,

$$k_aC_{eq}N(1-\theta) = k_dC_{eq}N\theta$$

Solving for $\theta$ gives,

$$\theta = \frac{aC_{eq}}{1+aC_{eq}} \qquad \text{Where } a = k_a/k_d$$

Since each site can only accommodate one molecule, the number of sites occupied per gram of adsorbent is equivalent to the number of grams of solute adsorbed per gram of adsorbent i.e.

$$q_e = x/m$$

$q_e$ = equilibrium solid phase solute concentration (g/g)
m = mass of adsorbent (g)
x = mass of adsorbate adsorbed (g)

$$\theta = q_e/Q = \frac{aC_{eq}}{1+aC_{eq}}$$

Q = Langmuir monolayer capacity (g/g)

$$q_e = x/m = \frac{QaC_{eq}}{1+aC_{eq}} \qquad \text{or}$$

$$\frac{C_{eq}}{q_e} = \frac{1}{k} + \frac{aC_{eq}}{k} \qquad \text{where } k=Qa$$

$$y = c + mx$$

Therefore by plotting $C_{eq}/q_e$ against $C_{eq}$, a graph can be obtained of slope 1/Q and intercept 1/Qa and hence the capacity of an adsorbent can be determined experimentally. Results of work carried out by Bowden [26] suggest that the adsorption of the gold thiourea complex onto modified peat and activated carbon follows the Langmuir Isotherm model. Although the Langmuir Isotherm model was developed to describe the adsorption of gases, it can be used as a tool to compare the adsorption characteristics of various compounds onto adsorbents. It is merely used as a useful model or standard by which various compounds can be compared.

The aim of the following experiments was therefore to determine the capacity of the activated carbon for thiourea, copper(II), iron(III) and a copper thiourea complex. This information would be useful as it would give an indication of the degree of adsorption of the species which would be typically adsorbed from a leach solution. Any species which is adsorbed would reduce the capacity of the carbon for the gold-thiourea complex since the number of available sites would be reduced.

The general method for determining the capacity of an adsorbent for a particular adsorbate involves three steps:

(a) The same mass of carbon is added to separate flasks, each containing different known concentrations of the adsorbate of interest.

(b) The contents are left to shake at a uniform temperature until equilibrium is reached.

(c) The carbon is separated from the system by filtration and the concentration of adsorbate left in the filtrate is determined.

It is important to choose a sufficient mass of carbon so that there is a "measurable" change in adsorbate concentration in the filtrate.

### 5.2.2 Thiourea Analysis

In acidic solutions, thiourea is oxidised by potassium iodate to give formamidine disulphide (RSSR) according to the equation

$$6Tu + KIO_3 \xrightarrow{H^+} 3RSSR + 3H_2O + KI$$

When all of the thiourea is used up, the $KIO_3$ reacts with the KI to release free iodine,

$$IO_3^- + 6H^+ + 5I^- \longrightarrow 3I_2 + 3H_2O$$

The released iodine exists as the $I_3^-$ anion,

$$I_2 + I^- \rightleftharpoons I_3^-$$

which forms an insoluble blue complex with starch and hence the end-point can be detected easily by direct titration.

### 5.2.3 Copper Analysis

Copper can be analysed with ethylenediamine-tetra-acetic acid [10]. Diluted ammonia was added to each analyte until the hydroxide formed disappeared. Titration was made immediately after addition of "Murexide" indicator until the colour changed from orange-yellow to bright violet.

Copper was also analysed by atomic absorption spectrophotometry using the normal calibration method.

### 5.2.4 Iron Analysis

Iron was analysed by atomic absorption spectrophotometry using the normal calibration method.

### 5.2.5 Copper-Thiourea complex analysis

The complex was analysed using both atomic absorption spectrophotometry and by titration with potassium iodate as before.

## 5.3 DETERMINATION OF THE CAPACITY OF "EUROCARB" ACTIVATED CARBON FOR THIOUREA

The aim of this experiment was to determine the capacity of activated carbon for thiourea using the Langmuir adsorption isotherm. The experiment was carried out at both pH=1 and pH=2.

### 5.3.1 Reagents

0.05 Molar thiourea from thiourea (SKW-Trotsberg)
Standard $KIO_3$ solution from $KIO_3$ (Riedel-De-Haen)
Activated carbon size 1.4-2.0mm (Eurocarb Products Ltd)
Sulphuric acid (Riedel-De-Haen)
Deionised distilled water (Elgastat U.H.Q)
Starch solution from Starch (B.D.H Chemicals)
1 Molar Phosphoric acid from Phosphoric acid (Riedel-De-Haen)

### 5.3.2 Experimental details

An approximate 0.05 M thiourea solution was made up and a 25cm$^3$ aliquot was titrated with a standard potassium iodate solution. 100, 80, 60, 40, 20, 10 and 5cm$^3$ of thiourea were pipetted into 7 grade "A" 100cm$^3$ volumetric flasks. Each solution was made up to the mark with distilled deionised water and transferred to a 250cm$^3$ conical flask. Activated carbon (2g) was weighed accurately and added to each solution. The flasks were sealed and left to shake until equilibrium had been reached after which a 10cm$^3$ aliquot was added to a 250cm$^3$ conical flask containing 50cm$^3$ of 1M phosphoric acid and titrated with a standard potassium iodate solution.

A simple BASIC program (TIOTRM) [25] was used into which the following information was entered for each experiment:

(1) The concentration of $KIO_3$ (Moles/$dm^3$).

(2) The total volume in each case ($cm^3$).

(3) The titration sample volume ($cm^3$).

(4) $cm^3$ of standard $KIO^3$ required to standardise 25$cm^3$ of the thiourea solution.

(5) The $cm^3$ of thiourea made up to 100$cm^3$ in each case.

(6) The mass of carbon (g) and titration result ($cm^3$).

(7) The number of flasks.

The equilibrium concentration of thiourea in Moles/$dm^3$, the mass of thiourea adsorbed per gram of carbon (x/m) and the equilibrium concentration divided by x/m was calculated for each titration result. It was found that a mass of 1g of carbon used with an approximate 0.05 M thiourea solution gave rise to a significant change in thiourea concentration while maintaining titration volumes that could be accurately measured.

The actual isotherm was plotted in each case by plotting x/m versus equilibrium concentration. The monolayer capacity of thiourea was determined by plotting the equilibrium concentration divided by x/m versus the equilibrium concentration. The capacity was found from the inverse of the slope of the graph.

## 5.4 Results and discussion

**Table 5.1**

pH=1, 24 hour contact.

| Mass Carbon (g) | Init.Conc. thiourea (Moles/dm$^3$) | Equil.Conc. thiourea (Moles/dm$^3$) | Mass Tu adsorbed (g) | Ceq/x/m (Moles/dm$^3$) |
|---|---|---|---|---|
| 1.002 | 0.06051 | 0.03999 | 0.1559 | 0.2569 |
| 1.001 | 0.05446 | 0.03398 | 0.1556 | 0.2185 |
| 1.000 | 0.04841 | 0.02866 | 0.1501 | 0.1911 |
| 1.000 | 0.04236 | 0.02455 | 0.1354 | 0.1814 |
| 1.000 | 0.03026 | 0.01423 | 0.1218 | 0.1168 |
| 1.000 | 0.02420 | 0.00998 | 0.1081 | 0.0923 |
| 1.000 | 0.01513 | 0.00458 | 0.0801 | 0.0572 |

**Table 5.2**

pH=2, 24 hour contact

| Mass Carbon (g) | Init.Conc. thiourea (Moles/dm$^3$) | Equil.Conc. thiourea (Moles/dm$^3$) | Thiourea adsorbed (g) | Ceq/x/m (Moles /dm$^3$) |
|---|---|---|---|---|
| 0.999 | 0.01114 | 0.00228 | 0.0673 | 0.03383 |
| 1.000 | 0.01670 | 0.00418 | 0.0951 | 0.04400 |
| 0.999 | 0.02784 | 0.01234 | 0.1178 | 0.10470 |
| 0.999 | 0.03341 | 0.01671 | 0.1269 | 0.13150 |
| 1.002 | 0.04454 | 0.02553 | 0.1445 | 0.17700 |
| 0.999 | 0.05568 | 0.03476 | 0.1589 | 0.21850 |

For the experiment carried out at a pH of 1, Figure 5.5 illustrates the dependence of surface coverage on the concentration of thiourea. It can be seen that the

**Figure 5.5** X/M Versus Thiourea Concentration (Moles/$dm^3$) at pH=1.

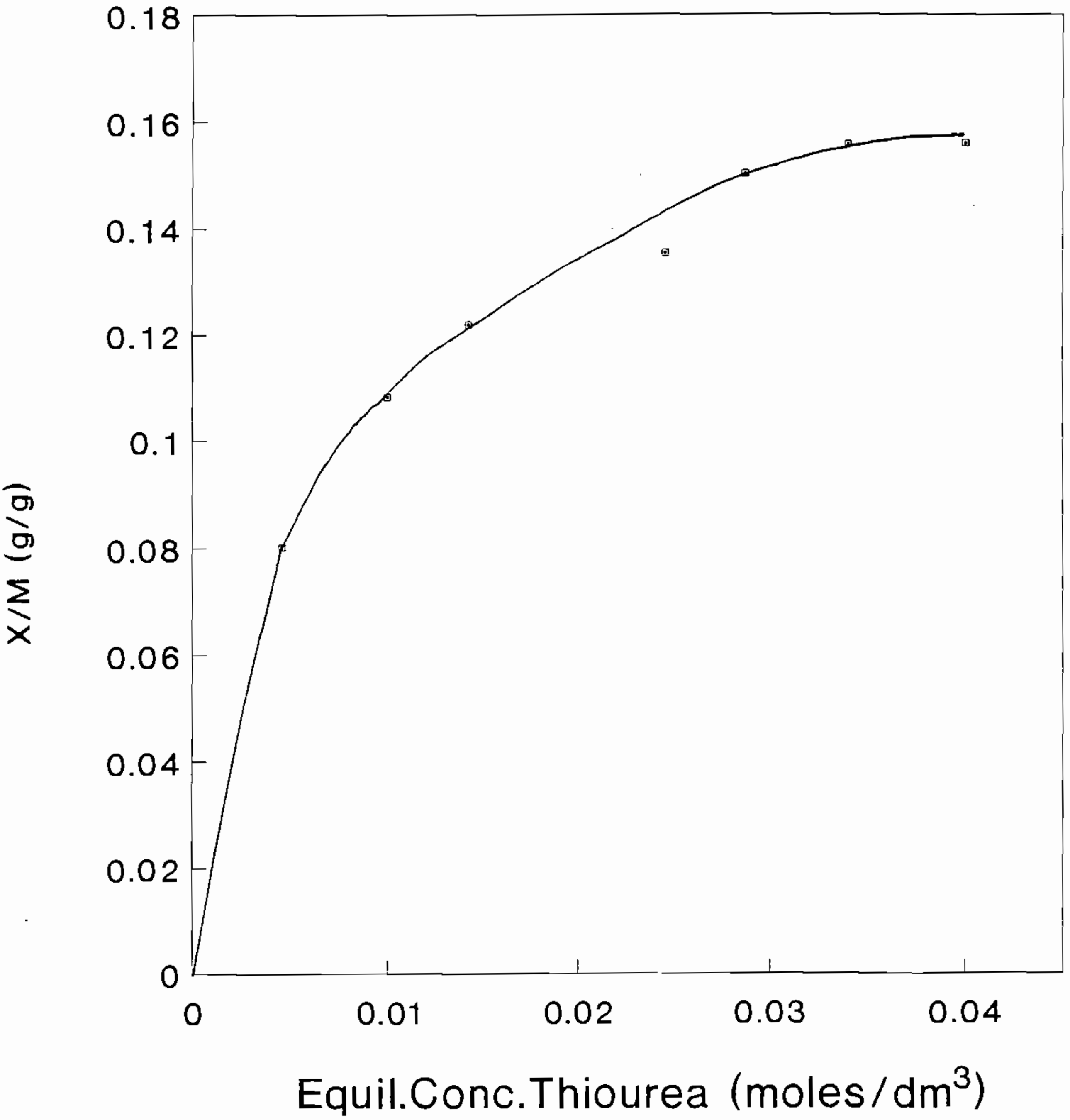


**Figure 5.6** $C_{eq}/(X/M)$ (Moles/dm$^3$) Versus $C_{eq}$ (Moles/dm$^3$) for Thiourea at pH=1.

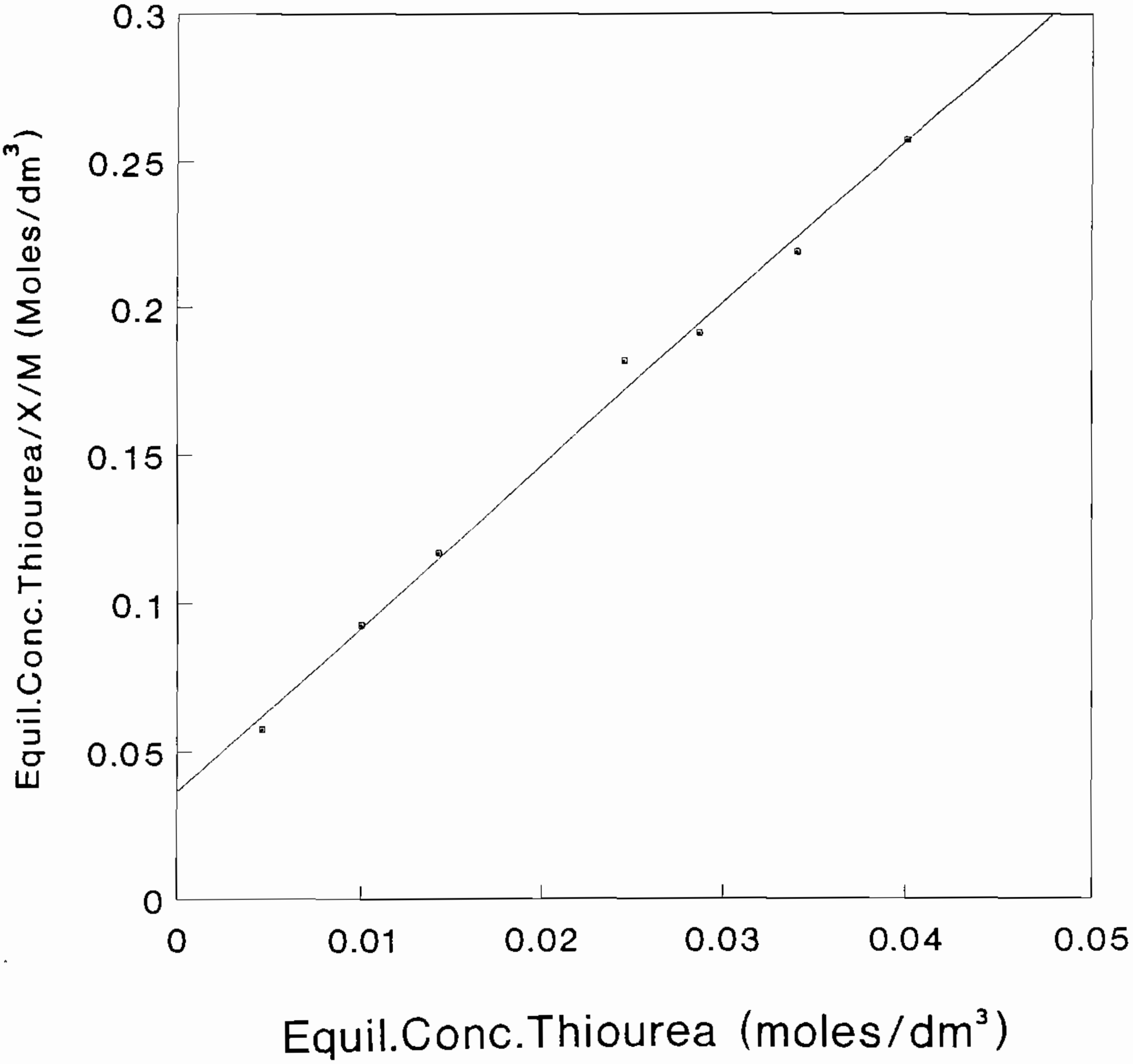


**Figure 5.7** X/M Versus Thiourea Concentration (Moles/dm$^3$) at pH=2.

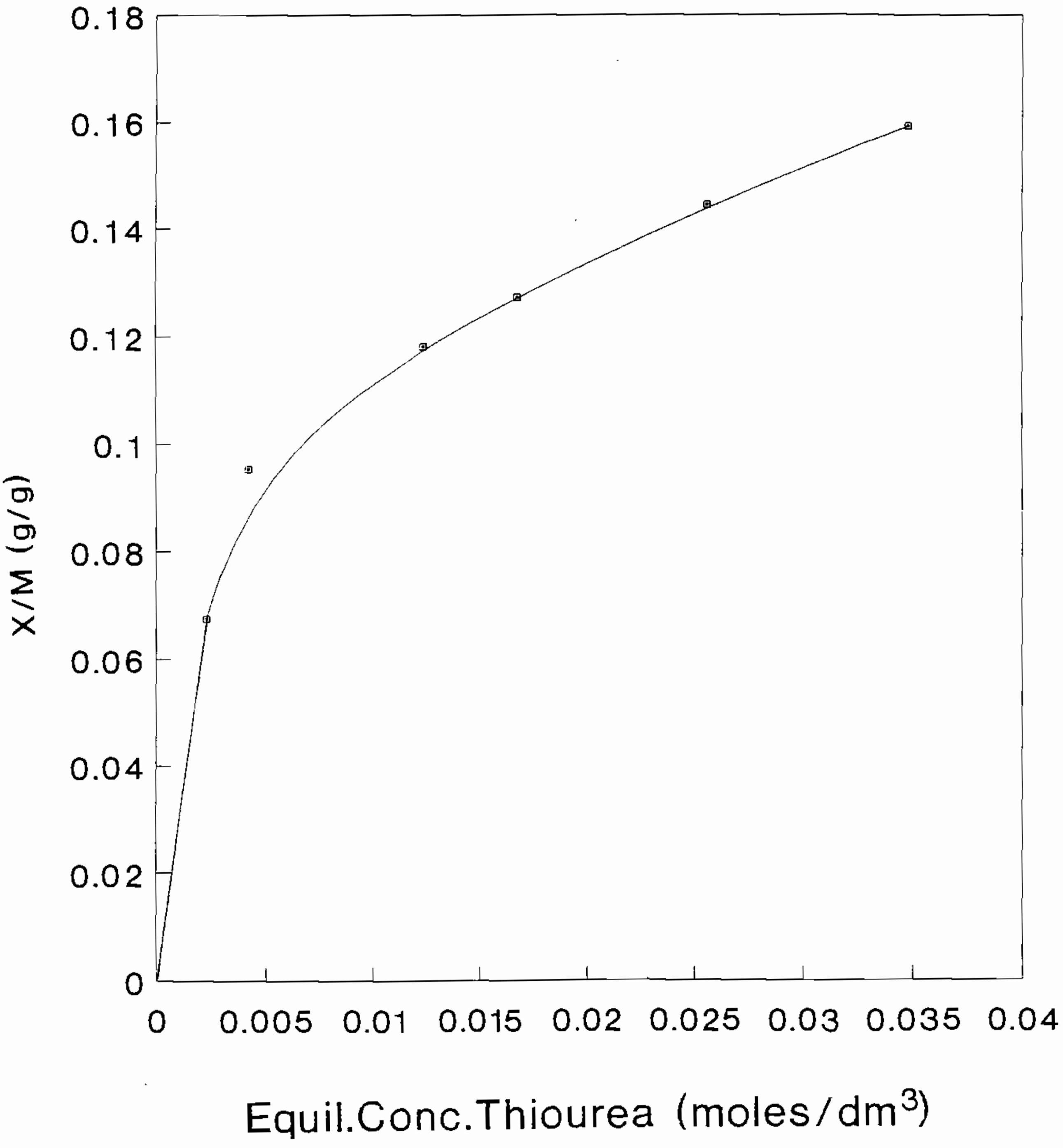
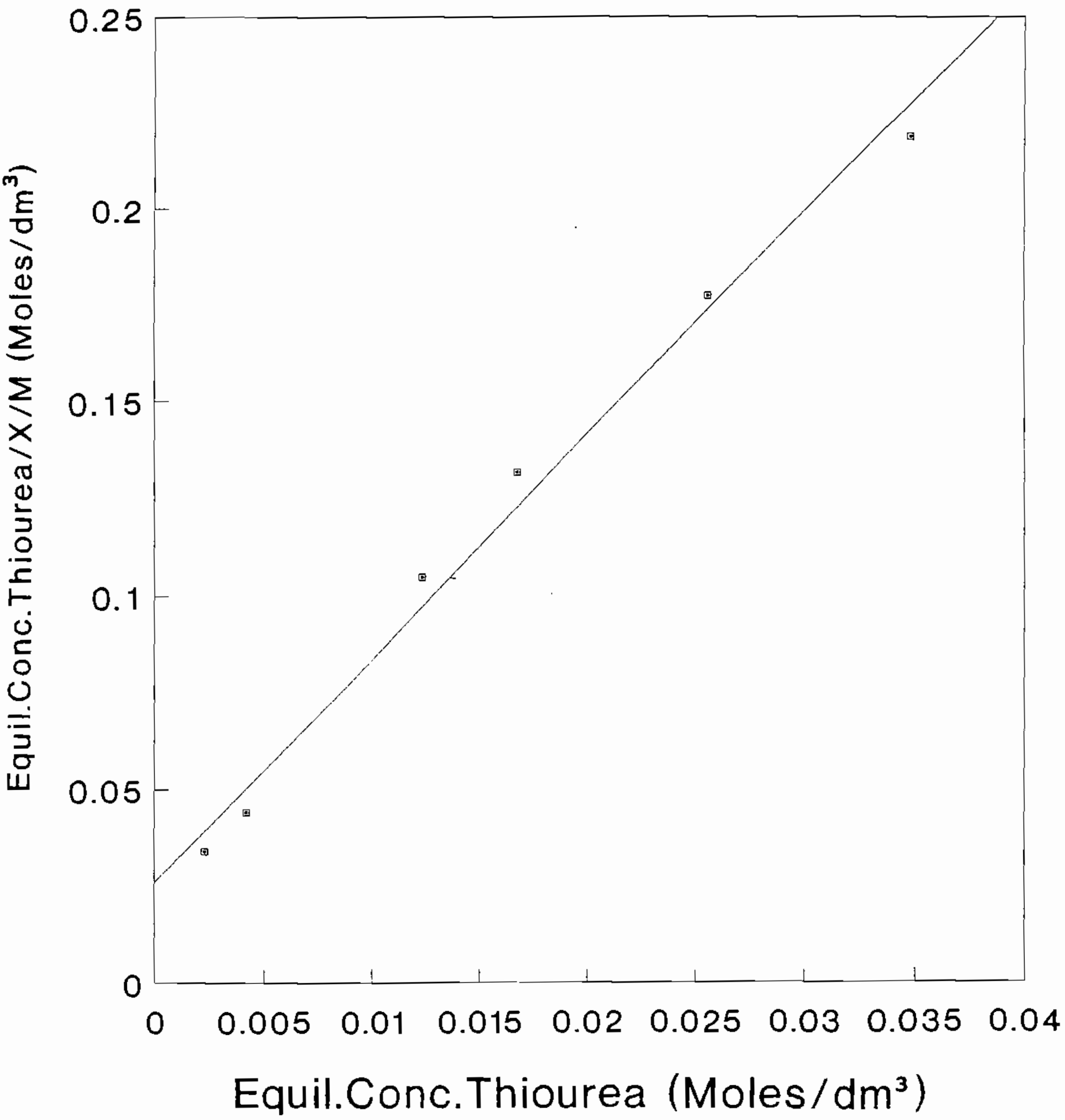


**Figure 5.8** $C_{eq}/(X/M)$ (Moles/dm$^3$) Versus $C_{eq}$ (Moles/dm$^3$) for Thiourea at pH=2.



surface coverage increases with concentration and approaches a limiting value as the concentration increases. The shape of the graph is typical of physical adsorption with filling of the micropores.

Figure 5.6 shows the linear relationship between equilibrium concentration divided by x/m and equilibrium concentration thus in accordance with the Langmuir Isotherm model. This is supported by the value of the correlation coefficient for the set of data i.e. 0.9956. From the inverse of the slope of the graph, the monolayer capacity was found to be 182 kg of thiourea per tonne of carbon.

For the experiment carried out at a pH of 2, Figure 5.7 illustrates similar behaviour to that in figure 5.5 although the levelling-off effect is not as pronounced. figure 5.8 again illustrates the correspondence with the Langmuir Isotherm model. (Correlation Coefficient=0.9947). The monolayer capacity was found to be 173 kg of thiourea per tonne of carbon.

## 5.5 DETERMINATION OF THE CAPACITY OF ACTIVATED CARBON FOR IRON(III)

The aim of this experiment was to determine the capacity of activated carbon for iron(III) (a typical component in the thiourea leach system) by use of the Langmuir Isotherm model.

### 5.5.1 Reagents

Activated carbon, size 1.4-2.0mm (Eurocarb Products Ltd.)
Sulphuric acid (Riedel-De-Haen)
1000 ppm Iron(III) solution from ferric sulphate (Riedel-De-Haen)
Deionised distilled water (Elgastat U.H.Q)

### 5.5.2 Instrumentation

Stuart Scientific shaker
Both samples were analysed using a Shimadzu AA670 Atomic Absorption/Flame Emission Spectrophotometer

**Instrument conditions**
Wavelength = 248.3 nm
Hollow cathode lamp current = 8 mA
Burner height = 10 cm
Slit width = 0.2 nm
Flame type = Acetylene/Air
Fuel flow rate = 1.6 $dm^3$/min.
Oxidant flow rate = 8$dm^3$/min.
Deuterium lamp ON

### 5.5.3 Experimental details

A 100 ppm solution of iron(III) was made up by adding 25$cm^3$ of the 1000 ppm iron(III) solution to a 250$cm^3$ grade "A" volumetric flask and making up to the mark with 0.01 Molar sulphuric acid. Volumes of 5,10,15,20,30 and 40$cm^3$ were added to six 100$cm^3$ volumetric flasks and each was made up to the mark with 0.01 M sulphuric acid.Each solution was transferred to a 250$cm^3$ conical flask to which was added 2g of carbon. The flasks were sealed and left to shake at speed 7 for 24 hours. After the time had elapsed, an aliquot of each flask was diluted appropriately and analysed for iron(III) by AAS using the normal calibration method. Graphs were plotted as in Section 5.3.

## 5.6 Results and discussion

**Table 5.3**
pH=1, 24 hour contact

| Init.Conc. Iron(III) (ppm) | Equil.Conc. Iron(III) (ppm) | Mass carbon (g) | x/m (g/g) (E-4) | $C_{eq}$/x/m (ppm) (E+4) |
|---|---|---|---|---|
| 5 | 2.846 | 2.002 | 1.076 | 2.644 |
| 10 | 6.989 | 2.002 | 1.504 | 4.648 |
| 15 | 9.820 | 2.001 | 2.588 | 3.794 |
| 20 | 13.65 | 2.003 | 3.169 | 4.308 |
| 30 | 20.93 | 2.001 | 4.533 | 4.618 |
| 40 | 29.18 | 2.001 | 5.408 | 5.395 |

From Figure 5.9, the relationship between the equilibrium iron(III) concentration and the mass of iron(III) adsorbed per gram of carbon can be seen after a 24 hour period. It appears that the value of x/m does not approach a constant value in this time period. This may suggest that equilibrium has not yet been reached. If it is assumed that equilibrium has in fact been reached, from figure 5.10, the capacity of carbon for iron(III) determined from the inverse of the slope is found to be approximately 1kg of iron(III) per tonne of carbon.

**Figure 5.9** X/M Versus Iron(III) Concentration (ppm).

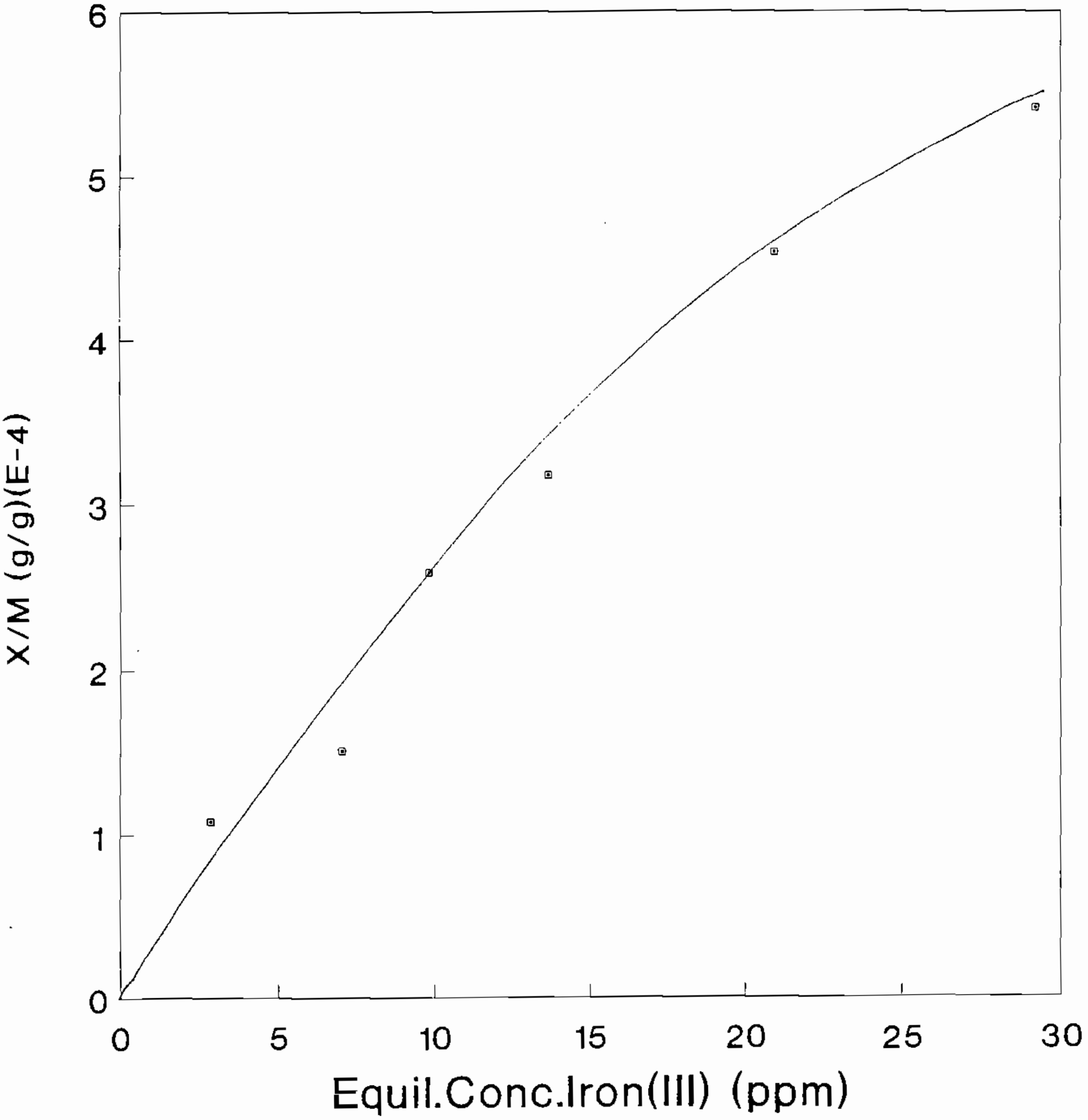
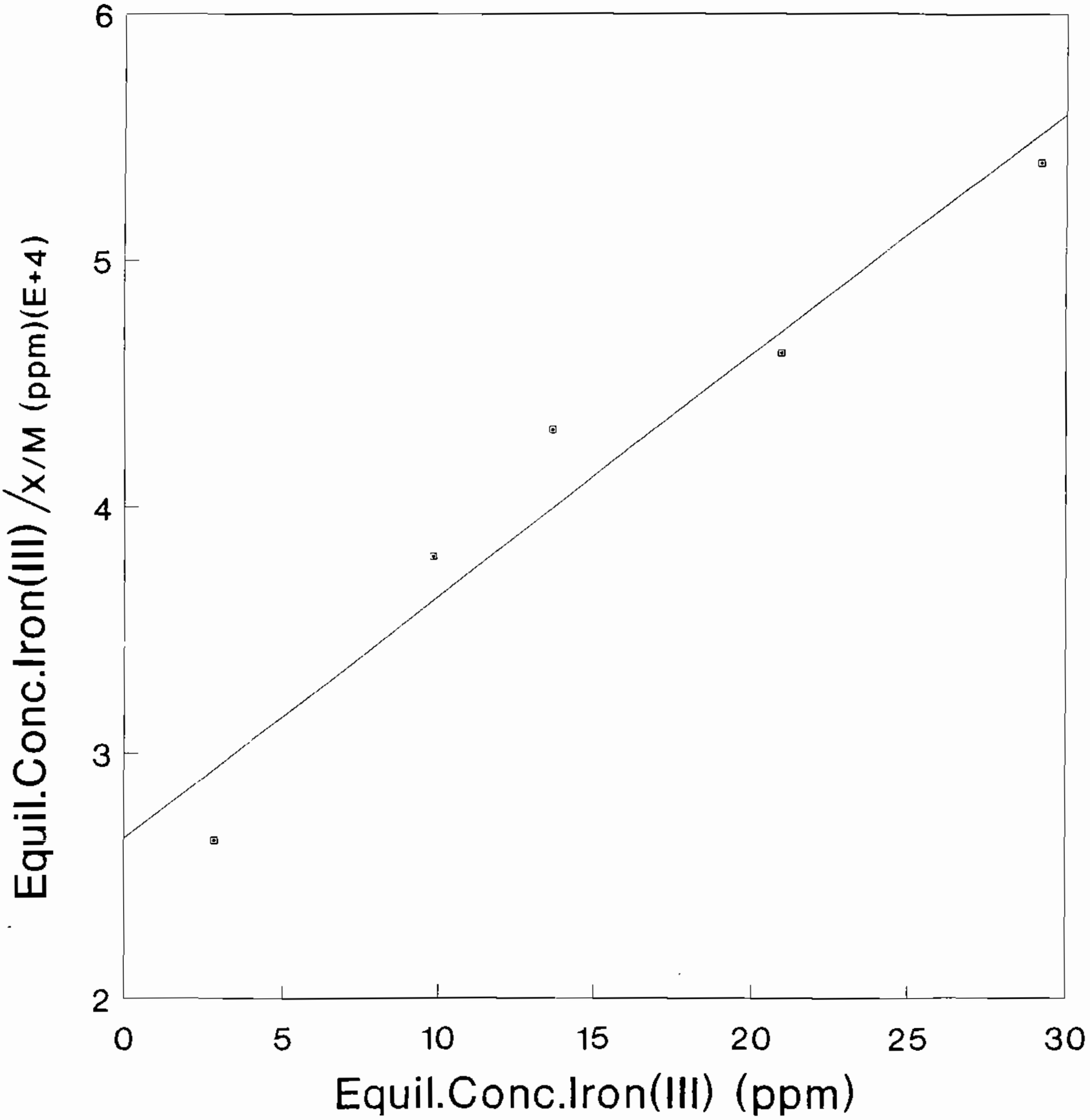


**Figure 5.10** $C_{eq}/(X/M)$ (ppm) Versus $C_{eq}$ (ppm) for Iron(III) at pH=1.



## 5.7 DETERMINATION OF THE CAPACITY OF CARBON FOR COPPER(II)

The aim of this experiment was to determine the capacity of carbon for copper(II) at pH's of 1 and 2.

### 5.7.1 Reagents

1000 ppm copper(II) solution from copper sulphate (Riedel-De-Haen)
0.003 Molar EDTA solution from ethylenediamine-tetra-acetic acid di-sodium salt (BDH Chemicals).
Concentrated ammonia solution (Riedel-De-Haen)
Activated carbon size 1.4-2.00 mm (Eurocarb Products Ltd).
0.1 and 0.01 Molar sulphuric acid from sulphuric acid (Riedel-De-Haen)
Deionised distilled water (Elgastat U.H.Q).

### 5.7.2 Instrumentation

Stuart Scientific shaker

### 5.7.3 Experimental details

A 1000 ppm copper(II) solution was made up with deionised distilled water. Volumes of 10, 20, 40, 50, 60, 70, 80 and 100cm$^3$ of the copper(II) solution were added in eight 100cm$^3$ grade "A" volumetric flasks. Each solution was made up to the mark with distilled deionised water and transferred to a 250cm$^3$ conical flask into which was added 2g of carbon. The pH of these solutions was 6.5. The flasks were sealed and left to shake at speed 7 for 24 hours. After 24 hours, each solution was filtered and two 10cm$^3$

aliquots of filtrate were added to two 250cm$^3$ conical flasks. Concentrated ammonia was added dropwise to each flask until the hydroxide formed disappeared resulting in a clear blue solution of the copper-ammonia complex. A very small quantity of solid "Murexide" indicator was added until an orange-yellow colour formed. The solution was titrated with standard EDTA solution until a bright violet colour formed. 10cm$^3$ of the stock solution were titrated similarly and the amount of copper adsorbed from the difference in actual and expected volumes of EDTA required for each titration.

The experiment was repeated at pH=2 using 0.01 M $H_2SO_4$ to make up the copper$^{2+}$ solutions. The experiment was also repeated at pH 1 using 0.1 M $H_2SO_4$ to make up the copper(II) solutions and each solution was analysed using AAS using the normal calibration method.

**Instrument conditions**

Wavelength = 324.8 nm
Hollow cathode lamp current = 3mA
Burner height = 10 cm
Flame type = Acetylene/Air
Fuel flow rate = 1.8 dm$^3$/min

Similar graphs were plotted as before where applicable.

## 5.8 Results and discussion

**Table 5.4**

pH=6.5, 24 hour contact.

| Init.Conc. Copper(II) (ppm) | Equil.Conc. Copper(II) (ppm) | Mass carbon (g) | x/m (g/g) | Ceq/x/m (ppm) |
|---|---|---|---|---|
| 100 | 11 | 2.002 | 4.45E-3 | 2.47E3 |
| 200 | 84 | 2.004 | 5.80E-3 | 1.45E4 |
| 300 | 166 | 1.998 | 6.71E-3 | 2.47E4 |
| 400 | 259 | 1.999 | 7.05E-3 | 3.67E4 |
| 500 | 355 | 2.003 | 7.24E-3 | 4.90E4 |
| 600 | 449 | 2.002 | 7.54E-3 | 5.96E4 |
| 700 | 547 | 2.000 | 7.65E-3 | 7.15E4 |
| 800 | 642 | 1.999 | 7.90E-3 | 8.13E4 |
| 900 | 743 | 2.000 | 7.85E-3 | 9.47E4 |
| 1000 | 832 | 2.000 | 8.40E-3 | 9.91E4 |

**Table 5.5**

pH=2, 24 hour contact.

| Init.Conc. Copper(II) (ppm) | Theoretical $cm^3$ EDTA required | Actual $cm^3$ EDTA required | Mass carbon (g) |
|---|---|---|---|
| 1000 | 54.08 | 54.32 | 1.998 |
| 800 | 43.26 | 43.12 | 2.001 |
| 700 | 37.86 | 38.09 | 2.000 |
| 600 | 32.45 | 32.50 | 2.003 |
| 500 | 27.04 | 27.24 | 1.999 |
| 400 | 21.63 | 22.00 | 2.002 |
| 200 | 10.82 | 11.23 | 2.002 |
| 100 | 5.41 | 5.75 | 2.001 |

**Table 5.6**

pH=1, 24 hour contact.

| Init.Conc. Copper(II) (ppm) | Equil.Conc. Copper(II) (ppm) | Mass carbon (g) |
|---|---|---|
| 5 | 5.06 | 2.002 |
| 10 | 9.86 | 2.003 |
| 20 | 19.55 | 2.001 |
| 30 | 29.27 | 2.002 |
| 50 | 49.37 | 2.002 |

From figure 5.11, at pH = 6.5 it can be seen that the value of x/m approaches a constant value suggesting filling of the micropores. From figure 5.12 it can be seen that the experimental data fit the Langmuir Isotherm model quite well (Correlation coefficient = 0.9971). From the slope, the monolayer capacity of copper sulphate 0.0326g/g of carbon i.e. the capacity of carbon for copper(II) is 8.3kg per tonne of carbon.

The results of the experiments at pH of 1 and 2 suggest that the copper(II) ion is not adsorbed at these pH's. This suggests that for the copper(II) ion, activated carbon has a low ion exchange capacity at these pH's. This result is not surprising since most metals are more soluble at low pH's. They have a higher affinity for acidic solutions rather than basic solutions. Therefore an increase in solubility at low pH's reflects a greater affinity between solute and solvent and acts to oppose the attraction between the carbon and the solute.

**Figure 5.11** X/M Versus $C_{eq}$ (ppm) for Copper(II) at pH=6.5.

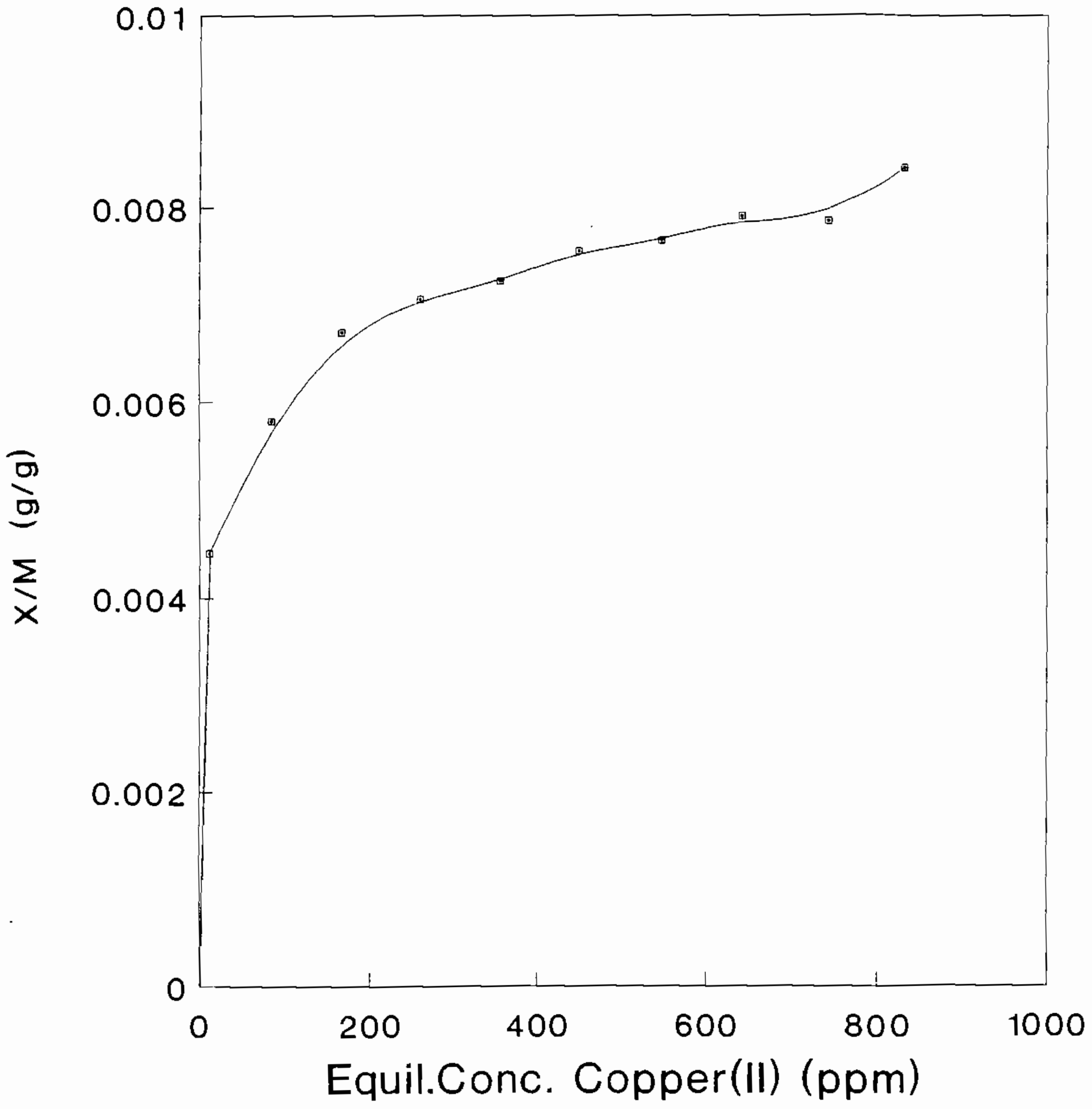
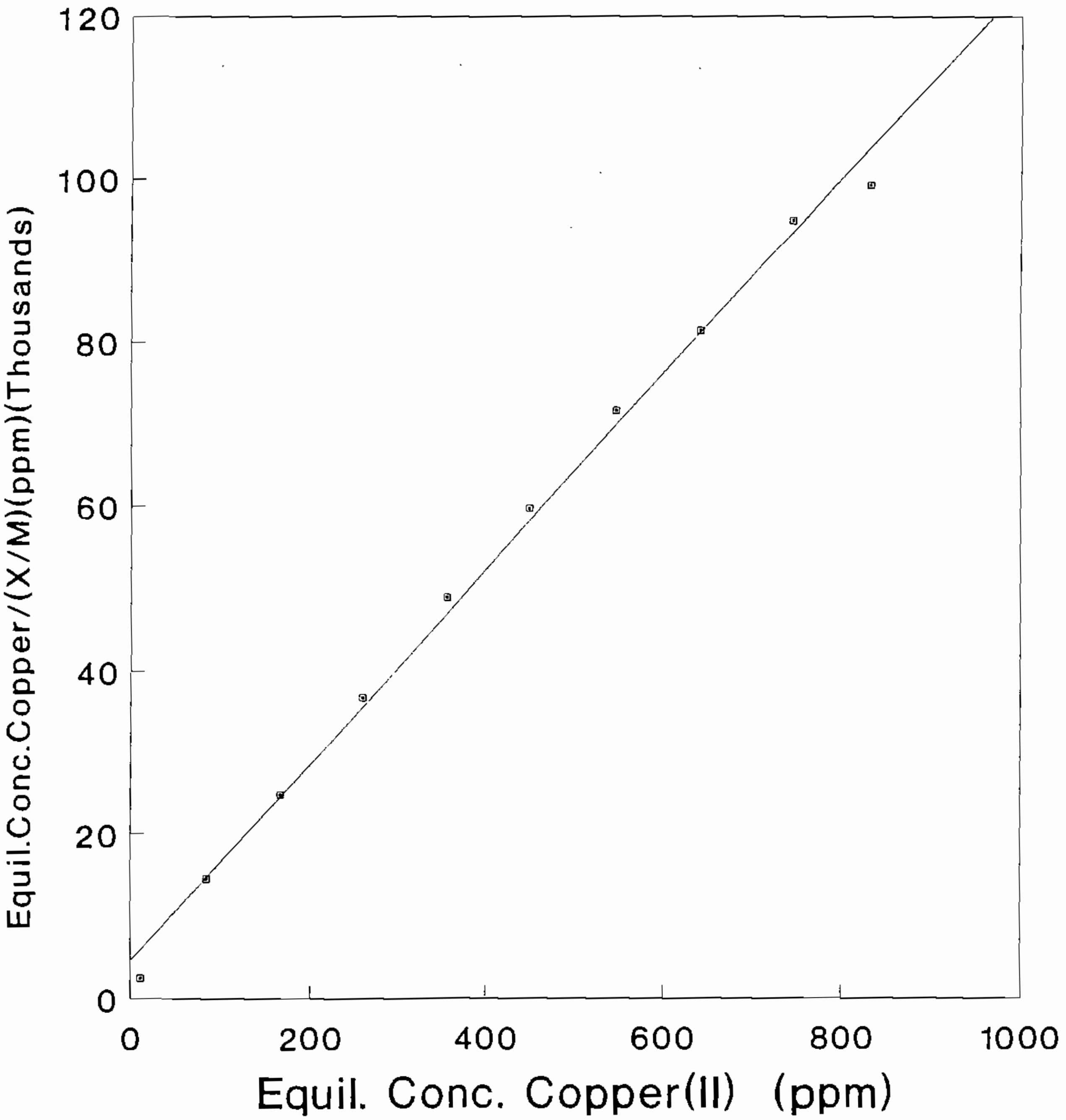


**Figure 5.12** $C_{eq}/(X/M)$ (ppm) Versus $C_{eq}$ (ppm) for Copper(II) at pH=6.5.



## 5.9 DETERMINATION OF THE CAPACITY OF CARBON FOR THE COPPER-THIOUREA COMPLEX $[Cu_2(Tu)_6]SO_4.H_2O$.

Thiourea is known to form many complexes with transition and non-transition metals. Copper(II) is reduced to copper(I) by thiourea as follows

$$2Cu(II) + 2Tu \rightarrow 2Cu(I) + RSSR + 2H^+$$

The copper(I) ion then forms many complexes with thiourea. An attempt was made to synthesise one of these complexes, the $[Cu_2(Tu)_6]SO_4.H_2O$ and determine the capacity of carbon for it.

### 5.9.1 Reagents

Copper sulphate (Riedel-De-Haen)
Thiourea (SKW-Trotsberg)
Distilled deionised water (Elgastat U.H.Q)
Sulphuric acid (Riedel-De-Haen)
Activated carbon size 1.4-2.00mm (Eurocarb Products Ltd.)
Potassium iodate (Riedel-De-Haen)
Starch solution from Starch (BDH Chemicals)

## 5.10 SYNTHESIS OF THE $[Cu_2(TU)_6]SO_4.H_2O$ COMPLEX

0.63 g of copper sulphate pentahydrate were dissolved in 100cm$^3$ of 0.01M $H_2SO_4$. 3g of thiourea were dissolved in 100cm$^3$ of 0.01M $H_2SO_4$. The copper sulphate solution was added to the thiourea solution and the resulting solution was cooled on ice for three hours. The resulting needle-like white crystals were filtered using a Buchner funnel and washed slowly with 200 $cm^3$ of cold methanol. The crystals were transferred onto a dry filter paper and left in a desiccator for 24 hours. The spectral identity was as previously reported [27]. The resulting crystals were analysed in the microanalytical laboratory in U.C.D.The procedure was repeated three times.

0.1373g of the copper-thiourea complex was dissolved in 0.1M $H_2SO_4$ and made up to the mark in a 500$cm^3$ volumetric flask. The resulting solution contained copper at 50 ppm. 10, 20, 40, 60, 80 and 100$cm^3$ of the stock solution were added to six grade "A" 100$cm^3$ volumetric flasks and each solution was made up to the mark with 0.1M $H_2SO_4$. Each solution was transferred to a 250$cm^3$ conical flask to which was added 0.5g of activated carbon. The flasks were sealed and left to shake at speed 7 for 24 hours. 10 $cm^3$ of the stock solution was titrated with 0.0004M $KIO_3$. The titration was carried out slowly since the reaction rate is slow because of the low concentrations of the species.

After the elapsed time, each solution was filtered and a 25$cm^3$ aliquot was titrated against standard $KIO_3$. Each filtrate was also analysed by AAS after an appropriate dilution in each case.

## 5.11 Results and discussion

**Table 5.7 Microanalysis results**

| Element | Theoretical % | Actual %<br>Sample number<br>1 | <br><br>2 | <br><br>3 |
|---|---|---|---|---|
| Carbon | 10.3 | 10.1 | 10.1 | 10.2 |
| Hydrogen | 3.7 | 3.7 | 3.8 | 3.7 |
| Nitrogen | 24.1 | 24.4 | 24.2 | 24.2 |
| Sulphur | 32.1 | - | - | - |
| Copper | 18.2 | 18.2 | 18.2 | 18.1 |

NOTE: Sulphur cannot be analysed in the presence of copper.

**Table 5.8**

| Mass carbon (g) | Init.Conc. Copper(II) (ppm) | Equil.Conc. Copper(II) (ppm) (by AAS) | $cm^3$ $KIO_3$ required before 24 hours | $cm^3$ $KIO_3$ required after 24 hours |
|---|---|---|---|---|
| 0.4996 | 50 | 47.65 | 24.4 | 0 |
| 0.5000 | 40 | 39.13 | 19.52 | 0 |
| 0.5001 | 30 | 29.15 | 14.64 | 0 |
| 0.5010 | 20 | 19.92 | 9.76 | 0 |
| 0.5002 | 10 | 10.03 | 4.88 | 0 |
| 0.5000 | 5 | 5.05 | 2.44 | 0 |

The results of the microanalysis in table 5.7 suggest that the $[Cu_2(Tu)_6]SO_4.H_2O$ complex had been synthesised since the actual % weight of each element found corresponded well to the theoretical % weight. When considering the adsorption of the complex using the $KIO_3$ titration, it appears that all of the complex in each solution was adsorbed. However, when analysed by AAS, it appears that there was in fact no adsorption and the level of copper in each solution remained the same. 25cm$^3$ of the 50 ppm copper stock solution required an average of 24.4cm$^3$ of potassium iodate whereas the analytes gave no end-point. This result suggests that even though thiourea is complexed to the copper(I) ion, it still becomes adsorbed onto the carbon surface with the release back into solution of the copper ion. The result may suggest that there is a ligand-exchange reaction occurring however further work would be required to confirm this.

## 5.12 Conclusions

(1) Thiourea is adsorbed very strongly by activated carbon at both pH 1 and 2 with a Langmuir monolayer capacity of 182 and 173 kg/tonne of carbon.

(2) Iron is very slightly adsorbed at a pH of 2 with a monolayer capacity of around 1kg/tonne of carbon.

(3) Copper is adsorbed at pH 6.5 with a capacity of 8.3 kg/tonne of carbon but is not adsorbed at all at either pH 1 or 2.

The physical implications of these conclusions from a process point of view is that the adsorption of the gold-thiourea complex will be poor in the presence of thiourea because of the reduction in the number of available sites on the carbon due to thiourea adsorption. This will be an inherent problem in a thiourea leach system which involves the recovery of gold with activated carbon.Formamidine disulphide, the oxidation product of thiourea would probably be adsorbed as strongly since it is a very similar compound.

Since iron is only very weakly adsorbed, it would appear that it does not play a significant role in the adsorption phase of the process.

Copper is not adsorbed at all at either pH 1 or 2 which may be good from a process point of view. Thiourea which exists in the form of the synthesised copper-thiourea complex appears to be adsorbed onto activated carbon with the release into solution of the copper ion, however, further work would be required to confirm this.

## REFERENCES CHAPTER 5

1. Dietz, V.R., Bibliography of solid adsorbents, United States cane sugar refiners and bone char manufacturers and National Bureau of Standards, Washington, D.C.: History of adsorbent carbon, p.ix ff;abstracts of reviews, histories and general discussions, pp.689-696, (1944).

2. Lowitz, Crell's Chem. Ann., 1:211 (1786).

3. Bussy, A., J. Pharm. Sci. Accessories, 8:257 (1822).

4. Hunter, J., J.Chem.Soc., 18:285 (1865).

5. Stenhouse, J., British patent 1395 (1856)., Chem. news, 3:78 (1861); 25:239 (1872).

6. Winser, F. and Swindells, J., British patent 835 (1868).

7. J. Gross and J.W Scott, "Precipitation of gold and silver from cyanide solutions on charcoal", Technical paper 378, US Bureau of mines, Washington D.C (1927).

8. W.N. Davis, "Use of carbon for the precipitation of gold from solution and subsequent burning", US Pat.227,963 (25 May 1880).

9. R.J. Adamson (ed.), Gold metallurgy in south Africa, Chamber of mines of South Africa, p.88, Johannesburg (1927).

10. W.D Johnson, "Abstraction of gold and silver from their solution in potassium cyanide", US Pat. 522,260 (3 July 1984).

11. Purification with activated carbon. John W. Hassler. 3rd edition, Chemical publishing Co., inc., pp 169, (1974).

12. British Patents 2037 (1855), 1287 (1857), 3164 (1857), 1409 (1865), 1103 (1869), 6687 (1888).
Belgian Patents 358,993, 385,944, 393,382, 444,407, 445,981.
Austrian Patents 134,282, 137,001, 158,209,
French Patents 357,432, 423,070, 475,184, 634,415.
German Patents 248,571, 491,971, 506,552, 528,505.
U.S Patents 1,087,486, 1,137,852, 1,151,553, 2,405,206.

13. References in chemical abstracts to literature since 1950 on activation:
Vol.44:1680e, 2208i, 2734d, 4658b, 5567d, 6606e, 8096b, 9138i, (1950)
Vol 45: 1274d, 4912i, 5913b, 5913d, 6368g (1951)
Vol 46: 8351f, 7281h, 6816a, 3781d (1952)
Vol 47: 2960c, 4586b, 7763b, 8998a, 10828c (1953)
Vol 48: 350h, 3666f, 6101c, 10310f, 13202f (1954)
Vol 49: 1310a, 4268e, 4268f (1955)
Vol 50: 1294a, 3742b, 5251a, 5276i (1956)
Vol 51: 12474d, 12474f, 14237e (1957)
Vol 52: 2384h, 5796e, 6768a, 7809b (1958)
Vol 53: 669a, 4791e, 5671h, 9651a (1959)

14. Mukherjee, S., and Bhattacharya, S., J.Sci. and Ind. Research (India), 4:235 (1945).

15. Blayden., H.E., Riley, H.L., and Taylor, A., J.Am. Chem. Soc., 62:180 (1940).

16. Riley, H.L., Trans Faraday Soc., 34:1011 (1938).

17. Biscoe, J., and Warren, B.E., J.Applied Phys., 13:364 (1942).

18. Berl, E., Trans Faraday Soc., 34:1040 (1938).

19. Hoffman, U., Wien. Chem. Ztg., 46:97 (1943).

20. J.J. Mattson and H.B. Mark, activated carbon, Marcel Dekker, New York (1971).

21. J.C. Bockris, in chemistry and physics of carbon, ed. by P.C. Walker, Vol 5, Marcel Dekker, New York (1969).

22. H.L. Riley, Chemistry and Industry, 58 No.17:391 (1939).

23. G.J. McDougall, Unpublished results.

24. Complexometric Assay methods with titriplex. E.Merck. A.G. Darmstadt p.35-36.

25. See Appendix 2.

26. Bowden, C., MSc. Thesis, Dublin Institute of Technology, (In Preparation).

27. Curran, A., "Studies into leaching of gold from Avoca Ore", MSc. Thesis, Dublin Institute of Technology, (1991).

# CHAPTER 6

# THIOUREA AND FORMAMIDINE DISULPHIDE ANALYSIS USING REVERSE-PHASE ION PAIR HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

## 6.1 Introduction

The basic principle of thiourea leaching and its economical viability depend on the careful control of the solution redox potential. This potential is caused by the simultaneous presence of both thiourea and formamidine disulphide. It has already been shown that at high redox potentials, formamidine disulphide undergoes an irreversible reaction to form thiourea, cyanamide and elemental sulphur. Control of this oxidation process is very important to minimise reagent consumption [1]. The standard method for determination of thiourea is by titration with potassium iodate. The determination of formamidine disulphide involves reduction by zinc to thiourea followed by titration with potassium iodate [2]. These methods are slow and often tedious and hence it was decided to attempt to develop a quick technique which would simultaneously determine both thiourea and formamidine disulphide in a typical leach system. A quick analytical method would be of great benefit in process control so that reagent consumption could be monitored during leaching. The method used to determine these compounds in a typical leach system was reverse phase ion pair chromatography.

The development of ion pair chromatography is generally attributed to Schill and his co-workers [1-7]. They found that excellent separation of ionic species could be obtained if silica gel and cellulose columns could be coated with a reagent capable of forming ion pairs while using non-polar mobile phases. Others illustrated its ability to separate a wide range of compounds such as dyestuffs, carboxylic acids and biogenic amines [8-13]. With proper use of the technique, complex separations can be achieved for ionic or ionizable compounds. In reverse phase IPC (RP-IPC), the stationary phase is non-polar. The mobile phase is composed of aqueous buffers containing a low concentration of counter ion. Both ionised and unionised components can be separated under the same chromatographic conditions. The basis of chromatographic separation is the "differential migration" of the various components of the sample through the column i.e. the components move through at different rates. Ionic or ionizable compounds which are usually only soluble in polar solvents become soluble in non-polar solvents due to the formation of hydrophobic "ion pairs" with the counter-ion. The neutral ion pair then partitions itself between the polar mobile phase and the non-polar stationary phase. By choosing a counter ion with a high UV extinction coefficient, an otherwise UV-transparent component can form a chromaphore with high sensitivity for detection. The counter ion may also be chosen to provide chromatographic selectivity characteristics.

### 6.1.2 Theory

The basic theory of ion-pair techniques has been discussed by Schill [4]. The exact mechanism by which separation is achieved by IPC has not been clearly established to date but two fundamental models have been proposed. The first model proposes that the counter ion partitions itself into the stationary phase with its ionic group orientated at the surface. The column then behaves like a liquid ion exchange column. The second proposal postulates that the solute molecule forms an ion pair with the counter ion in the mobile phase. The uncharged ion pair then partitions between the two phases i.e. there is an equilibrium distribution between the two phases. It has been suggested that the mechanism involves both postulates but micelle formation, adsorption and complexation of both the solute and counter ion make it more complex [14]. The ion pair formation is conceptually the easiest to understand however. The basic equations for a cationic species are as follows:

The cation ($R^+$) may be partitioned into a non-polar stationary phase as an ion pair ($R^+C^-$) formed with the counter ion ($C^-$).

$$R^+_{aq} + C^-_{aq} \rightleftharpoons [RC]_{aq} \rightleftharpoons [RC]_{org} \qquad .....(1)$$

The overall equilibrium constant, $k_{ip}$, may be expressed as,

$$K_{ip} = [RC]_{org}/[R^+]_{aq}[C^-]_{aq} \qquad .....(2)$$

The ratio of solute in the two phases may then be expressed as,

$$\frac{[RC]_{org}}{[RC]_{aq}} = K_{ip}[C^-]_{aq} \qquad .....(3)$$

The distribution of the ion pair therefore depends on the concentration of the counter ion.

The retention time of a component, $t_r$, in HPLC is given by,

$$t_r = \frac{L(1+k)}{\mu} \qquad .....(4)$$

L = Column length

$\mu$ = Linear velocity of eluent

k = Capacity factor, the number of moles of solute in the stationary phase divided by the moles in the mobile phase.

$$k = [RC]_{org}.Vs/[R^+]_{aq}.Vm \qquad .....(5)$$

Vs = Volume of stationary phase

Vm = Column void volume

By substitution we then get,

$$t_r = (L/\mu)[1 + (Vs/Vm)(K_{ip}[C^-]_{aq})] \qquad .....(6)$$

For a bonded phase column, Vs/Vm is constant and so the expression becomes,

$$t_r = (L/\mu)(1 + K[C^-]_{aq}) \qquad .....(7)$$

Where $K = K_{ip}(Vs/Vm)$

It can therefore be seen from the final expression that retention time depends on the concentration of the counter ion and the binding strength of the counter ion. The more soluble the ion pair is in the non-polar stationary phase, the longer it will be retained. Ion pairs which have a low affinity for the stationary phase will be eluted quickly. In general, increasing the size of the counter ion will increase retention, increasing the concentration of the counter ion increases retention up to a limit however experimental results reported by J.H Knox and G.R Laird [10] show that for certain counter ions, $t_r$ may actually decrease above a maximum concentration.

### 6.1.3 Choice of column packing

For ion pair chromatography applications, any reverse phase column can be used [14]. Homogeneously packed columns of small uniform particles should be used to minimise non-equilibrium effects. Packings containing monolayers of $C_8$ or $C_{18}$ alkyl groups are good choices while packings having polymeric coatings should be avoided since mass transfer is slow and peak shapes are generally poor. The major limitation of $SiO_2$ based packings is their limited pH range. Wahlund [15] reported that a $C_2$ bonded phase column had a lifetime of 1-2 weeks at a pH of 7.9. The lifetime of a column appears to be a function of the concentration of the counter ion and pH's above 7 should be avoided.

### 6.1.4 Choice of mobile phase

The more commonly employed solvent combinations in RP-IPC are water/methanol and water/acetonitrile. The major limitation is the solubility of the counter ion throughout the range of solvent conditions likely to be encountered during the analysis. The water/methanol mixture is the most common since problems with the counter ion solubility will be minimised. Acetonitrile/water combinations are more efficient due to lower viscosity, however many ion pair reagents are insoluble in it. The optimum concentration of counter ion may be dependant on the strength of the ion pair formed, the extent of adsorption on the stationary phase and the extent of micelle formation by the counter ion. It has been suggested that the optimum concentration for large counter ions is around 5mMolar and for small counter ions the optimum concentration is greater than 5mMolar. For small counter ions, the upper concentration limit may be the solubility or a change in the actual mechanism by the salting-out effect.

## 6.2 INVESTIGATION OF THE EFFECTS OF MOBILE PHASE COMPOSITION ON THE RETENTION TIMES OF VARIOUS COMPOUNDS

The aim of the following experiments was to look at the effects of the mobile phase composition and the counter ion concentration on the retention times of various species. The compounds of interest were thiourea, formamidine disulphide, hydrogen peroxide, copper(II) and iron(III). Having determined the optimum conditions, calibration curves for both thiourea and formamidine disulphide were established. The thiourea analysis was compared with direct titration and potentiometric titrations. The oxidation of a thiourea solution by hydrogen peroxide was followed using the IPC technique and finally thiourea and formamidine disulphide concentrations during a typical leach run were followed over a six hour period.

### 6.2.1 Reagents

1000 ppm thiourea solution from thiourea (SKW-Trotsberg).
100 ppm copper(II) solution from copper sulphate pentahydrate (Riedel-De-Haen).
100 ppm iron(III) from ferric sulphate (Riedel-De-Haen).
1000 ppm formamidine disulphide dihydrochloride from synthesised formamidine disulphide dihydrochloride.
Hydrogen peroxide solutions from 30% hydrogen peroxide (Riedel-De-Haen).
Sulphuric acid (Riedel-De-Haen).
100 ppm cyanamide from cyanamide (Aldrich).
Tetrabutyl ammonium hydrogen sulphate (Riedel-De-Haen).
HPLC grade methanol (Romil Chemicals).
Deionised distilled water (Elgastat U.H.Q).

### 6.2.2 Instrumentation

Shimadzu LC-6A chromatograph solvent delivery system.
Rheodyne fixed loop injector (20$\mu$l).
Waters Associates 441 fixed wavelength UV absorbance detector.
Shimadzu C-R5A chromatopac data processor.
Millipore filtration system fitted with a vacuum pump for filtering and degassing of mobile phase.

### 6.2.3 Mobile phase preparation

Each mobile phase was prepared by adding the appropriate volume of low-UV HPLC grade methanol to a grade"A" 500cm$^3$ volumetric flask to which was added tetrabutyl ammonium hydrogen sulphate in the range 2.5-5.5 mMolar. The solution was vacuum filtered through a 0.45$\mu$m membrane filter to remove any possible particulate matter. This filtration also degassed the solution. Dissolved gases in the system, especially in the detector cell can give rise to base-line oscillation. A build up of air in the pump can result in compression of the air by the piston rather than direct transmission of the force to the liquid. A flow rate of 1cm$^3$/min and a chart speed of 5mm/min were chosen. The detection wavelength was set at 214nm. Each sample was identified from its retention time, $t_r$. All samples were chromatographed at room temperature.

### 6.2.4 Experimental details

A series of 100 ppm solutions of thiourea, formamidine disulphide, hydrogen peroxide, copper(II) and iron(III) were made up in 100cm$^3$ volumetric flasks. 250cm$^3$ of 2.5 mMolar TBAHS mobile phases containing 0, 2, 5 and 10% V/V methanol were made up with deionised distilled water. The pH of each solution was 4. Each mobile phase solution was filtered and degassed prior to use. Each species of interest was injected into the system via the 20$\mu$l rheodyne fixed loop injector and the retention time was noted in each case. The procedure was repeated for each methanol/water mobile phase combination. When the mobile phase was changed, the fresh solution was pumped through the system for 45 minutes prior to injection of each sample. The procedure was repeated using 5mMolar TBAHS in each methanol/water mobile phase combination.

## 6.3 Results and discussion

**Table 6.1**

TBAHS Concentration = 2.5mM.

| % MeOH in Mobile Phase | $t_r$ Tu (Min) | $t_r$ RSSR (Min) | $t_r$ $H_2O_2$ (Min) | $t_r$ $Cu^{2+}$ (Min) | $t_r$ $Fe^{3+}$ (Min) |
|---|---|---|---|---|---|
| 0 | 3.44 | 2.00 | 2.58 | 2.00 | 2.67 |
| 2 | 3.28 | 2.01 | 2.57 | 2.01 | 2.70 |
| 5 | 3.15 | 2.02 | 2.56 | 2.04 | 2.60 |
| 10 | 2.95 | 2.00 | 2.54 | 2.04 | 2.61 |

**Table 6.2**

TBAHS Concentration = 5.0mM.

| % MeOH in Mobile Phase | $t_r$ Tu (Min) | $t_r$ RSSR (Min) | $t_r$ $H_2O_2$ (Min) | $t_r$ $Cu^{2+}$ (Min) | $t_r$ $Fe^{3+}$ (Min) |
|---|---|---|---|---|---|
| 0 | 3.50 | 2.10 | 2.60 | 2.09 | 2.79 |
| 2 | 3.34 | 2.11 | 2.60 | 2.09 | 2.76 |
| 5 | 3.17 | 2.11 | 2.60 | 2.11 | 2.72 |
| 10 | 3.02 | 2.12 | 2.55 | 2.12 | 2.62 |

From table 6.1 and 6.2, it can be seen that increasing the concentration of TBAHS slightly increases the retention times for all species with the exception of $H_2O_2$. Therefore the ion-pair reagent appears to have no effect on $H_2O_2$.

Increasing the concentration of methanol in the mobile phase causes a decrease in the retention time for thiourea and possibly for iron(III) but the others remain unchanged.

Interestingly, when deionised-distilled water only was used as mobile phase, both thiourea and formamidine disulphide gave similar retention times at approximately 3.2 minutes while $H_2O_2$, copper(II) and iron(III) all had retention times at approximately 2.5 minutes. This indicates that the ion-pair reagent appeared to affect the retention of formamidine disulphide, copper(II) and iron(III) to a lesser extent while the retention of thiourea may be due mainly to partition/adsorption effects on the bonded stationary phase.

It can also be seen from tables 6.1 and 6.2 that the retention times for both formamidine disulphide and copper(II) are almost identical at around 2 minutes. This means that copper(II) may be an interferant at high concentrations when analysing for formamidine disulphide and vice-versa.

In analysing solutions for both thiourea and formamidine disulphide, the peaks are separated by between 1 and 1.5 minutes depending on the % methanol in the mobile phase. There is also no significant advantage in using 5 mM TBAHS over 2.5 mM TBAHS, in fact, there is a better chance of precipitation of the ion pair reagent at the former. The increase in retention time is only very slight for each compound and so it was decided to use a mobile phase with an ion pair reagent concentration of 2.5 mMolar.

The separation between thiourea and formamidine disulphide is at a maximum when there is no methanol present in the mobile phase, however the peaks are well separated when using 5% methanol in the mobile phase. The advantage of this is that any unwanted organics in the system would be flushed through by the less polar mobile phase. It was therefore decided to use a mobile phase composition of 2.5 mMolar TBAHS in 5% V/V methanol/water for subsequent experiments.

## 6.4 CONSTRUCTION OF CALIBRATION CURVES FOR THIOUREA AND FORMAMIDINE DISULPHIDE

Having determined suitable conditions for analysis of both compounds, attempts were made to establish standard calibration curves for both compounds and determine the limits within which the detector response was linear.

### 6.4.1 Experimental details

Two stock solutions containing 1000 ppm thiourea were made up in deionised water and 0.01 M $H_2SO_4$. A series of standard solutions containing 25, 50, 75, 100, 150 and 200 ppm thiourea were made up using both stock solutions. A sample of each standard solution was injected onto the column. The thiourea peak was identified from its retention time and the peak area was noted in each case.

The procedure was repeated for formamidine disulphide dihydrochloride in 0.01 M $H_2SO_4$ because formamidine disulphide decomposes very rapidly at high pH's. The peak areas were plotted in each case against concentration.

### 6.4.2 Conditions

Eluent : 5% V/V methanol/water and 2.5 mM/dm$^3$ TBAHS
Flow rate : 1 cm$^3$/min.
Column : $C_{18}$ (10μm)
Injection size : 20μl
Detector wavelength : 214 nm

## 6.5 Results and discussion

**Table 6.3**

| Standard Conc. (ppm) | Peak area thiourea in dist. $H_2O$ (μV.S) | Peak area thiourea in 0.01 M $H_2SO_4$ (μV.S) | Peak area RSSR di-HCl in 0.01 M $H_2SO_4$ (μV.S) |
|---|---|---|---|
| 25 | 2525873 | 2597491 | 1354396 |
| 50 | 5059692 | 4959670 | 2792015 |
| 75 | 7663228 | 7529250 | 4111027 |
| 100 | 10066424 | 9821868 | 5401934 |
| 150 | 14817745 | 14892888 | 8120525 |
| 160 | 15817865 | 15789054 | 8662546 |
| 200 | 17679510 | 17860782 | 10784724 |

In table 6.3, the peak area for each sample injected is illustrated. By inspection it can be seen that there is no difference in peak area between thiourea samples in deionised water and thiourea in 0.01M $H_2SO_4$. The peak areas correspond very well. Figures 6.1 and 6.2 show the peak areas versus concentration for thiourea solutions made up in deionised water and 0.01M $H_2SO_4$ respectively. It

**Figure 6.1** Peak Area ($\mu$VS) Versus Thiourea Concentration (ppm) for Thiourea made up in deionised water.

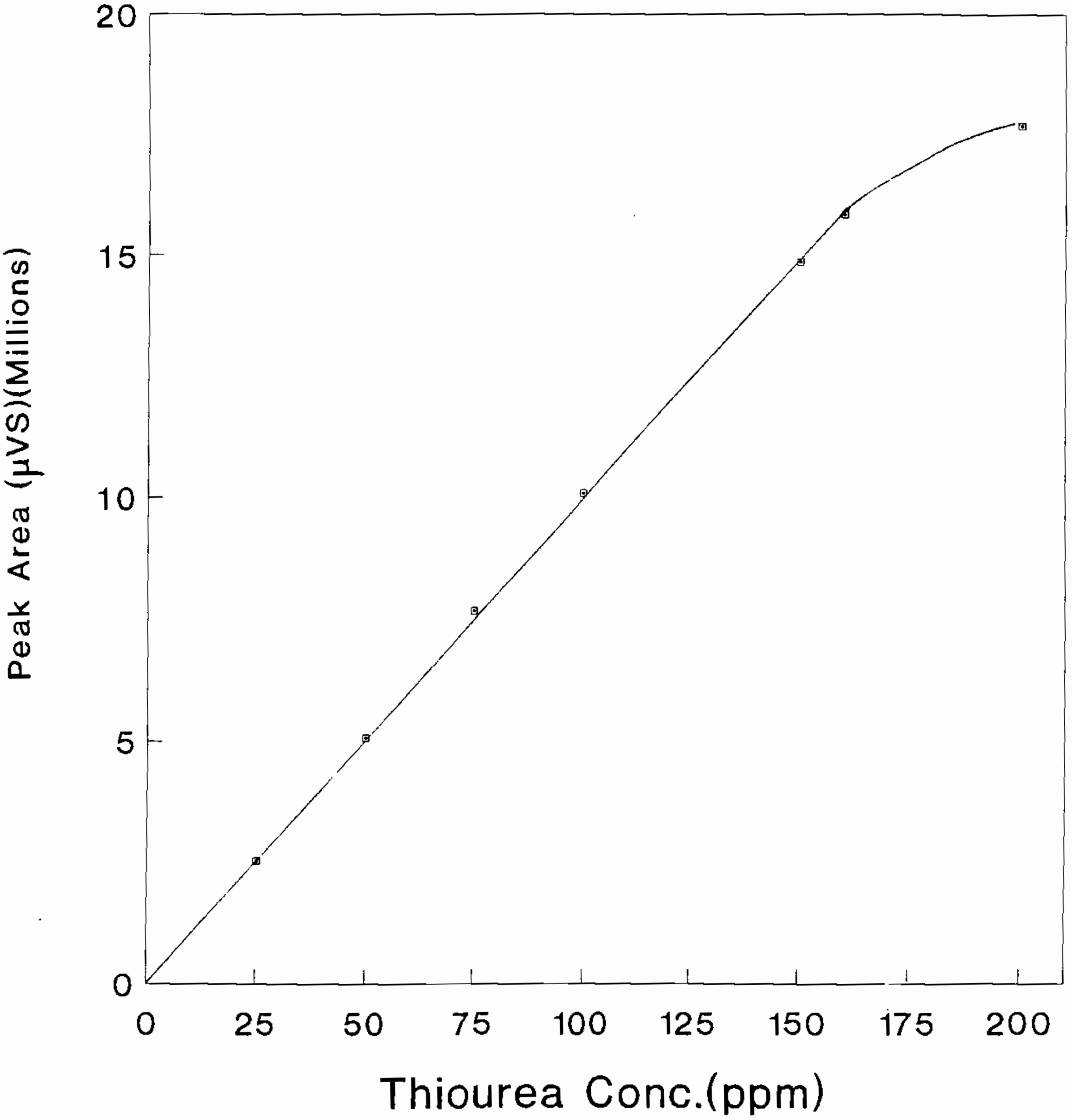


**Figure 6.2** Peak Area (μVS) Versus Thiourea Concentration (ppm) for Thiourea made up in 0.01M $H_2SO_4$.

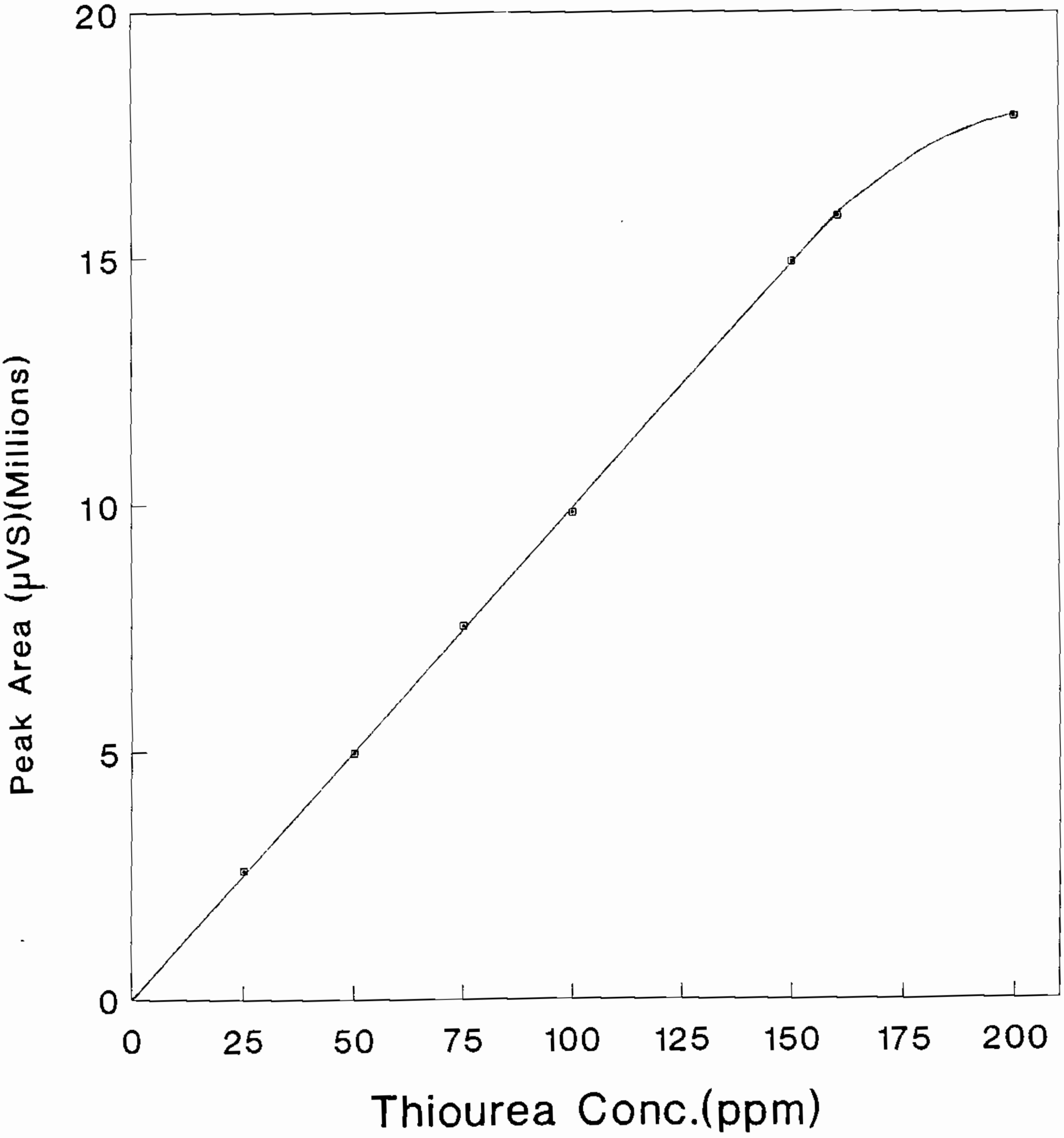


**Figure 6.3** Peak Area ($\mu$VS) Versus Thiourea Concentration (ppm).

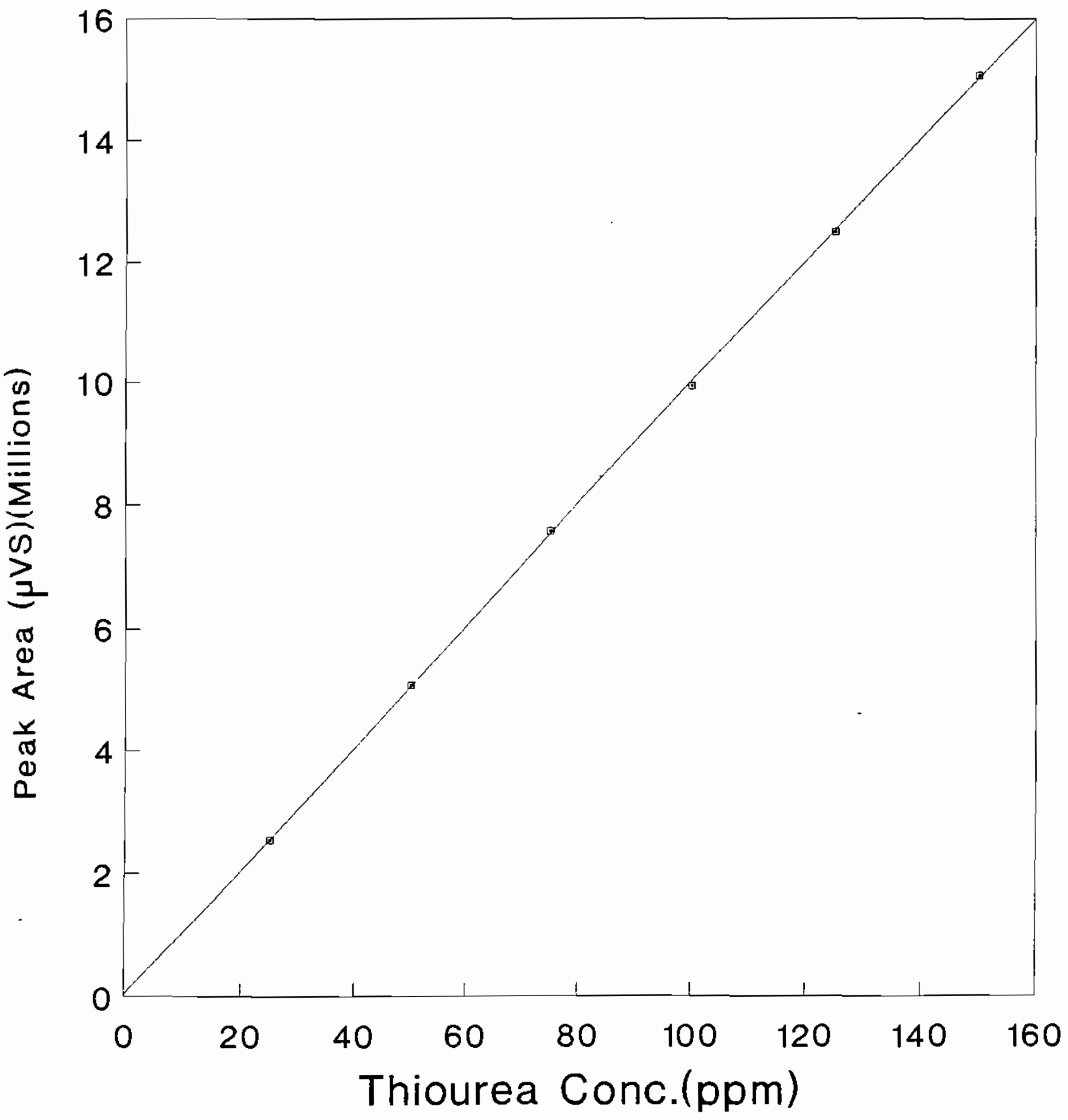


**Figure 6.4** Peak Area (μVS) Versus Formamidine Disulphide di-hydrochloride Concentration (ppm).

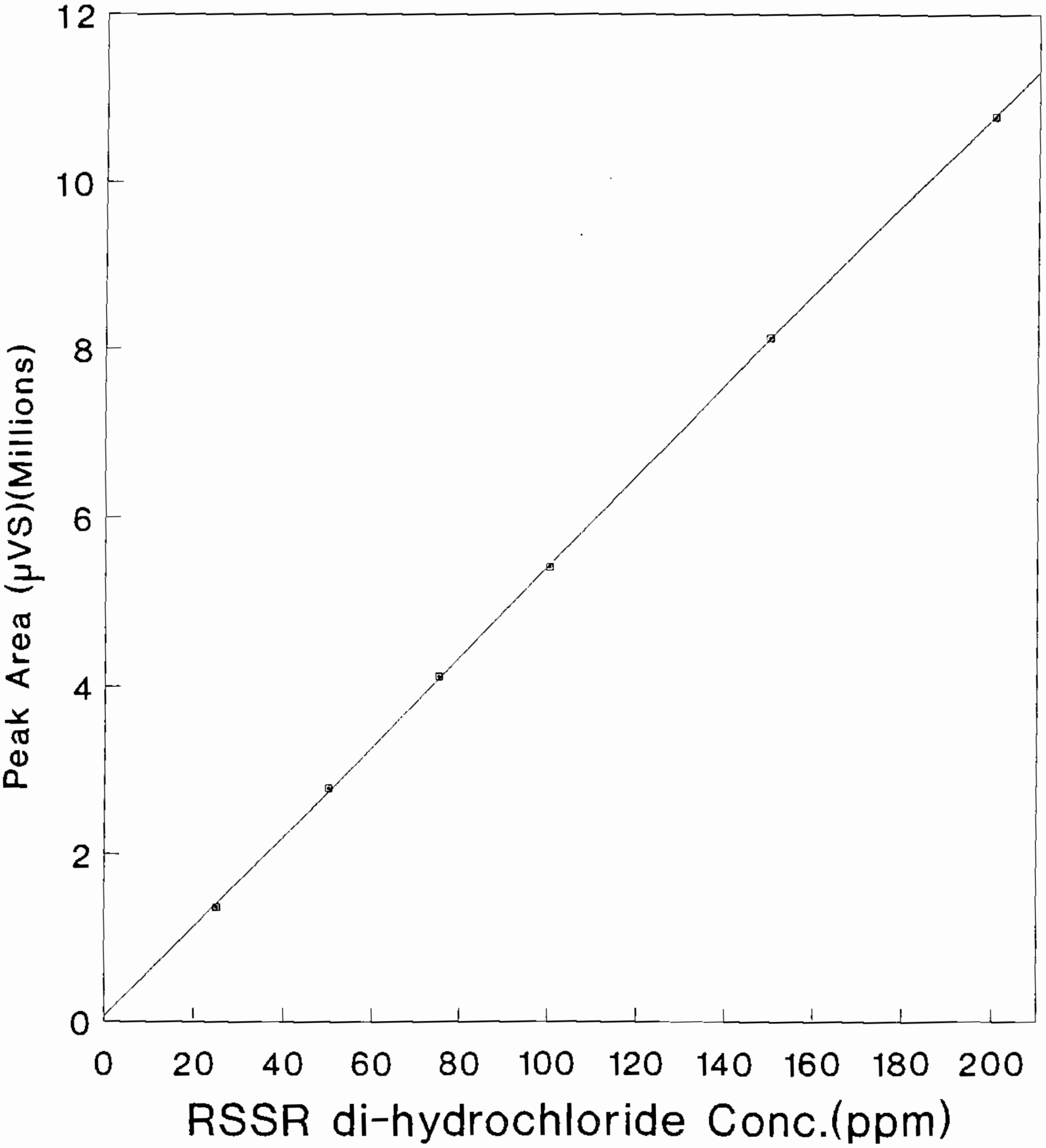
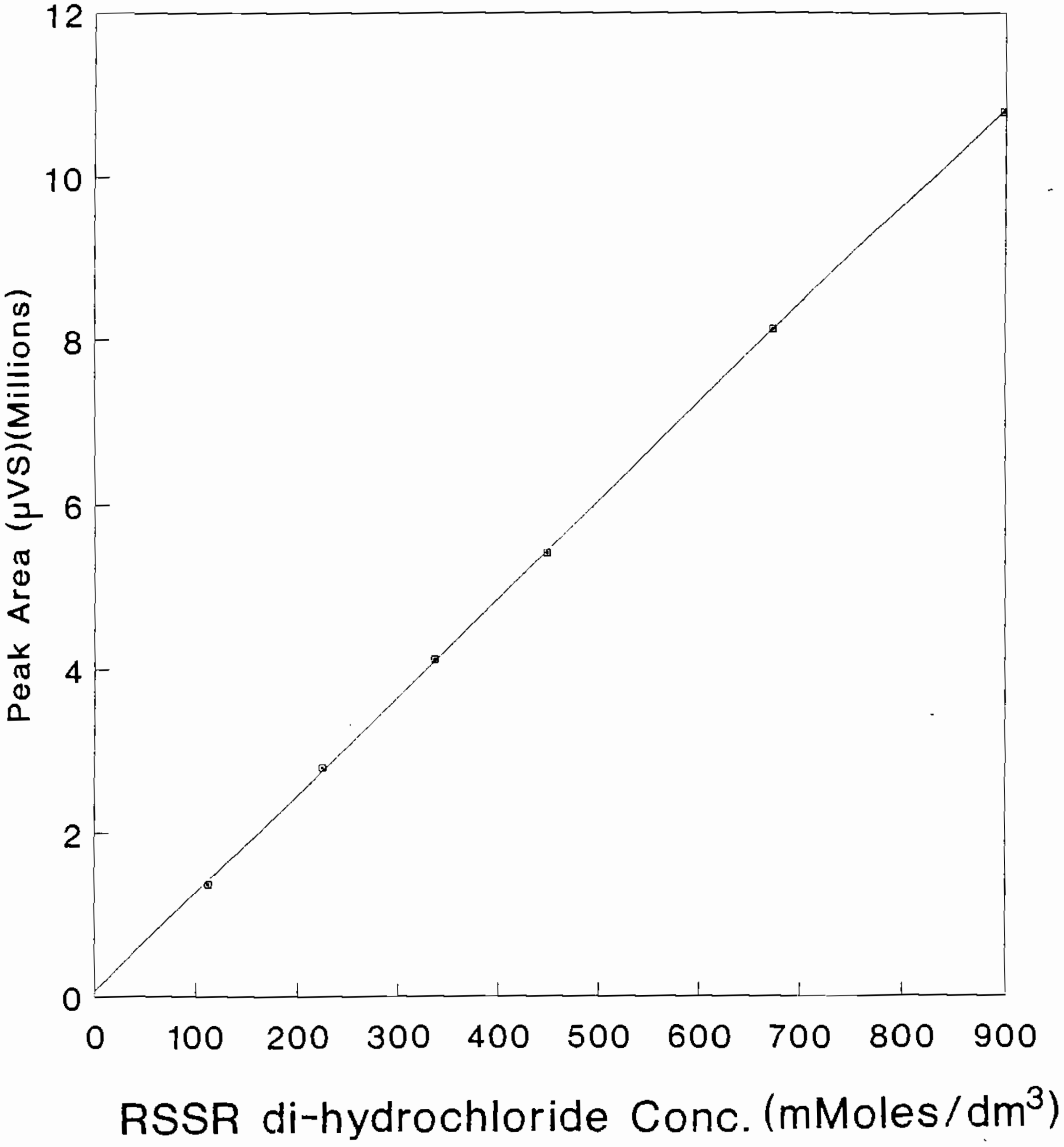


**Figure 6.5** Peak Area (μVS) Versus Formamidine Disulphide di-hydrochloride Concentration (mMoles/dm$^3$)



can be seen that the peak area tends to level off in both cases as the concentration exceeds around 160 ppm thiourea. The linear response region of the detector for this particular compound has been exceeded at this point. Figure 6.3 illustrates the results of a repeat of the experiment with standards made up to 150 ppm. The graph shows a correlation coefficient of 1 indicating good linearity.

Figure 6.4 illustrates the relationship between the formamidine disulphide dihydrochloride concentration in ppm and the peak area. The graph is linear with a correlation coefficient of 1. It would appear that the response of the detector is linear up to 200 ppm (0.897mMolar) for this compound. Figure 6.5 illustrates the results obtained when the graph was constructed for formamidine disulphide dihydrochloride concentrations expressed as mMoles/dm$^3$. This was done in order to obtain an equation for the estimation of formamidine disulphide concentrations as opposed to formamidine disulphide-dihydrochloride. This calibration curve was used to determine formamidine disulphide concentrations in subsequent experiments.

## **6.6 COMPARISON OF RP-IPC THIOUREA ANALYSIS WITH DIRECT AND POTENTIOMETRIC ASSAYS**

Having developed a reliable and reproducible calibration curve for thiourea analysis, it was decided to compare this RP-IPC method with a direct hand-titration method and a potentiometric method using an autotitrator. In order to evaluate the potential and reliability of the RP-IPC method for thiourea analysis, a comparison with the already standard methods of analysis had to be carried out and the general merits of each analysis evaluated.

### 6.6.1 Reagents

Potassium iodate (May & Baker Ltd.)
1000 ppm thiourea from thiourea (SKW-Trotsberg)
1 Molar phosphoric acid from phosphoric acid (Riedel-De-Haen)
Starch (Riedel-De-Haen)

### 6.6.2 Instrumentation

The potentiometric titration was carried out using a Mettler DL25 automatic titrator. The result of each titration was printed out automatically using an Epson LX-800 printer. The chromatographic conditions were as described in Section 6.2.2.

## 6.7 Results and discussion

**Table 6.4 (3 methods)**

( Direct Titration )

| Titration Number | cm$^3$ 0.004 M $KIO_3$ | Thiourea (ppm) |
|---|---|---|
| 1 | 27.59 | 1989 |
| 2 | 27.70 | 2004 |
| 3 | 27.60 | 1997 |
| 4 | 27.66 | 2001 |
| 5 | 27.60 | 1997 |
| 6 | 27.60 | 1997 |
| 7 | 27.59 | 1997 |
| 8 | 27.65 | 2000 |
| 9 | 27.68 | 2003 |
| 10 | 27.70 | 2004 |

( Autotitrator )

| Titration Number | Thiourea Conc. (ppm) |
|---|---|
| 1 | 2005 |
| 2 | 2009 |
| 3 | 2009 |
| 4 | 2007 |
| 5 | 2010 |
| 6 | 2012 |
| 7 | 2005 |
| 8 | 2007 |
| 9 | 2004 |
| 10 | 2005 |

(HPLC Determination by 1/25 dilution)

| Sample Number | Peak area (μV.S) | Thiourea Conc. (ppm) |
|---|---|---|
| 1 | 8107906 | 2023 |
| 2 | 8110798 | 2024 |
| 3 | 8074200 | 2015 |
| 4 | 8103209 | 2022 |
| 5 | 7998102 | 1995 |
| 6 | 8075654 | 2015 |
| 7 | 8045733 | 2007 |
| 8 | 7895889 | 1970 |
| 9 | 8083986 | 2017 |
| 10 | 8053516 | 2009 |

From the results obtained with the automatic potentiometric titrator, it can be seen that the standard deviation for the autotitrator has the lowest value i.e. 2.5 ppm. The mean result is 0.25% above the true thiourea concentration.

From the results obtained by direct titration, the standard deviation is only 4 ppm and the mean result is 3 ppm (0.15%) below the true thiourea concentration. For the HPLC determination, the standard deviation is 16 ppm and the mean value is 0.4% above the actual thiourea concentration. The larger standard deviation could be attributed to the fact that the HPLC determination involves a 1 in 25 dilution of the sample and so variations between results are more likely to occur. The fact that the mean result is 0.4% above the true value is not very important since most laboratory reagents are usually only 99% pure. Although the potentiometric titration appears to be the most reliable and most reproducible method of analysis, the difference between the means in the autotitration and HPLC methods is not experimentally significant and so it can be concluded that the HPLC method is a reliable method for the determination of thiourea. The analysis time is only around 4 minutes and does not require the use of phosphoric acid or the making up of a starch solution.

Having developed a reliable method for determining thiourea and formamidine disulphide, it was decided to look at the changes in the levels of each compound during leaching over a 6 hour period.

## 6.8 ANALYSIS OF THIOUREA AND FORMAMIDINE DISULPHIDE IN A TYPICAL LEACH SYSTEM

The aim of the experiment was to determine both thiourea and formamidine disulphide over a 6 hour leach period in a typical leach system. Both compounds were analyzed by the HPLC method developed and compared with the results obtained by potentiometric determination. Thiourea consumption occurs when formamidine disulphide undergoes irreversible oxidation to give secondary redox products. These redox products are lost from the formamidine disulphide-thiourea system since neither compound can be regenerated. Thiourea consumption can therefore be defined as

$$[\text{Thiourea}]_0 \quad - \quad ([\text{Thiourea}]_t \; + \; 2[\text{RSSR}]_t)$$

Where $[\text{Thiourea}]_0$ = Initial thiourea conc.(Moles/dm$^3$)
$[\text{Thiourea}]_t$ = Analyzed thiourea at time t (Moles/dm$^3$)
$[\text{RSSR}]_t$ = Analyzed RSSR at time t (Moles/dm$^3$)

Thiourea consumption was determined over the leaching period.

### 6.8.1 Reagents

Thiourea (SKW-Trotsberg)
4000 ppm iron(III) from ferric sulphate (Riedel-De-Haen)
The ore used contained 3.96 ppm gold.
0.01 Molar sulphuric acid from sulphuric acid (Riedel-De-Haen)
Zinc, granular 20 mesh A.C.S reagent (Aldrich)
1 Molar phosphoric acid from 60 % phosphoric acid (Riedel-De-Haen)
Potassium iodate (May & Baker Chemicals)

### 6.8.2 Formamidine disulphide analysis

The analysis of formamidine disulphide has been discussed by Mullins [16]. 5cm$^3$ of the leach filtrate was analyzed by the Mettler DL-25 automatic titrator. 10 cm$^3$ of the same filtrate was added to a 100 cm$^3$ conical flask to which was added 1g of granular zinc. The flask was sealed and shaken for 15 minutes at speed 7 on the flask shaker. 5 cm$^3$ of the solution was titrated against standard potassium iodate using the automatic titrator. The zinc metal was used as a reducing agent to reduce the formamidine disulphide back to thiourea.

$$RSSR + 2H^+ + Zn^0 \dashrightarrow 2Tu + Zn^{2+}$$

The difference between the initial and final concentrations in ppm of thiourea after reduction is therefore the formamidine disulphide concentration in ppm.

### 6.8.3 Leach conditions

3g/dm$^3$ thiourea
20% solid/liquid ratio
pH = 2
300 ppm Fe$^{3+}$

### 6.8.4 Experimental details

40g of ore were weighed out accurately in a 600 cm$^3$ glass beaker. 15 cm$^3$ of the 4000 ppm iron(III) solution were added. 0.6g of thiourea were weighed accurately and dissolved in 185 cm$^3$ of 0.01 Molar $H_2SO_4$. The solution was added to the ore. A magnetic follower was added and the beaker was placed on a magnetic stirrer. 30 cm$^3$ samples of the resulting slurry were taken and filtered on a Buchner funnel. 5 cm$^3$ of the filtrate was added to a 100 cm$^3$ grade"A" volumetric flask and the solution was made up to the mark with deionised water. A sample was injected onto the HPLC column and the thiourea and formamidine disulphide concentrations were analyzed as before. Both thiourea and formamidine disulphide were analyzed potentiometrically by the method outlined above.

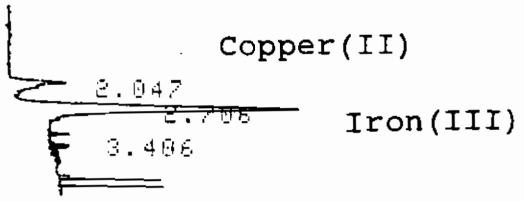
A blank leach was carried out without thiourea and a sample of the filtrate was injected onto the column. A 1 in 25 dilution was carried out on the filtrate and that too was injected onto the column. This was done in order to see if any species present in the ore slurry would interfere with the analysis of the two compounds of interest.

## 6.9 Results and discussion

**Table 6.5**

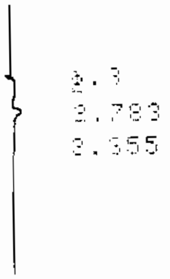
| | HPLC ANALYSIS | | | AUTOTITRATION ANALYSIS | | |
|---|---|---|---|---|---|---|
| Time (Min) | Tu Conc. (ppm) | RSSR Conc. (ppm) | Total Conc. (ppm) | Tu Conc. (ppm) | RSSR Conc. (ppm) | Total Conc. (ppm) |
| 40 | 2143 | 488 | 2631 | 2257 | 375 | 2632 |
| 100 | 1898 | 570 | 2468 | 2190 | 433 | 2623 |
| 225 | 1879 | 551 | 2430 | 2019 | 429 | 2448 |
| 330 | 1972 | 498 | 2470 | 2062 | 297 | 2359 |
| 360 | 1912 | 453 | 2365 | 2144 | 255 | 2399 |

**Figure 6.6** Samples of Peaks Obtained after a 3 hour leaching period in the presence and absence of Thiourea.

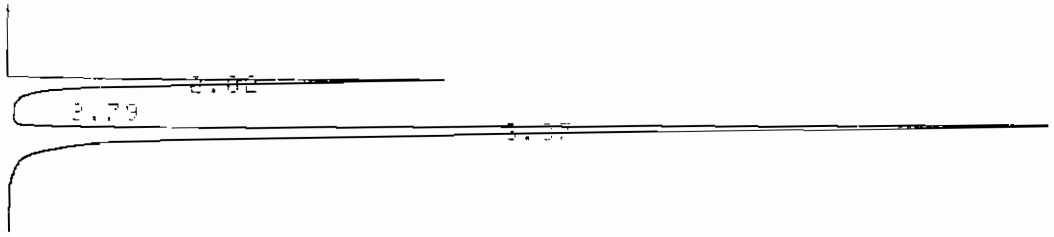


3 hour leach solution (no dilution).

Note the slow return to baseline after the Iron(III) peak.



1/25 dilution of leach in the absence of thiourea.



1/25 dilution of leach in the presence of thiourea.

Figure 6.6 illustrates the peaks obtained after a leach run in the absence of thiourea after a 3 hour period. The peaks are due to copper(II) and iron(III) as can be seen from their retention times of 2.05 and 2.7 minutes respectively. It would then be thought that copper(II) would interfere with the formamidine disulphide determination. However, when the solution is diluted by 1 in 25, the peaks become so diminished that they probably approach the noise level of the instrument and so would not interfere with the calculations.

From table 6.5, the results of the HPLC and autotitration analysis can be seen. Although there is a significant difference between the individual analysis results, the total concentrations of both compounds match quite well. The initial concentration of thiourea was 3000 ppm however, after 40 minutes, it can be seen that this has been reduced to somewhere between 2150 and 2250 ppm thiourea. The formamidine disulphide concentration at this time is between 400 and 500 ppm suggesting that reagent consumption is between 350 and 450 ppm or 13%. The loss of reagent is most likely due to irreversible oxidation of formamidine disulphide. It has been suggested that one of the products of the irreversible oxidation of formamidine disulphide is cyanamide. Under the chromatographic conditions used, cyanamide would be expected to appear at a retention time of 3.45 minutes but a peak is not visible at this retention time on the chromatogram. During the analysis however, a peak developed at a retention time of 2.71 minutes but would have interfered only very slightly with the analysis of the 2 compounds. It was also found that the baseline became noisy during the analysis and this was probably due to iron(III), the presence of which gave a peak with a slow return to baseline accompanied by baseline noise as can be seen from figure 6.7.

These are some of the possibilities which may explain the differences in the two methods and since the total concentrations of analytes is the same in both cases, it would appear that the analysis would be reliable if these problems were overcome. Since the analysis involved the use of a real ore sample, it is possible that some species in the ore may have interfered with the analysis and therefore the problem requires further work and investigation.

## 6.10 OXIDATION OF THIOUREA BY HYDROGEN PEROXIDE

It has been suggested that the use of hydrogen peroxide as an oxidant for gold is uneconomical because it reacts more rapidly than iron(III) and increases the redox potential, favouring the irreversible oxidation of formamidine disulphide to further oxidation products thus giving rise to reagent consumption [1]. The aim of this experiment was to look at the oxidation of thiourea by hydrogen peroxide using the RP-IPC method to follow the concentration of thiourea and formamidine disulphide with time.

### 6.10.1 Reagents

30% V/V hydrogen peroxide (Riedel-De-Haen)
Thiourea (SKW-Trotsberg)
0.01Molar $H_2SO_4$ from concentrated $H_2SO_4$ (Riedel-De-Haen)

### 6.10.2 Experimental details

An approximate 160 ppm thiourea solution was made up in 0.01M $H_2SO_4$. Four samples of the solution were injected onto the column and the average concentration was found from the calibration curve. Five drops of a 30 % V/V hydrogen peroxide solution were added. Samples of this solution were taken every few minutes and injected onto the column. The concentrations of both thiourea and formamidine disulphide were calculated in each case. The peak area of the unknown peak was also noted in each case. The sample was left to react overnight and samples were also taken the following day. The concentrations of both formamidine disulphide and thiourea were plotted against time. Since the concentration of the compound which gave rise to the unknown peak would be expected to be proportional to its concentration, its peak area was also plotted against time.

## 6.11 Results and discussion

**Table 6.6**

| Time (Min) | Thiourea Conc. (ppm) | RSSR Conc. (ppm) | Total Conc. (ppm) | Peak area Unknown ($\mu$V.S) |
|---|---|---|---|---|
| 0 | 158 | - | 158 | - |
| 5 | 153.7 | 3 | 156.7 | - |
| 10 | 137.1 | 13.6 | 150.7 | 410529 |
| 16 | 115.7 | 44.9 | 160.6 | 188902 |
| 27 | 89.6 | 72.7 | 162.3 | 345153 |
| 32 | 77.4 | 85.4 | 162.8 | 426935 |
| 37 | 68.2 | 95.3 | 163.5 | 489994 |
| 45 | 59.2 | 104.6 | 163.8 | 679478 |
| 52 | 51.1 | 112.4 | 163.5 | 790587 |
| 65 | 41.5 | 128.4 | 169.9 | - |
| 85 | 31.6 | 125.7 | 157.3 | 1243553 |
| 95 | 28.6 | 129.8 | 158.4 | 1249990 |
| 200 | 22.4 | 120.3 | 142.7 | - |
| 208 | 21.8 | 127.3 | 149.1 | 1888925 |
| 216 | 21.9 | 127.2 | 149.1 | 2064975 |
| 1506 | 20.1 | 55.1 | 75.2 | 5828204 |
| 1510 | 19.6 | 58.5 | 78.1 | 5660318 |
| 1646 | 19.9 | 48.8 | 68.7 | 5948030 |

Average peak area for thiourea = 15791806

Initial Concentration of thiourea = 157 ppm

**Figure 6.7**

Cyanamide peak at $t_r$ = 3.45 minutes.

Unknown peak at $t_r$ = 2.71 minutes.

Example of baseline noise.

**Figure 6.8** Concentrations of both Thiourea and Formamidine Disulphide (ppm) with Time (Minutes).

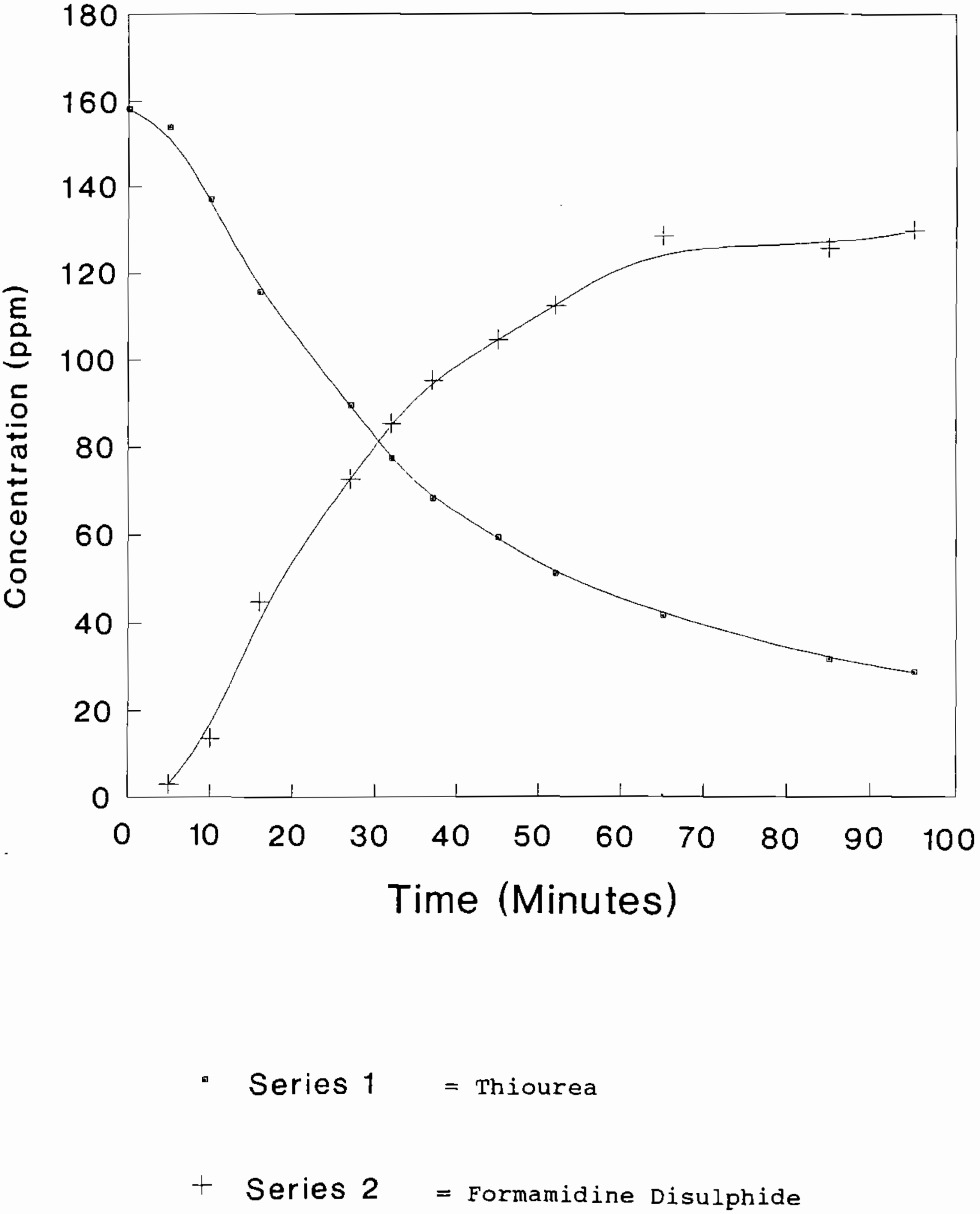


**Figure 6.9** Samples of peaks obtained during the oxidation of Thiourea by Hydrogen Peroxide.

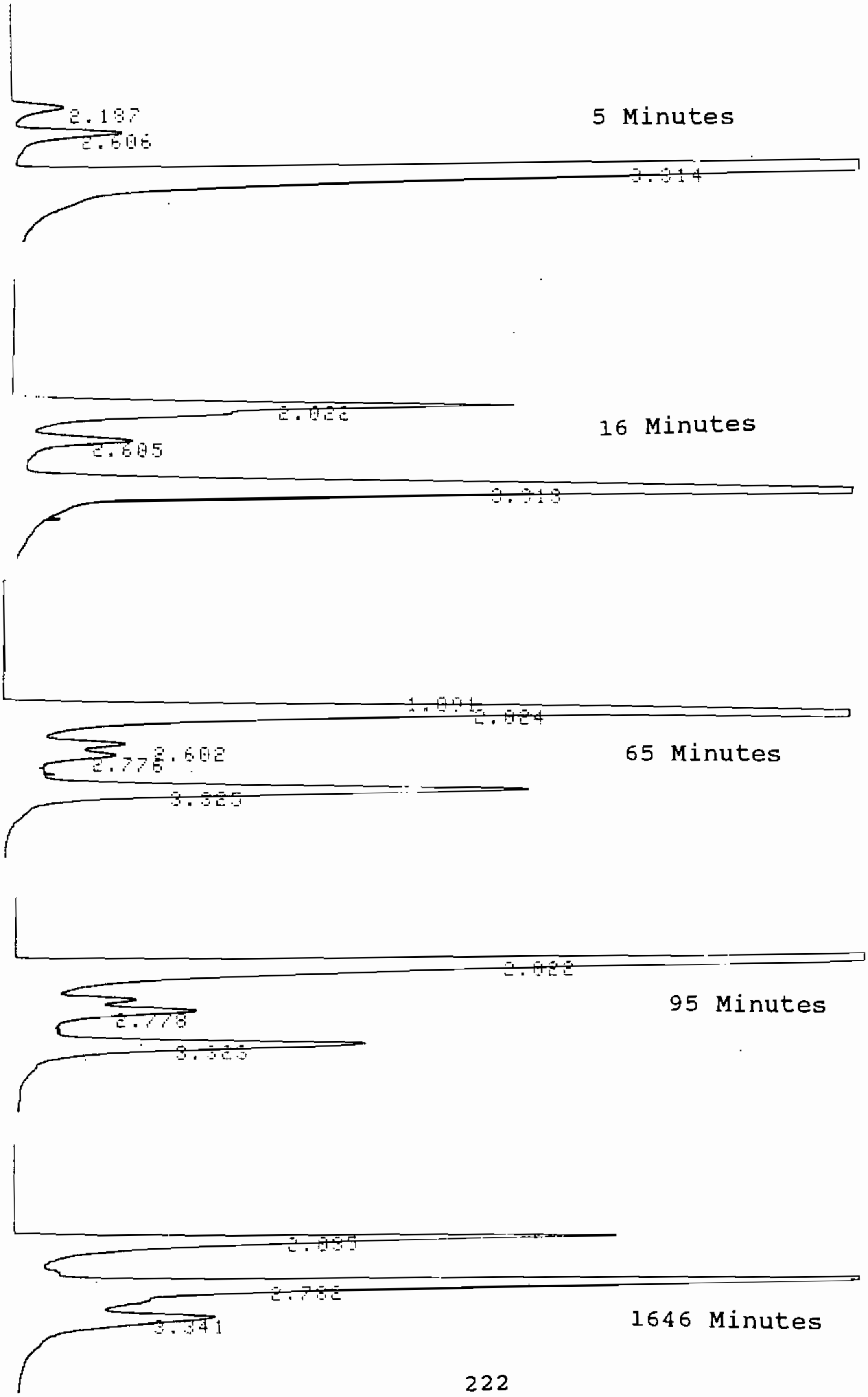


**Figure 6.10** Peak Area of Unknown ($\mu$VS) Versus Time (Minutes).

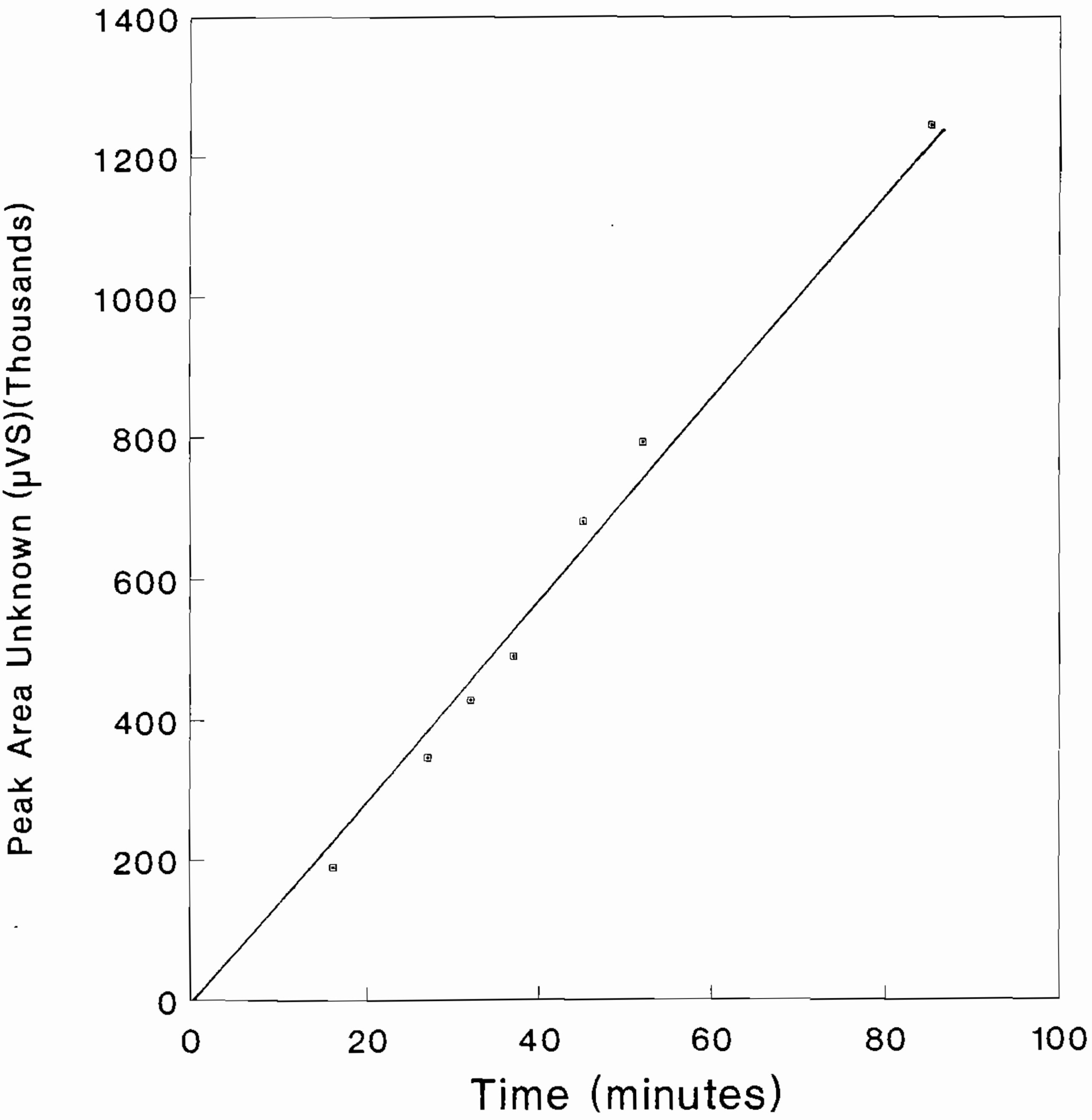


Table 6.6 illustrates the concentrations of both thiourea and formamidine disulphide and the peak area of the unknown with time. From the total concentration column in table 6.6, it can be seen that the total concentration of both thiourea and formamidine disulphide remains fairly constant between 150 and 160 ppm up to around 200 minutes. Figure 6.8 illustrates the concentration profile for both compounds with time. It can be seen that the thiourea concentration drops off very rapidly at first and then levels off to a constant value of around 20 ppm.The appearance of formamidine disulphide is also very rapid at first but again levels off to a constant concentration of around 130 ppm.

It should be noted that there is an increase in the area of the unknown peak with time. This increase could be due to the irreversible oxidation of formamidine disulphide with time to a further product. The hydrogen peroxide peak appeared at a retention time of 2.6 minutes. This peak was accompanied by the appearance of a peak at a retention time of 2.78 minutes. The peak was not recognised by the integrator under the peak processing parameters being used, until a time of 65 minutes into the reaction. The hydrogen peroxide peak then merged with this peak and so the area of the unknown peak was calculated by subtracting the area of the initial hydrogen peroxide peak from the area of the merged, unresolved peaks. Cyanamide appears at a retention time of 3.45 minutes as can be seen from figure 6.7 and so the unknown peak cannot be attributed to cyanamide. During the first 40 minutes of the reaction, the thiourea peak on returning to the baseline, stopped momentarily as can be seen from figure 6.9. This is possibly due to an unresolved cyanamide peak as it appears close to the retention time expected for cyanamide.

Figure 6.10 illustrates the peak area of the unknown product of hydrogen peroxide oxidation of thiourea with time. It can be seen that the concentration of the product grows linearly with time. From figure 6.9, it can be seen that having left the solution to react overnight, the formamidine disulphide concentration has halved to around 75 ppm and the thiourea peak has remained constant at a concentration of 20 ppm. It can also be seen that the peak area of the unknown has trebled from 2E+6 to 6E+6 uV.S. Although the hydrogen peroxide may still be oxidising thiourea, its concentration may be remaining constant since it is a product of the irreversible oxidation of formamidine disulphide. It may also be possible that the hydrogen peroxide has been used up and the formamidine disulphide is decomposing slowly to form a product other than thiourea. In terms of reagent consumption, it can be seen that the concentration of the thiourea-formamidine disulphide couple remains constant up to 95 minutes at around 158 ppm. After this time however, the total concentration begins to fall to around 150 ppm at 216 minutes. Although it was found that most of the gold dissolution takes place within the first hour of contact of the ore with the thiourea, in a recycle system, the use of hydrogen peroxide may not be favourable due to high reagent consumption with time. After 24 hours, the total reagent concentration was down to around 70 ppm. The effective figure for leaching purposes would be expected to be lower due to complexation.

It can be seen that the unknown peak at a retention time of 2.78 minutes has become very large after 1646 minutes and this was accompanied by a dramatic loss in the peak area for formamidine disulphide and thiourea. This result suggests that there is some further redox or decomposition reaction occuring however further work would be required to explain these findings. It was also noticed during the analysis that some of the peaks developed "shoulders", which is likely to be due to the presence of an unresolved smaller peak in the presence of a larger peak. The appearence of these smaller peaks may be due to the formation of further oxidation products of thiourea. This can be seen from figure 6.11. During the work, an attempt was made to construct a calibration curve for formamidine disulphide by oxidation of thiourea with hydrogen peroxide but the method proved to be unsuccessful because of the appearance of the unknown peak at 2.78 minutes. The formamidine disulphide peaks appeared to be composed of two unresolved peaks and so the method was disregarded. It can therefore be concluded that although hydrogen peroxide does oxidise thiourea to formamidine disulphide, it also gives rise to the appearance of other products resulting in reagent consumption and thus rendering it unsuitable to be used as an oxidant for gold in the thiourea leach system.

## REFERENCES CHAPTER 6

1. Charley, W.R., "Hydrometallurgical extraction of precious metals using thiourea", Prac.Hydromet. 7th annual symposium. p.p 75-80, (1983).

2. Mullins, K., "Precious metal extraction", M.Sc. Thesis, Dublin Institute of Technology, (1989).

3. Denkert, M., Hachzell, I., Schill, G. and Sjogren, E., J.Chromatog., 218, 31-34, (1981).

4. Eksborg, S., Lagerstrom, P.O., Modin, R. and Schill, J.Chromatogr., 83, 99, (1973).

5. Eksborg, S. and Schill,G.,Anal Chem., 45, 2092, (1973).

6. Schill, G., in "Assay of drugs and other trace compounds in Biological Fluids", edited by E.Rad, North Holland publishing Co. New York (1976).

7. Wahlund, K.G. and Lund, U., J. Chromatogr., 122, 269 (1976).

8. Wahlund, K.G., J.Chromatogr. 115:411 (1975).

9. Frannson, B., Wahlund, K.G., Johansson and Schill, G., J.Chromatog., 125, 327(1976).

10. Persson, B.A. and Karger, B.H., J. chromatog. Sci., 12, 521,(1974).

11. Kraah,J.S. and Huber, J.F.K., J.Chromatogr., 102, 333(1974).

12. Knox, J.H. and Laird, G.R., J.Chromatog., 122, 17, (1976).

13. Juraud, J., in high pressure liquid chromatography in clinical chemistry, Academic press, New York, P.F.Dixon Editor(1976).

14. Wittman, D.P., Nuessle, N.O. and Horey, W.G., Anal.Chem., 47, 1422;(1976).

15. Fitzgerald, E., Anal.Chem. 48, 1734,(1976).

16. Gloor, R. and Johnson, E.L, J.Chromatog.Sci., 15, 413-423 (1977).

17. Annual book of ASTM Standards, part 23, D2230, American society for testing materials, Philadelphia, 606-611, (1971).

# APPENDIX 1

Factorial designs are widely used in experiments involving several factors where it is necessary to study the joint effect of these factors on a response. There are several special cases of the factorial design which are important because they are widely used in research work. The two cases used in this work were where k factors, each at two levels called a $2^k$ factorial design were studied and k factors, each at three levels called a $3^k$ factorial design were studied. In the analysis of these two designs it is assumed that:

1. The factors are fixed.

2. The designs are completely randomised.

3. The usual normality assumptions are satisfied.

## The $2^k$ design

Consider a design in which two factors A and B are each run at two levels. By convention, the effect of a factor is denoted by a capital latin letter. Therefore "A" refers to the effect of factor A, "B" refers to the effect of factor B and "AB" refers to the interaction effect of A and B. The low and high levels of A and B are denoted by 0 and 1 on the A and B axes. The representation can be seen in figure 1. Treatment combinations are usually denoted by lower case letters. The high level of any factor is denoted by its corresponding lower case letter. Therefore, "a" represents the treatment combination of A at the high level and B at the low level, ab represents both factors at high level and (1) is used to denote both factors at the low level.

**Figure 1** Representation of a $2^k$ Factorial Design.

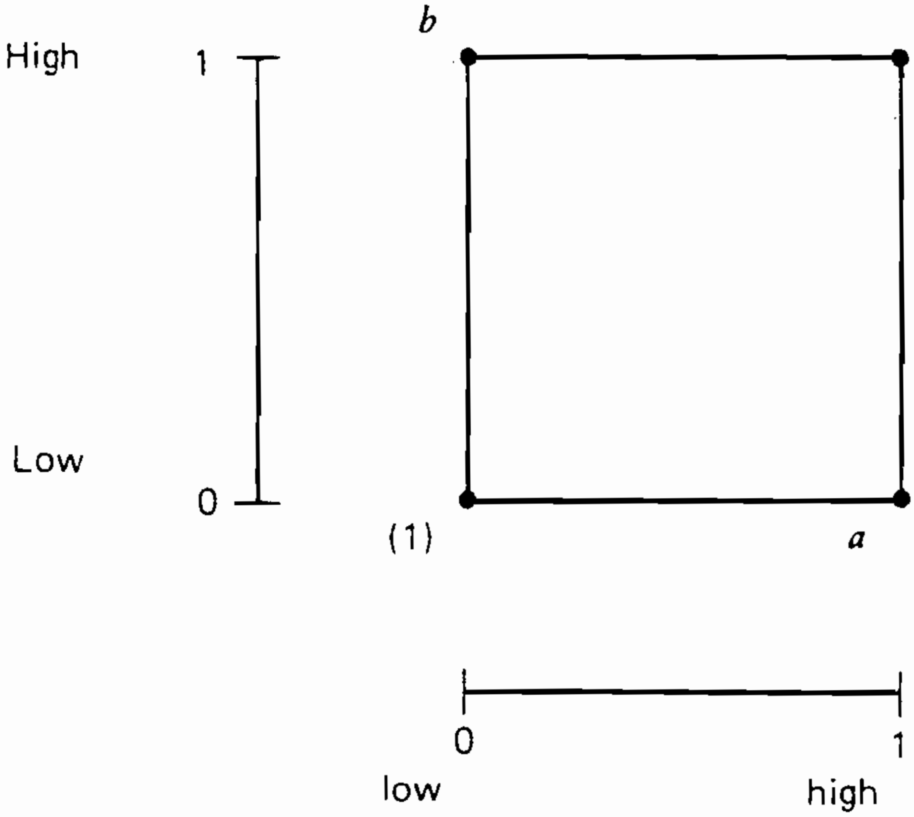


**Table 1** Analysis of Variance for a $2^k$ Factorial Design.

| Source of Variation | Sum of Squares | Degrees of Freedom |
|---|---|---|
| $k$ Main Effects | | |
| $A$ | $SS_A$ | 1 |
| $B$ | $SS_B$ | 1 |
| $\vdots$ | $\vdots$ | $\vdots$ |
| $K$ | $SS_K$ | 1 |
| $\binom{k}{2}$ Two-Factor Interactions | | |
| $AB$ | $SS_{AB}$ | 1 |
| $AC$ | $SS_{AC}$ | 1 |
| $\vdots$ | $\vdots$ | $\vdots$ |
| $JK$ | $SS_{JK}$ | 1 |
| $\binom{k}{3}$ Three-Factor Interactions | | |
| $ABC$ | $SS_{ABC}$ | 1 |
| $ABD$ | $SS_{ABD}$ | 1 |
| $\vdots$ | $\vdots$ | $\vdots$ |
| $IJK$ | $SS_{IJK}$ | 1 |
| $\vdots$ | $\vdots$ | $\vdots$ |
| $\binom{k}{k} = 1$ $k$-Factor Interaction | | |
| $ABC \ldots K$ | $SS_{ABC \ldots K}$ | 1 |
| Error | $SS_E$ | $2^k(n-1)$ |
| Total | $SS_T$ | $n2^k - 1$ |

The average effect of a factor is defined to be the change in response produced by a change in the level of that factor averaged over the levels of the other factor. The effect of A at the low level of B is [A-(1)]/n where n is the number of replicates. The effect of A at the high level of B is [ab-b]/n. The average of these 2 gives the effect of A,

$$A= \frac{1}{2n} \{[ab-b]+[a-(1)]\} \qquad (1)$$

$$= \frac{1}{2n} [ab+a-b-(1)] \qquad (2)$$

Similarly the effect of B is

$$B= \frac{1}{2n}[ab+b-a-(1)] \qquad (3)$$

The interaction effect is defined as the average difference between the effect of A at the high level of B and the effect of A at the low level of B i.e.

$$AB = \frac{1}{2n}[ab+(1)-a-b] \qquad (4)$$

The factor in brackets in equation (1) is known as the "contrast" or the "total effect of A". The contrast sum of squares for any contrast is equal to the contrast squared divided by the number of observations in each total in the contrast times the sum of squares of the contrast coefficients, or

$$SS_c = \frac{\left(\sum_{i=1}^{a} c_i Y_i\right)^2}{n \sum_{i=1}^{a} c_i^2}$$

$Y_i$ represents the total of the observations under the ith treatment and $c_i$ represents the contrast coefficient. Consequently we have,

$$SS_A = \frac{[ab+a-b-(1)]^2}{4.n}$$

$$SS_B = \frac{[ab+b-a-(1)]^2}{4.n}$$

$$SS_{AB} = \frac{[ab+(1)-a-b]^2}{4.n}$$

The total sum of squares is found from,

$$SS_T = \sum_{i=1}^{2} \sum_{j=1}^{2} \sum_{k=1}^{n} Y^2_{ijk} - \frac{Y^2_{...}}{4n}$$

$SS_T$ has 4n-1 degrees of freedom. The error sum of squares is computed by subtraction as,

$$SS_E = SS_T - SS_A - SS_A - SS_B - SS_{AB}$$

and has 4(n-1) degrees of freedom. The mean square, MS, is calculated by dividing the sum of squares, SS, by the number of degrees of freedom. The analysis of variance for a $2^k$ design can be seen in table 1.

### The $3^k$ design

This design is a factorial arrangement of k factors each at 3 levels. The 3 levels are usually referred to as low, intermediate and high respectively. An example of the treatment combinations in a $3^3$ design can be seen in figure 2. Each main effect has 2 degrees of freedom, each two-factor interaction has 4 degrees of freedom and the three-factor interaction has 8 degrees of freedom. If there are n replicates, there are $n3^3-1$ total degrees of freedom and $3^3(n-1)$ degrees of freedom for error. The sum of squares, SS, may be calculated using the standard methods for factorial designs. The analysis of variance for a $3^k$ design can be seen in table 2.

**Figure 2** Representation of a $3^k$ Factorial Design.

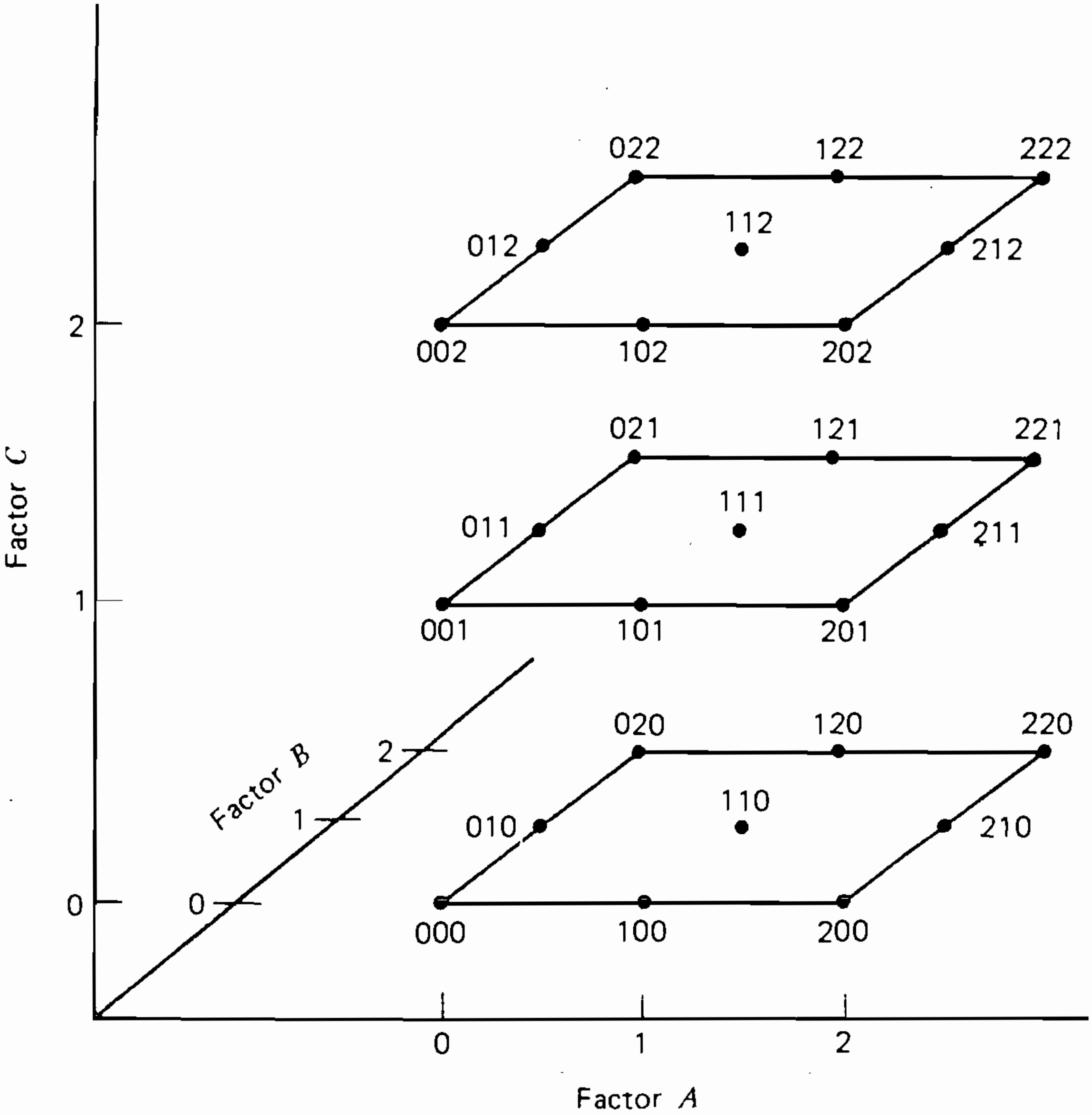


**Table 2** Analysis of Variance for a $3^k$ Factorial Design.

| Source of Variation | Sum of Squares | Degrees of Freedom |
|---|---|---|
| $k$ Main Effects | | |
| $A$ | $SS_A$ | 2 |
| $B$ | $SS_B$ | 2 |
| $\vdots$ | $\vdots$ | $\vdots$ |
| $K$ | $SS_K$ | 2 |
| $\binom{k}{2}$ Two-Factor Interactions | | |
| $AB$ | $SS_{AB}$ | 4 |
| $AC$ | $SS_{AC}$ | 4 |
| $\vdots$ | $\vdots$ | $\vdots$ |
| $JK$ | $SS_{JK}$ | 4 |
| $\binom{k}{3}$ Three-Factor Interactions | | |
| $ABC$ | $SS_{ABC}$ | 8 |
| $ABD$ | $SS_{ABD}$ | 8 |
| $\vdots$ | $\vdots$ | $\vdots$ |
| $IJK$ | $SS_{IJK}$ | 8 |
| $\vdots$ | $\vdots$ | $\vdots$ |
| $\binom{k}{k} = 1$ $k$-Factor Interaction | | |
| $ABC \ldots K$ | $SS_{ABC \ldots K}$ | $2^k$ |
| Error | $SS_E$ | $3^k(n - 1)$ |
| Total | $SS_T$ | $n3^k - 1$ |

# APPENDIX 2

## List of BASIC Program "TIOTRM"

```
10  MODE 3
20  @%=&00406
30  INPUTTAB(10,15)"WHAT'S THE TOTAL VOLUME IN cm^3 IN EACH
    CASE"TVOL
40  CLS
50  INPUTTAB(10,15)"WHAT'S THE CONCENTRATION OF POTASSIUM
    IODATE IN MOLES dm^3"
60  CLS
70  INPUTTAB(10,15)"WHAT'S THE TITRE SAMPLE VOLUME IN cm^3 IN
    EACH CASE"TIV
80  CLS
90  INPUTTAB(10,15)"HOW MANY cm^3 OF POTASSIUM IODATE
    STANDARDISE THE THIOUREA SOLUTION"VK
100 CLS
110 LET MTU=(KIO*VK*6)/TIV
120 INPUTTAB(10,15)"HOW MANY FLASKS HAVE YOU GOT"NF
130 CLS
140 DIM MLST(NF),MC(NF),MLSK(NF)
150 PRINTTAB(10,15)"TYPE IN cm^3 OF THIOUREA MADE UP TO
    100cm^3"
160 FOR A=1 TO NF
170 INPUTTAB(10)MLST(A)
180 NEXT A
190 CLS
200 PRINTTAB(10,15)"TYPE IN MASS OF CARBON(g) AND TITRE
    FIGURE(cm^3)"
210 FOR B=1 TO NF
220 INPUTTAB(10) MC(B),MLSK(B)
230 NEXT B
240 REM
250 REM CALCULATIONS
260 CLS
```

```
261 INPUTTAB(10,15)"DO YOU WANT THESE RESULTS PRINTED OUT
    (Y/N)"A$
262 IF A$="Y" THE 268 ELSE 270
268 VDU2
270 PRINT
280 PRINT
290 PRINT"MASS OF INIT.CONC. EQUIL.CONC. MASS TU  MASS ADS
    Ceq/X/M"
300 PRINT"CARBON  THIOUREA   THIOUREA    ADSORBED /g CARBON "
310 PRINT"   (g)    MOLES/dm$^3$   MOLES/dm$^3$     (g)         (g/g)
    MOLES/dm$^3$"
320 PRINT
330 FOR C=1 TO NF
340 LET ICTU=(MTU*MLST(C))/TIV
360 LET MOLTUADS=(ICTU-EQTU)*TVOL/1000
370 LET MASSTUADS=MOLTUADS*76
380 LET XM=MASSTUADS/MC(C)
390 LET CXM=EQTU/XM
400 PRINT MC(C)"     "ICTU"    "EQTU"    "MASSTUADS"     "XM"    "CXM
410 NEXT C
420 VDU3
430 END
```