SOLVENT IMPREGNATED RESINS FOR THE RECOVERY OF GOLD FROM GOLD(I)THIOUREA SOLUTIONS.

by

Fiona Fitzpatrick. School of Chemistry, DIT Kevin St.

A Thesis presented to Dublin City University for the award of M.Sc.

Prepared under the supervision of Dr M.B. Foley,

School of Chemistry, DIT Kevin St., Dublin 8, Ireland.

December 1997

Thesis Declaration

I hereby certify that this material, which I now submit for assessment on the programme of study, leading to the award of M.Sc is entirely my own work and has not been taken from the work of others, save to the extent that such work has been cited and acknowledged within the text of my work.

Signed:____________________
Candidate

Acknowledgements

Many thanks to all who helped with the preparation of this thesis. In particular, I would like to express my sincere gratitude to my supervisor, Dr. Barry Foley, for his guidance, support and encouragement. Thanks also to the lecturers of the School of Chemistry, DIT Kevin St., for their help and advice and to Dr. Malcolm Smith, Dublin City University for his time and interest in my work.

A special word of appreciation to the chemistry technicians and postgrads in Kevin St, for their help and friendship and for all the good times I've had with them. Thanks also to my friends, especially my flatmates, who've put up with me rambling on about gold recovery and resins for the past few years - I hope it all finally makes sense!

I also wish to acknowledge the financial assistance of the DIT, through their Strategic Research and Development Programme.

Finally, a very special thank you to my family, in particular my mother and my late father, for their love, support and encouragement always.

Chapter 1 Introduction

Chapter 2 Phase Transfer Systems for Precious Metal Recovery

Chapter 3 Impregnation of Amberlite XAD 2, XAD 4 and XAD 7 Resins

Chapter 4 The Recovery of Bis-Thiourea Gold Perchlorate Using Solvent Impregnated Resins

Chapter 5 The Capacity of Solvent Impregnated Resins for Gold and the Recovery of Gold from the Resins

Chapter Six The Effect of Interfering Species on the Efficiency of Gold Recovery by Solvent Impregnated Resins.

Solvent Impregnated Resins for the Recovery of Gold from Gold(I)Thiourea Solutions

Fiona Fitzpatrick,
School of Chemistry, Dublin Institute of Technology, Kevin St, Dublin 8.

Abstract

Solvent Impregnated Resins (SIRs) are high surface area, macroporous, polymeric resins which have been physically impregnated with an organic solvent. In this research, three resins have been impregnated with Di-2-ethylhexyl phosphoric acid, a solvent which has shown selectivity to gold. The ability of the resins to recover gold(I)thiourea perchlorate from solution has been investigated.

The resins have been studied both bare and when impregnated with the solvent and their efficiency was seen to increase significantly upon impregnation. The overall efficiency of the resins was found to be pH dependent. It is also related to the level of impregnation of the resins. Recovery by the resins compares favourably with liquid/liquid solvent extraction using the same solvent. The overall capacity of the resins was estimated by determination of the maximum gold loading of the resins. Gold from the resins was eluted by washing with methanol and mass balances of gold approaching 100% have been achieved.

The effect of interferents in solution, in particular, excess thiourea and ferric and cupric ions was also investigated. Scanning electron micrographs and X-Ray fluorescence spectra of the bare and impregnated resins were obtained and the effect of sulphur formation on the resins was established.

Chapter 1
Introduction

1.1 The History of Gold Mining

Before the late 19th century, the reclamation of gold from the earth's resources was mainly restricted to the recovery of placer deposits from rivers and streams. These deposits occurred where particles of gold were washed from mother lodes and veins in the earth's surface by floodwaters etc. (1). Rocks and other barriers in the river allowed stream water to carry away suspended loads of lightweight particles, while trapping denser particles such as gold into the bed load. In effect, gold in the river was gravimetrically concentrated and could then be recovered by sifting through the river sediment, washing lighter materials from the silt to leave the heavier gold deposits behind. If the gold was part of a composite ore, the deposit was milled to liberate the gold particles before it was concentrated. If the deposit proved to be extensive, the river was dredged by dragging large containers along the bottom of the river bed to remove the gold bearing silt (2).

Prospectors could often tell whether the mother lode was close, by inspecting the shape of the gold nuggets. Alluvial deposits, that is, deposits away from the source or vein were rounder and flatter because of the pounding effect of the moving river on the nugget. Eluvial deposits i.e. deposits found near to the bedrock source were sharper and more angular. By following the trail of gold upstream, it was often possible to source the mother lode (1).

In the 1800's, the discovery of a new gold deposit drew thousands of hopeful prospectors to a particular area in what became known as gold rushes. One of the most famous of these rushes was the 1848 California gold rush, sparked by the discovery of gold by James Wilson Marshall at Sutter's Mill, California. The promise of gold had such an impact on the locality that it resulted in the small town of San Francisco growing to a city of 25,000 people in just one year (3). So many miners went to California during the gold rush that the territory had enough people to be admitted as a state in 1850. Gold rushes in California and other places led to the development of mines and communities in many parts of the world including Australia, South Africa, West Africa, Malaya, Mexico and Siberia (3).

1.2 Gold Mining in Ireland

Gold mining in Ireland over the last two hundred years has mainly concentrated on one placer deposit in Ballinvally, Co. Wicklow. The deposit was first discovered in 1795 in a minor river which has since become known as the Gold Mines River. The find led to a gold rush in which 80kg of gold is estimated to have been recovered in just six weeks. The government then stepped in and dispersed the gold diggers. The ore was worked intensely by the state between 1796 and 1803 and was then worked intermittently by locals and by private mining companies. The gold occurred as free particles of a minute scale although some larger grains and nuggets were also reported, some as large as 0.75kg. The total mass of gold extracted from the ore is estimated to be near 300kg, though the true figure may be higher (4).

Other significant discoveries in Ireland include Avoca, Co. Wicklow, in the late nineteenth century. Although the ore was primarily copper, gold was found in pyritic and chalcopyritic ores as well as free gold. The ore typically contained 0.3g gold/t though some pyritic rocks contained up to 0.75g /t. More recently, attempts to recover gold from the tailings pond by leaching with thiourea have been reported. It is estimated that the tailings contain between 2 and 3 Mt grading 0.85 to 28.35g Au/ton (5).

Curraghinalt, Co. Tyrone has long been recognised as a minor source of alluvial gold, however prospecting in 1982 revealed that bedrock gold, associated with pyrite minerals, was also present. Drilling and underground exploration have outlined over 900,000 t grading 10g Au/t . The discovery of this deposit led to a major resurgence of gold exploration in Ireland.

Lecanvey, Co. Mayo was reported as a source of gold in 1984 by Tara Prospecting Ltd. It was an unusual discovery in that no previous record of gold existed for that region. A programme of panning and prospecting led to the discovery of visible quartz veins and drilling of the best site revealed a reserve of 498,000 t grading 9.94g Au/t.

A gold deposit in Cavancaw, Co. Tyrone was discovered in 1987 and a geological resource of 2Mt at 6.9g Au/t has been determined. Large scale trenching and diamond drilling have confirmed the existence of 360,000 t, grading 7.52g Au/t . The mine is operated by Omagh Minerals and a license for open pit mining was recently granted to the company. The estimated lifetime of the pit is eight years (5).

1.3 Environmental Considerations of Mining in Ireland

Mining in Ireland has received mixed public reaction over the past couple of decades. The prospect of employment in rural areas in a time of economic recession has not always been enough to pacify the environmental concerns of local communities and environmental groups when mining companies apply for exploration licenses. They cite cases such as the lead and zinc mine in Tynagh near Loughrea, Co. Galway as an example of the real costs of mining on a community. The mine, which was the source of much excitement when it opened in 1965 as one of the most significant deposits of its kind in the world, was developed by Northgate Exploration Ltd. After nine years of open cast mining and six years of underground mining, the site was abandoned in the early 1980's. Very little decommissioning of the mine was undertaken after its closure and a tailings pond of approximately 160 acres was left untreated. Environmental groups estimate that as much as 2,000 acres of what had been valuable agricultural land was poisoned by lead and zinc disturbed by the mine, though this estimate may be disputed by current mining companies who claim it has been overstated (6).

However, Tynagh mine was one of the first large scale mines in this country and it was developed at a time when no proper planning or environmental controls were in place to force mining companies to clean up. As the population became aware of the environmental implications of mining, legislation was put in place to prevent any repeat of such irresponsible mining practises. Relevant legislation includes The Minerals Developments Acts (1940 and 1979), Mines and Quarries Act (1965), Wildlife Act (1976), Local Government (Water Pollution) Acts (1977 and 1989), Local Government (Air Pollution) Act (1987), Safety, Health and Welfare at Work Act (1989) and The Environmental Protection Agency Act (1992) (7). The legislation now in place ensures mining operations in Ireland will conform to regulations which are among the strictest in the world.

Nevertheless, concerns still exist and the polluting effects of mining, along with objections to mining in environmentally sensitive areas, have led to vociferous opposition to some mining applications. The application for a mining license by Burmin Exploration and Development plc is a well publicised example. They applied for permission to develop a gold mine at Croagh Patrick in Co. Mayo, as part of the Glaspatrick gold deposit. The proposed siting of the mine resulted in national controversy and an application to renew a licence for exploration was refused, partly because of public opposition to the setting up of a gold mine in an environmentally and historically significant area such as Croagh Patrick (8).

Public concerns centre around the visual and environmental impact of modern gold mine practices, which involve overground leaching of gold using potentially toxic chemicals such as cyanide. The development of a non toxic gold extraction procedure suitable for mining would be of particular significance since it would allay justifiable concerns about using dangerous chemicals and would also allow the leaching of gold from the ore to be carried out underground. If safer mining practises could be established, it is hoped that public opinion regarding gold mining in Ireland and other countries could become more positive and that the industry could work with the support and backing of governments and local communities. A significant step forward in this overall aim is the development of alternative extraction lixiviants such as thiourea to replace cyanide as the main method of gold extraction.

1.4 Modern Methods of Gold Extraction

Gold is present in trace amounts throughout the earth's lithosphere and hydrosphere. The average content of the earth's crust is 5 parts per billion (ppb), however, economically recoverable gold needs to be in concentrations of over a thousand times higher. The minimum operating grade in a gold mine depends on the current price of gold and also on the cost effectiveness of the operation. In recent years, grades of about 7 parts per million and better have constituted standard ore. The development of more effective mining techniques, however, allows the threshold of minimum enrichment to be decreased all the time (4).

1.5 Cyanidation

The advent of cyanide extraction in 1890 revolutionised the gold mining industry. It was developed and patented by J.S. MacArthur and W. and F.W. Forrest and was first introduced to the Witwaterstrand mine in South Africa (9). Its impact on the industry was so great that world-wide gold production rocketed from 9,870t in the latter half of the nineteenth century to 34,172t in the first half of the twentieth century (10).

Cyanide extraction was successful because it allowed the mining of gold ores which would have previously been rendered uneconomic. This was possible because it can selectively dissolve gold from the ore. It has remained the predominant method of gold extraction since its development and while much work has been put into optimising the procedure, the overall process remains essentially the same as MacArthur's original proposal.

1.5.1 The Extraction of Gold by Cyanide

Extraction occurs in alkaline solution. It is an oxidative leaching process, i.e. oxygen is required for the reaction to occur. Atmospheric oxygen is usually sufficient. The overall reaction between gold and cyanide can be expressed as:

$$4Au + 8CN^- + O_2 + 2H_2O \longrightarrow 4Au(CN)_2^- + 4OH^-$$

The aurocyanide ion formed is an extremely stable linear complex (10).

The reaction can be separated into the anodic dissolution of gold:

$$4Au + 8CN^- \longrightarrow 4Au(CN)^-_2 + 4e^-$$

supported by the reduction of oxygen as the cathodic reaction:

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \text{ (11)}$$

The process is recognised for its economy and process simplicity, its selectivity and its suitability for the recovery of gold and silver from solution (12).

1.5.2 Disadvantages of Cyanide Extraction for Gold Mining

However, cyanide leaching is by no means an ideal method of extraction and there are many disadvantages attached to the process. Of these, the dangers of working with cyanide is the most controversial, since it is a toxic chemical and must be handled carefully to avoid damage to the environment and to humans. Great care is needed to prevent its release into the surrounding environment through seepage from tailings ponds etc.. The ore heaps need to be formed on an impervious site which usually involves forming an impenetrable layer with compacted clay or asphalt (11). When working with cyanide solutions, it is necessary to control the pH of the solution so that it remains above the pKa of hydrogen cyanide gas, since this is a highly toxic form of cyanide which, if inhaled, can lead to death in minutes. The effect of cyanide on the environment has been the subject of many studies (12), (13), (14). Howe et al (14) described the contamination of the Whitewood Creek in South Dakota in the United States. As a result of six decades of receiving mine effluent, the river had been declared "biologically dead" in 1960. The effects of cyanide on vegetation surrounding the mine is discussed and a link between cyanide in the soil and its uptake by certain plantlife is established. Because of the environmental problems associated with cyanide, the US environmental protection agency forces mining companies in the US to provide options for non-polluting methods of gold leaching (15).

The toxic nature of cyanide also prevents its use for in-situ mining of gold, that is, the underground mining of gold from within the earth’s crust without removing it to heap (16). This type of mining would allow for the extraction of low grade gold ores since the cost of extraction is minimised by reducing transport and other costs associated with conventional extraction techniques.

Another significant problem with conventional cyanide extraction is its inability to economically extract gold from certain refractory ores without first pretreating the ore. When gold is present in refractory ores, that is, complex ores containing other compounds such as base metals, sulphides, arsenopyrite, pyrite, carbonaceous sulphides etc., cyanide consumption becomes so high that it becomes uneconomical to mine these ores without first pretreating in order to oxidise and thus deactivate the refractory materials (17). Techniques used include roasting, oxidative acid leaching and bioleaching, all of which add to the overall cost of extraction and can cause other problems such as the generation of toxic gases (18). The need to pretreat these ores often means it is no longer economically viable to mine the ore. In particular, copper minerals, which are often associated with gold ores, consume significant quantities of cyanide to form a mixture of cyanide complexes, ferrocyanide, cyanate or thiocyanate depending on the mineral present. The pre-treatment methods for removing copper prior to cyanidation or post treatment methods of recovering copper and cyanide from solution are generally unsatisfactory or uneconomic (19).

Because of the problems associated with cyanide extraction, in particular its toxic nature and excessive consumption for complex ores, considerable effort has been put into the development of alternative lixiviants which might overcome these problems.

Methods proposed include, thiourea, halide, thiosulphate and thiocyanate extraction. Of these, thiourea extraction has shown the most promise and a processing plant for the extraction of gold using thiourea has been set up for the recovery of gold from a concentrate containing antimony and arsenic (20). It has also been proposed for the recovery of gold from chalcopyrite concentrates (21). The other methods of extraction have been widely researched but little application to actual ores has been reported.

1.6 The Extraction Of Gold By Thiourea

The thiourea leach process for the extraction of gold has been widely studied since its first application by Plaskin in 1941 (22) and of the processes studied as alternatives to cyanide, it has gained the most attention. Its most obvious advantages over cyanide include low toxicity, fast kinetics and its insensitivity to impurity interferences. The dissolution of gold by thiourea is approximately 10 times faster than cyanide, it also appears to be less sensitive to impurities than cyanide and so does not require the expensive and environmentally damaging pre-treatment steps often required for cyanide extraction. Although thiourea is classified as a suspect animal carcinogen, it is not a highly toxic compound and it is not likely to cause acute toxic effects since the level of toxicity is low (LD_{50}= 1,830 mg/kg) (23).

1.6.1 Thiourea Extraction Mechanism

When comparing the leaching chemistry of thiourea with cyanide, Schulze (24) makes three important points:

1. Thiourea uses condensed phase oxidants, e.g. ferric iron or hydrogen peroxide, while cyanide takes gaseous oxygen from the air.
2. The charge of the thiourea complex is cationic, while cyanide yields negatively charged complex anions.
3. Kinetically, the rate of thiourea leaching should be a function of both the concentration of thiourea and of the oxidant.

Thiourea extracts gold in an acidic medium (pH 1) and at a solution oxidation potential such that its oxidation product formamidine disulphide (RSSR) is formed. Oxidants used include ferric iron (25), (26), hydrogen and sodium peroxide (25), (26) and dissolved oxygen (25). The rate of gold dissolution is rapid and increases with increasing concentrations of thiourea and oxidant. The rate of dissolution is related to the pH of the solution and above pH 1.5 decreases significantly (27). Rates are similar in hydrochloric and sulphuric acid media although nitric acid appears to retard the process (26). There is a relationship between the temperature of the leach solution and the rate of dissolution; Schulze (24) reported that for every 10°C increase in leaching temperature the rate of dissolution of gold by thiourea doubles.

Formamidine disulphide (RSSR or $(CSNH_2NH)_2$) is an oxidation product of thiourea and is required for dissolution of gold in thiourea (25). Dissolution involves a redox reaction between gold and thiourea with RSSR. The process can be separated into:

1. Oxidation of Thiourea

$$2CS(NH_2)_2 \longleftrightarrow (CSNH_2NH)_2 + 2H^+ + 2e^-$$

(in the presence of an oxidising agent, e.g. Fe^{3+} or H_2O_2).

The oxidising agent most commonly used for the formation of RSSR is ferric iron (Fe^{3+}).

2. Dissolution of Gold

$$2Au + 2CS(NH_2)_2 + (CSNH_2NH)_2 + 2H^+ \longrightarrow 2(Au(CS(NH_2)_2)_2)^+$$

Groenewald (25) suggests that RSSR is the active oxidant for the dissolution of gold in thiourea solutions. The initial rate of dissolution of gold in an acidic solution of thiourea and ferric iron is rapid and is only limited by the rate of diffusion of the oxidant to the surface of the gold. Ferric iron appears to be more effective in a sulphate rather then a chloride medium (26).

1.6.2 The Application of Thiourea to Gold Concentrates

Thiourea extraction has found its application for the processing of gold from ores which cannot be economically mined using cyanide. One of the first mines reported to use thiourea for gold extraction was the New England Antimony Mine in New South Wales in Australia which opened in 1969. Initially, the ore was treated by flotation to recover antimony only, but increasing gold grades and prices led to the installation of a gravity concentration circuit for the recovery of gold in 1976. An investigation into the recovery of gold from the concentrate showed that cyanide extraction was not economically viable and other lixiviants were tested. Thiourea extraction was found to be the most effective and a leach plant was commissioned in 1982. A high thiourea and ferric ion concentration system was used and a leaching time of less than 15 minutes was found to be sufficient. Thiourea consumption of less than 2kg/t were normal. The leach solution was recirculated after readjustment of the redox potential with hydrogen peroxide. Gold was recovered by adsorption onto activated carbon and sold as a concentrate containing 6 to 8kg gold/t. Gold recoveries of between 50% and 80% were achieved depending on the exposure of gold in the concentrate. Problems with the adsorption of gold onto chlorite in the flotation concentrate were initially encountered but these were overcome by using Aero depressant 633 in the flotation and a small addition of diesel oil to the leach. High recoveries of gold have been achieved with pregnant solutions assaying as low as 0.5ppm (20).

Deschênes et al investigated thiourea for the extraction of gold from a chalcopyrite concentrate from the Chibougamau mine in Canada. The conventional method of processing gold bearing chalcopyrite ore is smelting. Cyanidation is not economical because yields are low (71%) and cyanide consumption is high (18.8kg/t). This is due to the leaching of copper from the mineral which was reported to be as high as 5.3g/l.

An investigation of the leaching with thiourea gave a maximum gold recovery of 89%, with a thiourea consumption of 9.84Kg/t. Pre-processing of the concentrate with acid before leaching reduced the presence of interfering ions such as iron and copper. The concentration of copper leached by thiourea was significantly lower and concentrations of 160ppm in the leachate were typical (21).

1.6.3 Disadvantages of Thiourea for Gold Mining

While thiourea may appear to solve many of the problems of conventional gold extraction methods, it is not without its disadvantages. In particular, the oxidation of thiourea, which while necessary to produce RSSR, becomes a nuisance when RSSR is irreversibly oxidised to elemental sulphur, hydrogen sulphide or cyanamide in the presence of weak oxidising agents, or to urea and sulphate if the oxidising agents are stronger (e.g. MnO_4^- or CrO_7^-). The decomposition of thiourea in the extraction process not only increases its consumption, but also leads to extraction and recovery problems. Elemental sulphur is formed in the solution as a fine suspension and can coat the surface of the feed material resulting in passivation. The presence of sulphur in the leach is blamed for suppressed recovery of gold and silver (24).

In order to minimise thiourea consumption, the second (irreversible) oxidation step must be avoided or, at least, controlled. Methods of achieving this include:

1. Adding a very low initial concentration of thiourea ($\leq 1g/dm^3$) (29).

2. Limiting reagent oxidation in the presence of a suitable reductant e.g. SO_2, sulphite and sodium metabisulphite ($Na_2S_2O_5$). It has been reported that the oxidation of thiourea in the presence of SO_2 does not go to completion but attains equilibrium at approximately 50% conversion to RSSR. This is

reported to be the key factor in achieving a high leaching rate at low consumption (24), (30).

3. Using high concentrations of thiourea and recycling the solution at the end of the process (30).

4. The addition of urea and K-lignin sulphonate (30).

Another disadvantage of thiourea leaching is the adsorption of the cationic gold and silver thiourea complexes formed onto clay minerals. This is a problem for commercial thiourea leaching and can lead to misinterpretation of test data for thiourea leaching systems. This effect can be overcome by sequential washing of the solids with warm dilute thiourea to desorb the gold and silver (31). Schulze (33) reported that leach recovery of gold by thiourea increased from 88% to 98% after washing the solids with warm thiourea.

Despite initial problems, thiourea remains one of the most promising alternatives to cyanide extraction for the gold industry. It is a non toxic lixiviant, it can leach at a faster rate than cyanide and under certain conditions it will extract gold more efficiently than cyanide. It is likely that the increasingly strict regulations on water quality and pollution control will force the gradual replacement of toxic processes such as cyanide with safer alternatives. The advantages of thiourea over cyanide under these circumstances, along with its other advantages, should help establish thiourea as a standard method of gold extraction.

1.7 Halide Extraction

1.7.1 Chloride

Chloride leaching has been applied to precious metal recovery for many years, especially in the treatment of complex metal sulphide ores. The chlorine complex of gold is much weaker than either the cyanide or thiourea complexes (28). It requires highly oxidising conditions for gold dissolution and reprecipitation of metallic gold will occur unless oxidising conditions are maintained throughout the leach. A brine solution is used as the source of chloride and chlorine is used as the oxidant. The reaction for the dissolution of gold by chloride is given below:

$$3Cl_2 + 2Au + 2Cl^- \longrightarrow 2AuCl_4^-$$

The rate of dissolution of gold is rapid under acidic conditions and complete dissolution of gold can be achieved in one hour.

The main disadvantage of chlorine extraction is the excessively high reagent consumption in the presence of oxidisable materials in the leach. Pyrite and other sulphides dissolve at a similar rate to gold and if they are not completely dissolved, they can cause the reduction of gold back to elemental gold. The corrosive nature of the acidic chlorine solutions means that the materials used in the construction must be capable of withstanding extremely hostile conditions. Developments in the plastics industry however, should allow for large scale leaching vessels. The toxic nature of chlorine gas must also be a consideration when chloride extraction is employed.

Recovery of gold from the leach solution by activated carbon yields high loadings (>50 kg Au/t). The carbon is burnt to recover the gold bullion (28).

1.7.2 Bromine

Bromine has been known as a lixiviant for gold dissolution since 1846 (31). It can be added in several forms including the addition of a bromide salt with chlorine or hypochlorine to convert bromide to bromine. The rate of leaching is greatly enhanced by the addition of a protonic cation such as NH_4^+ and an oxidant and leaching is not affected by pH. Other bromine systems proposed include the commercial Bio-D leachant which is reported to be more effective than reagents such as bromocide (a disinfectant) because it can be recycled and Geobrom®3400, a liquid bromine carrier (31). Bromine leaching has particular relevance to the mining of black sand concentrates which can have adequately high gold recoveries to justify higher reagent consumptions. Black sand concentrates contain mainly magnetite (nearly Fe_3O_4) and ilmeno-hematite (Fe_2O_3 with up to 25% $FeTiO_3$ component) as well as other minerals. Dadgar et al report leaching and recovery of gold from a black sand concentrate using a bromine system (34). They achieved 95% solubilization of gold after three four-hour leaches and recovered gold by loading onto ion exchange resins and eluting with acetone/HCl (100%) and thiourea/HCl (90%). The cost of the bromine required to leach 1kg of gold is given as $325, in comparison to $800 for cyanide extraction (including the cost of cyanide detoxification) (34). The advantages of bromine include rapid dissolution of gold, non-toxicity and adaptability to a wide range of pH values.

1.7.3 Iodine

Iodine forms the most stable gold complexes of all the halogens and its redox potential is about half that at which gold dissolves in acidified chlorine solution. Iodine can leach gold over a wide range of pH values. Good recoveries of gold using iodine are possible, however it is an expensive reagent and must be recovered efficiently for recycling in order to remain a cost effective process (31).

1.8 Thiosulphate Extraction

The dissolution of gold by thiosulphate is given as:

$$Au + 2S_2O_3^{2-} \longrightarrow [Au(S_2O_3)_2]^{3-} + e^- \qquad (19)$$

Thiosulphate is a non toxic and inexpensive bulk chemical. Its use in the leaching of gold goes back to the 1880s when it was used in the Russell and the von Patera processes (31). Abrantes et al reports that thiosulphate can extract gold from low grade oxide ores; it has also shown some promise for the economic processing of low grade carbonaceous gold ores (19).

The gold leaching chemistry of thiosulphate has been found to be very complicated. Dissolution is sensitive to thiosulphate and Cu^{2+} concentration and also has a complex dependency on temperature (19). Although thiosulphate was tested for an in-situ leach project, there are no known commercial scale ore operations using the reagent (31).

1.9 Thiocyanate Extraction

The dissolution of gold by thiocyanate was first demonstrated by White in 1905 (32). It has recently been reinvestigated and shows some promise as a technically viable lixiviant for gold. The oxidation of thiocyanate in the presence of iodide proceeds through the formation of several intermediate species which act as both oxidant and upon reduction, as complexing agent for gold. The instability of these intermediates toward hydrolysis is one of the major drawbacks of the thiocyanate/Fe^{3+} system although it may be prevented by the addition of small amounts of I^- or I_2. Research on gold extraction using thiocyanate is limited and no commercial processes are known (19).

1.10 The Recovery of Gold from Leach Solutions

With the establishment of cyanide as the main method of gold leaching, techniques in gold recovery have not changed dramatically over the past 100 years, again, because their simplicity and economic viability as part of the cyanide process meant their was no great need for change. Conventional methods of recovery include zinc cementation and activated carbon.

1.11 Zinc Cementation

Zinc precipitation or cementation was patented by MacArthur et al in the 1890's at the same time he patented cyanidation as an extraction technique. The process has been improved and redeveloped over the years to become what is known today as the Merrill-Crowe process (9). Its recovery may be represented by the reaction:

$$2Au(CN)^-_2 + Zn \longrightarrow 2Au + Zn(CN)_4^{2-}$$

The technique involves the addition of a fine zinc dust into the pregnant leach solution. The emulsion formed is pumped through a filter system and the gold-zinc slime is then filtered from solution. The barren filtrate is recycled for further extraction of gold. The zinc-gold precipitate is then smelted to separate the gold from the zinc. Clarification and de-aeration of the pregnant liquor is necessary to eliminate colloidal constituents which would coat the zinc particles, inhibiting precipitation and also to prevent oxidation of zinc and redissolution of precipitated gold (9).

The process suffers from drawbacks in that sulphide, sulphate, thiosulphate and ferrocyanide ions can cause passivation of the zinc surface and thus inhibit cementation. Very low quantities of arsenic and antimony (1ppm) can also reduce the recovery of gold from cyanide solutions (17).

While zinc cementation has worked well for the recovery of gold from cyanide extraction solutions, it has been found to be unsuitable for gold recovery from thiourea solutions because of the generation of hydrogen gas due to the acidic nature of the solution. This results in an excessively high consumption of zinc (35).

1.12 Activated Carbon

The sorption of gold onto activated carbon is a simple process, dating back to 1880 when it was first patented for the recovery of gold from chlorination leach liquors (36). It was patented for recovery of gold from cyanide solutions in 1894 (37). Its initial success was limited by the low surface area and low abrasive strength of early carbons and also by the lack of a suitable procedure for elution of gold from the loaded carbon (36). It was useful, however, for the recovery of gold from slimy ores, which were difficult to treat using conventional Merrill Crowe techniques because filtration and clarification was difficult. Early use involved loading the carbon with gold and selling as a gold concentrate, however this was discontinued when a recycling process, first suggested by Zadra in 1952 (38), was made commercially viable in the 1970s by the effective reactivation of the loaded carbon by heating to 900°C in an air free environment (39). The rapid development of carbon recovery systems in recent times can be attributed to the work of Zadra in developing a process for the recovery of gold and silver from activated carbon by leaching and electrolysis (38) and also the development of high surface area, abrasion resistant carbon products. Sources of activated carbon include wood, nut shells, coal and petroleum coke. The most popular source however is coconut shells since these give high recovery capacities and have good long term durability for gold recovery.

The steps involved in the recovery of gold from cyanide liquors using activated carbon are:

1. Pre-screening,
2. Carbon adsorption,
3. Carbon acid -washing and elution,
4. Gold electrowinning or precipitation and
5. Carbon reactivation (40).

Pre-screening removes oversize material which might block the screens on the adsorption contactors which retain the activated carbon while allowing the pulp to flow freely. Adsorption involves the effective recovery of dissolved gold from the leach liquor onto the activated carbon. Elution and acid washing procedures strip the recovered gold from the carbon. Gold electrowinning and precipitation recovers elemental gold from the elution mixture and carbon reactivation reactivates the carbon by heating to 900°C, allowing it to be reused in the recovery process (40).

Loading of gold onto the carbon surface can be accomplished from clean leach liquors with carbon in column systems, from leach pulps with carbon in pulp systems and even when leaching is still in progress with carbon in leach systems. Carbon in column recovery is used in heap leaching where the solutions are filtered and so do not contain suspended solids. Carbon in pulp is common for slimes, ground ores and calcine containing ores. Carbon in leach is used when the ore contains carbonaceous material which could rob the gold from the pregnant solution. Elution of gold from the loaded carbon is performed at atmospheric or elevated pressures using sodium cyanide or sodium hydroxide solution. Electrowinning and zinc cementation are used to recover the gold from the eluant (17).

The most widely used of these recovery methods is the carbon in pulp (CIP) process. Activated carbon is added directly to the leach solution and moved counter current to it. The CIP method of recovery has several advantages over zinc cementation:

1. Carbon can adsorb gold cyanide without being affected by the common ions and complexes found in leaches, such as copper and nickel cyanide, which can cause problems during recovery by zinc cementation.

2. The expensive clarification step needed for zinc cementation is eliminated since the carbon is added directly into the leached pulp.

3. Soluble gold losses are usually significantly lower than for zinc precipitation (36).

The recovery of gold from thiourea process solutions using activated carbon has not been as successful as for gold cyanide complexes. Adsorption of thiourea onto the carbon can be higher than 30% resulting in excessively high consumption of thiourea (35). While it is possible to wash free thiourea from the carbon, this must be done in an oxygen free environment (24). Although high recoveries of gold have been reported (41), excess thiourea in the presence of an oxidant such as ferric iron, can very significantly reduce the capacity of the recovery medium. This is due to the oxidation, by ferric iron, of excess thiourea to RSSR which is strongly retained by the carbon and undergoes decomposition to elemental sulphur which deposits in the pores of the carbon structure, preventing the diffusion and adsorption of the gold thiourea molecule. Activated carbon also appears to catalyse the degradation of thiourea to elemental sulphur which again leads to increased consumption of thiourea and inhibited gold recovery.

1.13 Alternative Methods of Gold Recovery

Conventional gold extraction using cyanidation achieved satisfactory levels of recovery with both zinc cementation and activated charcoal. These methods of recovery dominated gold recovery and improvements over the years meant that recovery rates were steadily increasing. When thiourea was proposed as an alternative to cyanide, problems with recovery were encountered using conventional methods and therefore it became necessary to find a more satisfactory process for gold recovery. Methods proposed include solvent impregnated resins, ion exchange, solvent extraction, precipitation, electrowinning and hydrogen pressure reduction. Ion exchange and solvent extraction will be discussed in more detail in chapter 2, along with solvent impregnated resins which are the main subject of this study. A brief discussion of other methods of recovery is given below.

1.14 Precipitation

Chemical precipitation of gold using zinc is not suitable for thiourea leaches since hydrogen evolution results in high acid consumption. Precipitation using other metals including aluminium, lead and iron have been proposed. Tests by the US Bureau of Mines on the precipitation of gold from thiourea leaches using aluminium gave up to 99% precious metal recovery for a 30g/L thiourea solution at pH 1.5, containing 42ppm Au and 45ppm Ag. 6.4lbs of aluminium powder were required per pound of metal in solution (42). A final gold content in the cement of approximately 2% was reported by Van Lierde (43). The low gold content meant that refining of the aluminium cement was uneconomical. Deschênes reports that aluminium is more effective than activated carbon for the recovery of gold from a pyrite concentrate leach (17).

Tests with lead powder showed that recovery was dependent on the powder surface area and a minimum activity is needed to have high recovery (17). Deschênes (15) reported that no gold was recovered using lead powder with a particle size less than 0.38μm, even at elevated temperatures (60°C) . Lead shot recovered 76% of gold in solution after 4 hours but it was not economically viable (15).

Recovery of gold using iron cementation has been suggested for thiourea solutions of low gold content (17). Recovery of gold onto iron wool was also reported (41) but problems with hydrogen evolution and wool recovery from the slurry caused problems. Iron plate was found to be as fast as activated carbon but iron and acid consumptions were high (41).

1.15 Electrodeposition

The electrodeposition of gold from thiourea solutions, through the reduction of gold(I)thiourea occurs through the following reaction:

$$Au(CS(NH_2)_2)_2{}^{+} + e^{-} \longleftrightarrow Au + 2CS(NH_2)_2 \qquad (26)$$

This is a diffusion controlled reaction with a cathodic potential ranging from between -0.15 and -0.35 V. If the cathodic overpotential is increased to between -0.5 to -0.6V, gold deposition occurs, along with hydrogen evolution. Formation of an unidentified polymer related to the presence of gluconate or citrate ions in solution (used in buffers), which is a problem when acidic cyanide solutions are used (44), appears to be inhibited by the evolution of hydrogen when thiourea solutions are used (26). If the voltage is maintained above these values, the deposition of gold approaches 100%. Thiourea does not directly contribute to the cathodic reaction of gold, but its oxidation product, formamidine disulphide can be reduced on the cathodic surface. It is necessary to separate the anode and cathode compartments of the electrolytic cell to avoid incorporation of sulphur in the gold plate and to prevent the dissolution of gold by the oxidants formed at the cathode (26). Pilot plant testing on gold recovery by electrolysis of thiourea solutions from commercially recycled waste products has been reported (17).

1.16 Hydrogen Pressure Reduction

Pressure reduction has been previously reported for the recovery of platinum, rhodium, palladium and silver (45) (46). While it is not possible to recover precious metals from cyanide solutions because of the stability of the complexes, its use for recovery from thiourea solutions has been more successful. The reduction of the gold(I)thiourea complex in an acidic solution is given as:

$$Au(CS(NH_2)_2)_2^+ + \tfrac{1}{2}H_2 \longleftrightarrow Au + 2CS(NH_2)_2 + H^+$$

The reaction is catalysed by platinum and nickel and 98% reduction of gold in one hour using platinum has been reported. The effect of excess thiourea in solution adversely affects gold recovery at concentrations of 45g/l and higher.

References

1 Physical Geology, Second Edition. R. Foster Flint and B.J. Skinner. John Wiley and Sons (1977).

2 The New Encylopædia Britannica. Volume 21. 15th Edition, (1992).

3 The World Book Encyclopedia. Volume 8, World Book - Childcraft International Inc., (1978).

4 Gold In Ireland: The Potential for Mineralisation. P. McArdle, J.H. Morris, P.R. Gardiner. Geological Survey of Ireland. Series RS/87 (1987).

5 Gold in Ireland. Internet Website: http://www.cosmedia.ie/mineral/

6 Gold Mining in Mayo. G. Donnellan BSc (Final year project). DIT Rathmines, (1993).

7 Mining and the Environment in Ireland. Irish Association for Economic Geology. Fact Sheet 5, (1992).

8 "Mining Company to Sue State over Croagh Patrick". D. Coghlan. Irish Times. (May 23, 1990).

9 Gold Metallurgy in South Africa. R.J. Adamson, (Ed). Chamber of Mines of South Africa, (1972).

10 Dissolution Chemistry of Gold and Silver in Different Lixiviants. J. Brent Hiskey and V.P. Atluri. Mineral Processing and Extractive Metallurgy Review. Vol. 4, pp 95-134, (1988).

11 Hydrometallurgical Extraction and Reclamation. E. Jackson. Ellis Horwood Series in Industrial Metals, (1986).

12 Environmental Considerations for Alternatives to Cyanide Processing. Emerging Process Technologies for a Cleaner Environment. J.B. Hiskey and F.W. DeVries. SME- AIME, Chp 11, pp 73-80, (1992).

13 Environmental Aspects of Cyanide. D. R. Baker. American Mining Congress Mining Convention. Denver, Colorado, September 27-30, (1981).

14 Effect of Cyanide Residue on Vegetation Bordering a Black Hills Stream. M. Howe and D. Noble. Society of Mining Engineers of AIME. Salt Lake City, Utah, October 19-21, (1983).

15 Investigation on the Potential Techniques to Recover Gold from Thiourea Solution. G. Deschênes. Proc. of Intl. Symp. on Gold Metallurgy. R.S. Salter (Ed.), CIM, Montreal, pp 359-377, (1987).

16 Underground Leaching of a Gold Sulphide Ore by Thiourea. L. Tremblay, G Deschenes, E. Ghali, J. McMullen and M. Lanouette. Personal Communication (1996).

17 Literature Survey on the Recovery of Gold from Thiourea Solutions and the Comparison with Cyanidation. G. Deschênes. C.I.M. Bulletin, Vol. 79, pp 895, (November 1986).

18 Modern Trends In Gold Processing- Overview. M.S. Prasad, R. Mensah-Biney and R.S. Pizarro. Minerals Engineering, Vol. 4, No. 12, pp 1257-1277, (1991).

19 Evaluation of Cyanide and Non Cyanide Lixiviants for Gold Extraction from Complex and Refractory Gold Ores. L.M. Abrantes and Y.Z. Zhang. Personal Communication (1996).

20 Recovering Gold with Thiourea. R.J. Hisshion and C.G. Waller. Mining Magazine, pp 237-243, (September 1984).

21 A Preliminary Techno-Economic Evaluation of the Extraction of Gold from a Chalcopyrite Concentrate using Thiourea. G. Deschenês, D. Bernard, P.J.H. Prud'Homme and D. Laforest. Minerals Engineering, Vol. 7, No. 4, pp 435-448, (1994).

22 The Solubility of Gold and Silver in Thiourea. I. Plaskin and M. Kozukhowa. Doklady, Akademii Nauk. SSSR, Vol. 31, No. 7, pp 671-674, (1941).

23 The Merck Index. An Encyclopedia of Chemicals, Drugs and Biologicals. Eleventh Edition. Susan Budavari, (Ed.).

24 New Aspects in Thiourea Leaching of Precious Metals. R.G. Schulze. Journal of Metals, Vol. 6, pp 62-65, (1984).

25 The Dissolution of Gold in Acidic solutions of Thiourea. T. Groenewald. Hydrometallurgy, Vol. 1, pp 271-274, (1976).

26 Potential Applications of Thiourea in the Processing of Gold. T. Groenewald. Journal of the South African Institute of Mining and Metallurgy, pp 217-232, (June 1977).

27 A Kinetic Study of the Leaching of Gold from Pyrite Concentrate using Thiourea. G. Gabra. Precious Metals. Mining Extraction and Processing: Metall. Soc. AIME, pp 145-172, (1984).

28 A Comparison of Cyanide, Thiourea and Chlorine as Lixiviants for Gold. A.O. Filmer, P.R. Lawrence and W. Hoffman. The Aus. I.M.M. Perth and Kalgoorlie Branches, Regional Conference on Gold Mining, Metallurgy and Geology, (October 1984).

29 Leaching of Precious Metals from Complex Sulphide Ores: On the Chemistry of Gold Lixiviation by Thiourea. Z.H. Fhang and M. Muhammed. Mineral Processing and Extractive Metallurgy Review. Vol. 11, pp 39-60, (1992).

30 Evaluation of Thiourea Consumption for Gold Extraction from Complex and Refractory Gold Ores. Y.Z. Zhang. Personal Communication (1996).

31 The Prospects for Alternative Leach Reagents. Can Precious Metals Producers Get Along Without Cyanide? H. von Michaelis. Engineering & Mining Journal, pp 42-47, (June 1987).

32 The Solubility of Gold in Thiosulphates and Thiocyanates. H.A White. J. Chem. Metall. Min. Soc. S. Africa, Vol. 6, pp 109, (1905).

33 Increasing the Amenability of Gold Ores for Thiourea Leaching. R.G. Schulze. TMS-AIME Annual Meeting, New Orleans, March 1986.

34 Leaching and Recovery of Gold from Black Sand Concentrate and Electrochemical Regeneration of Bromine. A. Dadgar, B.M. Sanders, J.A. McKeown, R.H. Sergent and R.H. Jacobson. Advances In Gold And Silver Processing, Proc. Sympgold Tech 4, Society of Mining, Metallurgy & Exploration Inc., (Sept 10-12, 1990).

35 Research and Development Activities for the Recovery of Gold from Non-Cyanide Solutions. R. Y. Wan and M. LeVier. Hydrometallurgy: Fundamentals, Technology and Innovations. Editors: J.B. Hiskey and G.B. Warren, Chapter 27. SME (1993).

36 Gold Complexes and Activated Carbon: A Literature Review. G. J. McDougall and R. Hancock. Gold Bulletin 14, Vol. 14, Part 4, pp 138-153, (1981).

37 W.D. Johnson. U.S. Patent 522, 260, (1894).

38 Process for Recovering Gold and Silver from Activated Carbon by Leaching and Electrolysis. J.B. Zadra, A.L. Engel and H.J. Heinen. Report of Investigation 4843, United States Bureau of Mines, (1952).

39 Recovery of Gold and Silver from Cyanide solutions: A Comparative Study of Various Processes. M.C. Jha. 1st I.S.P.M.R., Reno, Nevada, (June 1984).

40 Carbon in Pulp Processes in South Africa. P. A. Laxen. Hydrometallurgy, Vol. 13, pp 169-192, (1984).

41 New Aspects in Thiourea Leaching of Precious Metals. R.G. Schulze. Journal of Metals, Vol. 6, pp 62-65, (1984).

42 Gold and Silver Recovery from Thiourea Leach Solutions. W.W. Simpson, L. Peterson, R.G. Sandberg (US Bureau of Mines). Pacific Northwest Metals and Minerals Conference, Portland, Oregon, (April 29-May 2, 1984).

43 Development du Nouveau Procédé de Traitment pour le Minerai de Salsigne. A. Van Lierde, P. Ollivier and M.V. Lesoille. Ind. Min., Les Tech. Vol. 1a, pp 399-419, (1982).

44 Polymer Codeposited with Gold During Electroplating. G.B. Muiner. Plating, Vol. 56, pp 1151-1157, (1969).

45 The Use of Hydrogen to Recover Precious Metals. M. Findlay. Precious Metals, M.I. El Guinday, Pergamon Press, Toronto, pp 477-501, (1982).

46 Homogeneous Catalytic Activation of Molecular Hydrogen in Aqueous Solutions by Silver Salts. III. Precipitation of Metallic Silver from Solutions of Various Silver Salts. A.H. Webster and J.V. Halpern. Journal of Physical Chemistry, Vol. 61, pp 1245-1248 (1957).

Chapter 2

Phase Transfer Systems for Precious Metal Recovery

2.1 Phase Transfer Systems

The phase transfer of metallic species from an aqueous to an organic phase is widely used by the hydrometallurgical industry for the extraction, separation and recovery of metals. Two main processes are employed: ion exchange and solvent extraction. Both methods involve similar chemical principles, but differ in technological practises.

The recovery of metallic species using solvent impregnated resins (S.I.R.s) is also a phase transfer process. Solvent impregnated resins were developed as a technological alternative to ion exchange and solvent extraction processes and ideally incorporate the advantages of both techniques. As such, they are inextricably linked to both ion exchange and solvent extraction techniques. A discussion of the relevance of solvent impregnated resins for the hydrometallurgical industry and in particular for the recovery of gold from thiourea solutions is, therefore, not complete without first examining the relevance of ion exchange and solvent extraction to these processes.

2.2 Ion Exchange Systems

Ion exchange is based on the reversible exchange of ions in solution for similarly charged ions on an exchange medium. The exchange phase is usually a polymeric resin containing an ionic functional group which is responsible for the exchange (1). The two main characteristics of an exchange resin are:

(a) its selectivity, i.e. the affinity of the resin for a particular type of ion and
(b) its capacity, i.e. the extent to which ions are exchanged per unit quantity of resin.

The selectivity of the resin is controlled by the functional group of the resin and manipulation of that group, known as chemical functionalisation, affects the selectivity of the resin for the recovery of a particular ion. The exchange proceeds on an equivalent basis, i.e. for each exchangeable ion on the resin (known as the counter ion), there is an equivalent fixed ion of opposite charge, attached to the functional group skeleton. Ion exchange of metal complexes takes place between a solution, usually aqueous, containing metallic ions and a second phase known as the ion exchanger, usually a polymeric resin.

The most widely used type of exchange resins are cationic and anionic resins which are capable of exchanging positively and negatively charged ions respectively. Cationic or acidic exchange resins contain a carboxylic, phenolic or sulphonic group as an integral part of the resin, along with an equivalent number of cations, usually a H^+ ion. The resins are termed weak or strong acid resins depending on the strength of the acid group attached. Anionic or base resins contain weak or strong base groups such as an amine or quaternary ammonium group and an equivalent number of anions such as chloride, hydroxyl, or sulphate ions. Other types of ion exchange resins include chelate or electron exchangers, in which the oxidation number of the exchanged ions is affected and also non-ionic resins, which interact co-ordinatively with ions and molecules rather than adsorptively and so are akin to ion exchangers.

The fundamental requirements of a useful resin are:

1. the resin must be sufficiently cross-linked to have only a negligible solubility,
2. the resin must be sufficiently hydrophilic to permit diffusion of ions through the structure at a finite and useable rate,
3. the resin must contain a sufficient number of accessible ionic exchange groups and it must be chemically stable and
4. the swollen resin must be denser than water (2).

The practical application of ion exchange resins to the mining industry is concentrated mainly on the recovery of uranium (3). Its potential application to gold mining has been established by studies by Green et al (4), and Matsuda et al (4). In particular, the development of a resin in pulp system (RIP) for the recovery of gold, analogous to carbon-in-pulp (CIP) systems already used in the industry, would be relevant since no major refitting of equipment would be required.

Flemming (6) lists a number of the advantages of resins over activated carbon for the recovery of gold. These include:

1. The rate and equilibrium loading of resins is greater than activated carbon. This allows for a decrease in the volume of resin required and for a reduction in the size of elution plants in comparison to carbon recovery processes. At the same time, the concentration of resin in the leach solution can be significantly higher than concentrations of carbon generally used. An increase from an approximate volume of 6% for carbon recovery to 30% for resin systems can be achieved without any loss in interstage screening or any increase in resin breakage. This means the recovery tanks can be decreased in size by up to five times without any loss in recovery efficiency.

2. Resins are not poisoned by organic species such as humates, flotation reagents and other organic solvents present in the leach, which can severely inhibit the recovery of gold onto activated carbon. Also, shales, or clay type minerals which affect the efficiency of loading onto carbon have no effect on exchange resins.

3. Gold is eluted from the resins at atmospheric pressure and at a temperature of approximately 60°C while carbon elution requires higher temperatures (120°C to 130°C) and elevated pressures.

4. Resins can be used to co-extract other metal complexes efficiently and could be used to clean up tailings ponds, creating more environmentally acceptable effluent and forming cleaner excess leach solutions for recycling.

5. Resin losses from an RIP system are much less than carbon losses in CIP. This is because resins do not require a thermal regeneration step, which causes losses of carbon of up to 50%. Loss of resins in recovery systems are mainly due to fracturing of the beads, due to either osmotic shock or mechanical impact. Losses of this type can be kept to a minimum by choosing a resin which is resilient enough to withstand the type of process it is being used in. Also, appropriately designed equipment must be used.

6. Resin pumping and handling is easier since the smooth, spherical nature of the resins allows them to flow more readily through the pulp. The resins are also less dense than the pulp, aiding recovery of the resins from the pulp.

There are also some disadvantages associated with the use of resins in place of activated carbon. The resin beads are smaller than carbon granules and so the pre and interstage screening of the resins need finer filtration screens. Since the screens already create a bottleneck in CIP operations, this could create a limiting constraint on RIP processes. Also, the development of ion exchange resins has not progressed far past basic cationic and anionic resins and their selectivity for gold over base metals present in the leach liquor is not as good as has been achieved using activated carbon. Resins are also up to five times more expensive than activated carbon, though this should be negated by the significant decrease in losses of resin in comparison to carbon (6).

2.3 Ion Exchange Resins for the Recovery of Gold

The aurocyanide ion formed in cyanide extraction is a negatively charged ion and requires an anionic exchange resin for recovery. It has been found that weak anionic resins give greater loading than stronger ones (3). Also, resins with lower functional group conversions are reported to be more efficient. This can be explained in terms of steric hindrance, caused when larger functional groups inhibit the movement of the aurocyanide ion through the pores of the ion exchange resin.

Much of the work on ion exchange for the recovery of gold from aurocyanide solutions has been carried out by the Council for Mineral Technology (Mintek) in South Africa. Their work was prompted by the increasing quantities of gold solution being produced in South Africa which contained poisons and so were not suitable for conventional carbon recovery and they have produced tough resilient ion exchange resins with both strong and weak base functional groups. The gold selectivity characteristics of these resins are reported to be so good, that their capacities for gold are higher than activated carbon, even when interfering base metal cyanide complexes are present in solution (6).

The recovery of gold by a strong base resin developed by Mintek is discussed by Green et al (7). They report high loading of gold (20,000ppm), selectivity against copper, iron and cobalt and efficient elution of gold using thiourea. A decrease in the levels of base metal loading (Co, Ni, Zn) with successive cycles was also reported. A 15% decrease in the gold loading capacity of the resin was noted when the resin was contacted with eluant for a long period of time (15 days, at 60°C), however since this level of exposure is equivalent to one years elution time it should not significantly affect resin costs.

Mintek have also developed a weak base resin which shows good selectivity to gold. This is a major development because it allows for the recovery of gold cyanide at the high pH values (pH 10-11) which are typical of cyanide leach liquors, unlike strong base resins which can only operate below pH 8 and therefore need a preacidification step before recovery is possible. Weak base resins also have an easier elution step and gold can be stripped using a simple sodium hydroxide solution (6).

For the extraction of the thiourea gold complex, cationic exchange resins must be used, since gold is present as part of the cationic gold thiourea complex. The resins used are usually strong acid resins containing sulphonic acid groups. Studies on the recovery of gold from thiourea leach solutions using cationic resins include Simpson and co-workers working with the US Bureau of Mines (USBM) (8) and Deschênes (9).

Simpson and co-workers reported loading of up to 31 oz of gold per ton of resin (0.878kg Au per metric tonne) from a leach solution containing 11.4ppm of gold. The tests were carried out on a strong acid cationic resin, Ag-50W-X8, contact time was 50 minutes and the resin was used in a batch system. The loading capacity of the resin was found to decrease with increasing thiourea concentration. When thiourea concentration increased from 20 to 60 g/l, gold recovery decreased from 96% to 90%. Column adsorption tests on the same resin, for a one hundred bed volume system, gave loadings of 113oz per ton (3.15 kg Au per metric tonne), representing 93% gold recovery. Stripping of the resin with 6 bed volumes of a 0.2M NaCN/0.2M NaOH solution at pH 12 recovered 95% of gold from the resin. The loading capacity of the resin could be periodically regenerated by washing with 6N NH_4OH, followed by 1% Na_4(EDTA) in HCl at 70°C for 1 hour. This stripped the resin of any strongly attached metal ions which might build up over time (8).

Deschênes (9) studied eight different resins. Batch tests were run by contacting 15ml of resin with 150ml of solution for 60 minutes and agitating the solution at

500ppm. Six strong acid cationic resins, one weak acid cationic resin and one chelate polystyrene-divinylbenzene resin were tested. The characteristics of the resins are given below.

Resin	Manufacturer	Type	Active Group	Standard Mesh Distribution
HCR-S	Dow Chemicals	SAC	Sulphonic	20-50
50WX8	Dow Chemicals	SAC	Sulphonic	20-50
MSC-1	Dow Chemicals	SAC	Sulphonic	20-50
TG 650C	Dow Chemicals	SAC	Sulphonic	22-32
AG50W-X8	Bio-Rad	SAC	Sulphonic	100-200
AG50W-X16	Bio-Rad	SAC	Sulphonic	200-400
Lewatit OC1014	Bayer	Chelate*	polystyrene-DVB	12-48
Duolite GT73	Rohm & Haas	WAC	polystyrene	14-48

SAC: Strong Acid Cationic; WAC: Weak acid Cationic; *thiourea in resin

Table 2.1 Resins studied for the recovery of gold from thiourea solution (9).

The recovery efficiency of all eight resins was above 93%. The highest gold recovery was with the Bio-Rad AG50W-X16 resin which recovered 98.6% of gold. This resin also had the lowest gold loading, and it was suggested that this was due to the smaller bead size of that resin. The best gold loading was with the AG50W-X8 resin, in agreement with Simpson (8). Interferents in solution included excess thiourea, iron and copper, all of which were retained by the resins. The chelate Bayer Lewatit OC1O14 resin had the lowest thiourea loading (5.66kg/t) with above average gold loading (0.953kg/t). The weak acid resin Duolite GT 73 had the highest level of thiourea adsorption (44.7kg/t). Strong acid cationic resins had thiourea loadings of between 20 and 31kg/t, the AG50W-X8 resin had the highest thiourea loading for these type resins at 30.73kg/t. Copper loading ranged from between 0.62 to 0.93 kg/t for the strong acid cationic resins, again the AG50W-X8 had the highest loading. The chelate resin loaded 1.07kg/t of copper and the weak acid resin loaded 0.99kg/t of copper.

Deschênes discusses the selectivity of the resins in terms of the size of the ions in solution. Hanic and Durcanska report that the copper thiourea ion is a binuclear complex, i.e. $Cu_2[SC(NH_2)_2]_6^{2+}$ and is likely to be larger than the gold(I)thiourea complex (11). Deschênes suggests that the larger copper thiourea complex will not be retained as strongly as the gold thiourea complex. Copper loading on the Dowex HCR-S strong acid resin was three times less than gold. Iron in solution was also recovered but, in spite of having an iron concentration of about 250 times higher than gold, loading was only approximately twice as high. Deschênes reported that loading of iron and other base metals on the resin changed after equilibrium. He suggests that this was due to elution by thiourea. He also reports that the decrease in the base metal loadings on the resin allowed the loading of gold to increase.

The highest elution of gold from the resins was achieved with a 5% solution of sodium thiosulphate at pH 9 on the HCR-S resin; 97% of gold was recovered.

Mensah-Biney and co-workers (10) studied the recovery of gold from a gold thiourea solution. They reported theoretical loadings ranging from 189 to 256 kg Au/t for cationic exchange resins, based on Langmuir and Freundlich Isotherms. The best resin tested was the Ionac C249 resin, which is an isothiouronium chelate matrix, containing a sulphonate ionic exchange group. These loadings are higher than any previously reported, however this study was not undertaken on an actual ore leachate and no discussion on the effect of interfering ions in solution was included.

The main problem encountered with ion exchange resins for the recovery of gold from gold(I)thiourea solution, is the formation of elemental sulphur due to the decomposition of thiourea. Fine particles of sulphur formed in solution are retained on the resins surface and diffuse through the resin pores. This leads to passivation of the resin and inhibited gold recovery. The effect of sulphur formation is one of the main drawbacks to the application of ion exchange resins for the recovery of gold from thiourea solutions (12).

2.4 Solvent Extraction

Solvent extraction is a technique in which a solution is brought into contact with a second immiscible solvent, so that a substance or substances in the first phase can be extracted into the second phase. Extraction occurs by mixing the two phase solution for a given period of time, often just a few minutes. The two phases can then be separated in a separation funnel. Solvent extraction offers a simple, clean, rapid and convenient method of separation and it can be similarly applied to the recovery of high and trace concentrations of a particular solute.

The separation of solute particles from aqueous solutions into an organic phase is based on the formation of species which are more stable in an organic environment than in an aqueous one. The miscibility of the two phases should be minimal since they have different polarities. For systems involving two organic solvents, miscibility is kept to a minimum by saturating each solvent with the other. Procedures involving the extraction of organic species are not generally as selective as metal extraction systems and the determination of metals as minor and trace constituents in inorganic and organic materials remains the most popular application of solvent extraction (13).

For the solvent extraction of metallic cations from an ionic environment into a nonpolar solvent, it is necessary to neutralise the cationic charge on the metal ion. This is achieved by the formation of neutral chelate complexes or by ion association. In chelation complexes, the metal ion co-ordinates with a polyfunctional organic base to form a stable ring compound. The factors which affect the formation of the metal chelate complex are summarised as:

1. The basic strength of the chelating group. The stability of the chelate complexes formed by a given metal ion usually increase with the basic strength of the chelating agent.

2. The nature of the donor atoms in the chelating agent. Ligands which contain donor atoms of the soft-base type, form their most stable complexes with small groups of soft acid type metal ions e.g. Pd^{2+}, Ag^{+}, Hg^{2+}, Cu^{+}, Bi^{3+} and Pb^{2+}. Soft bases are donors having low electronegativity and high polarisability, they are also easily oxidised. These metals are selectively extracted by solvents such as diphenylthiocarbazone (dithiozone).

3. In the case of ringed chelate groups, five and six membered conjugated chelate rings are most stable since these have minimum strain. The functional groups of the ligand on a ringed chelate ion must also be situated to permit the formation of a stable ring.

4. Resonance and steric effects. The stability of chelate structures is enhanced by contributions of resonance structures of the chelate ring.

Ion association complexes are complexes in which the species is neutralised by association with oppositely charged ions. Such complexes form clusters with increasing concentration, resulting in an agglomeration of large, neutral species which are suitable for migration into a non-polar environment (13). These complexes can be categorised into three main groups. These are:

1. Those which form large organic ions, e.g. tetraphenylarsonium and tetrabutylammonium ions, which form large ion aggregates or clusters with suitably charged ions. These ions do not have a primary hydration shell and cause disruption of the hydrogen bonded aqueous phase. This causes the organic species to be pushed into the aqueous phase. These large association systems lack specificity since any large unhydrated, univalent cation will be extracted into the organic phase, although polyvalent cations will not be easily extracted since they have a greater hydration energy.

2. Those involving a cationic or anionic chelate complex of a metal ion. Chelate ions containing two uncharged donor atoms, such as 1:10 phenanthroline, form cationic chelate complexes which are large and hydrocarbon like. Ternary complexes are similarly formed.

3. Those in which the solvent molecules are directly involved with the formation of the ion association complex. In this case the co-ordinating ability of the solvent is of vital importance. Most of the solvents which participate in this way contain donor oxygen atoms e.g. ethers, esters, ketones and alcohols. Molecules containing the semi-polar phosphoryl functional group, which has a basic oxygen atom with good steric availability, exhibit very marked solvating properties e.g. tri-butyl phosphate. This type of ion association differs significantly from types 1 and 2 since these involve co-ordinately unsolvated large ions (13).

2.4.1 Practical Considerations when Choosing a Solvent

The choice of solvent for extraction should be governed by the following criteria:

1. A high distribution ratio for the solute and a low distribution ratio for any impurities in the solution.
2. Low solubility in the second phase.
3. Sufficiently low viscosity and difference in density to prevent the formation of emulsions.

4. Low toxicity and flammability.
5. Ease of recovery of solute from the solvent for subsequent treatment.

Consideration of the boiling point and ease of chemical stripping are relevant here. Often a mixture of two solvents improve the overall suitability of an extraction systems.

2.4.2 Solvent Extraction with Monoacidic Dialkyl Phosphates

Monoacidic dialkyl phosphates $(RO)_2P(O)OH$ have proven valuable for the solvent extraction and separation of metallic species. Studies of the extraction behaviour and of ir data show that they exist in organic solvents as hydrogen bonded dimers H_2X_2, which at low loading, extract metal cations M^{n+} to form $M(X_2H)_n$ complexes. Systems at higher solvent concentration exhibit more complex behaviour involving polynuclear complex formation and anion extraction.

The general extraction equation of dialkyl phosphates is given as:

$$M^{n+}{}_{aq} + n(H_2X_2)_{org} \longleftrightarrow MX_{2n}H_{n\ org} + nH^{+}{}_{aq}$$

The acid is given the dimeric form since this is the most stable form of dialkyl phosphates in non-polar solvents (at low loading) (14).

Dialkyl phosphates used in extraction systems include di (2-ethylhexyl) phosphoric acid (D2EHPA), di (n-butyl) phosphoric acid (DBP) and di (para 1,1,3,3, tetramethyl butyl phenyl) phosphoric acid (15). Studies on the extractive properties of these solvents and others have been carried out by Drysen (16), Peppard (15), (17) and Hardy (18).

Of these D2EHPA is one of the most widely used dialkyl phosphate solvents. Its use for the recovery of uranium from leach solutions is well documented (19) (20). It is used commercially for cobalt nickel separation (20), for the removal of metal cation impurities from cobalt sulphate leach liquors (21), for zinc extraction from sulphate and perchlorate solutions (22) and to recover trace scandium from stibnite ores (23). It is also used with tri-butyl phosphate for uranium extraction in a procedure known as the Dapex process. Distribution ratios are enhanced several times using the synergistic D2EHPA-TBP mixture in comparison with systems using only D2EHPA or TBP (19).

Many other process have been proposed including zinc, cadmium and mercury recovery (24), molybdenum/tungsten recovery (25), zinc/copper separation (26), (27) and manganese/cobalt separation (28). It has also been proposed for the removal of iron from acid solutions (29) and for the recovery of lanthanides (30).

2.4.3 Solvent Extraction of Gold

Solvent extraction processes for the recovery of gold from cyanide leach solutions have not generally been used on a commercial scale, however its potential for the industry has been recognised (31). Solvents systems studied mainly involve tertiary and quaternary amines. These solvents undergo protonation reactions and therefore their activity is dependent on pH. The extraction of $Au(CN)^{-}_{2}$ may be represented as:

$$(R_3N.HCl)_{org} + (Au(CN)^{-}_{2})_{aq} \longleftrightarrow (R_3N.HAu(CN)_2)_{org} + Cl^{-}_{aq}$$

and

$$(R_4N.Cl)_{org} + (Au(CN)^{-}_{2})_{aq} \longleftrightarrow (R_4N.Au(CN)_2)_{org} + Cl^{-}_{aq} \text{ (31)}$$

An order of affinities for the tertiary amine tri-n-alkyl-amine has been determined by Plaskin (32) as:

$$Au(CN)^{-}_{2} > Ag(CN)^{-}_{2} > Cu(CN)^{-}_{2} > Zn(CN)^{-}_{4} > Fe(CN)^{4-}_{6} > CN^{-}$$

The order of affinity indicates that there is a strong specific reaction between the amine and the aurocyanide ion. This is confirmed by the high extraction efficiencies seen from highly alkaline recovery solutions in which a very large proportion of the amine is in the free base and therefore unreactive form (31). Gold can be stripped from the alkaline solution with a 10% solution of thiocarbamide in 10% H_2SO_4 (20).

30% diisobutyl ketone (DIBK) in kerosene was reported as a modifier for the extraction of gold from alkaline cyanide solutions using the quaternary ammonium salt, Aliquat 336. The optimum solvent mixture minimised third phase formation and increased the gold extraction when compared to the use of an alcohol modifier. Gold was eluted by washing with a mixture of sulphuric acid and thiourea (33).

Gold is extracted from acidic cyanide solutions as $HAu(CN)_2$, after acidification with HCl, HNO_3 or H_2SO_4. Extraction increases in the order:

ethers > esters > alcohols > ketones > aldehydes (20)

An increase in equilibrium pH leads to an increase in the extraction coefficient, it is also affected by the acid used and increases in the order:

$HCl > HNO_3 > H_2SO_4$

Studies on the extraction of gold from $NaAu(CN)_2$ using alcohols and ketones at various levels of acidity showed that cyclohexanone was the best of the ketones and isononyl alcohol was the best of the alcohols. Gold was stripped from the solutions using dilute sulphuric acid up to 5% (20).

Other systems proposed for the recovery of gold include dibutyl carbitol for the recovery of gold from aqua regia solutions, gold was stripped from the solvent by oxalic reduction (20). Ethyl ether and isopropyl ether have also been reported for the extraction of gold from a gold chloride solution, gold was stripped by the addition of kerosene, toluene or other similar diluents followed by precipitation with sodium sulphite. When present, iron and tellurium were co-extracted with gold (34).

2.4.4 Solvent Extraction of Gold from Gold(I)Thiourea Solutions

The solvent extraction of gold from gold(I)thiourea solutions has been tested with several reagents, of these D2EHPA and TBP have proved the most effective. Tributyl phosphate has been used in hydrochloric acid solutions and has been industrially applied to the recovery of gold from a solution containing gold, silver, copper, iron, zinc and nickel (35). Extraction increased from 67% to 99% when the pH was increased from 1 to 8 and with increased contact time. The rate of recovery was comparable to activated carbon but the loading was much lower.

Di-2-ethylhexyl phosphoric acid has also been studied for the recovery of gold(I)thiourea from solution. Balakireva selectively extracted gold from impure gold(I)thiourea solutions and stripped the solution with HCl (36).

The extraction of gold by D2EHPA is a cationic exchange process, involving the exchange of the cationic metal complex with the hydrogen ions of the reagent dissolved in the organic phase. Sung-Gyu et al (37) reports that the gold(I)thiourea complex is solvated with five molecules of the D2EHPA monomer and that the extracted species are not associated with each other. The extraction is given as:

$$[Au(CS(NH_2)_2)_2{}^+]_{aq} + 3[R_2H_2]_{org} \longrightarrow [Au(CS(NH_2)_2)_2R.5RH]_{org} + [H^+]_{aq}$$

The equilibrium constant was given as 0.398.

The US Bureau of Mines studied a mixture of D2EHPA and TBP for gold recovery (8). Extraction increased from 50% with a D2EHPA:TBP ratio of 10:1 to 68% for a 12:1 ratio. A 1:1 organic to aqueous solution was used for stripping and 99% of the gold was stripped from the organic phase using 1.5M HCL in 30 min. When the HCl concentration was decreased to 0.37M and the contact time increased to 60 minutes, 95% of gold was recovered. Deschênes (9) studied the extraction of gold from solvent mixtures containing 10% TBP and D2EHPA concentrations ranging from 25% to 60%. Recovery improved with increasing D2EHPA concentrations, increasing from 47.6% to 77.1%. A 15% D2EHPA, 50% TBP solution gave a recovery of 77.4%, however high concentrations of TBP lead to phase precipitation in the organic layer. Kinetic tests for a 40% D2EHPA / 10% TBP mixture indicated that equilibrium was reached in less than 10 seconds. By maintaining the contact time to less than 5 minutes, iron impurities in the organic extractant were kept to less than 200mg/l. An increase in temperature decreased the efficiency of gold recovery and increased iron extraction. 85% of gold was stripped from the solvent with a 10% to 20% HCl solution at a 1:1 aqueous to organic ratio. 98% gold recovery was achieved with an increase in the organic phase ratio to 10:1 using a 10% HCl solution.

Selective stripping of gold, useful when iron is present in the organic phase, is achieved by using low acidity stripping solutions (9).

Solvent extraction gives better mass transfer rates, it is faster and it requires smaller equipment than ion exchange. However, problems such as phase disengagement and reagent losses often renders solvent extraction impractical. Solid extraction techniques, i.e. ion exchange, have lower mass transfer rates and take longer. Their advantages lie in the simplicity of the equipment required and the ease of operation, also, problems with phase disengagement and reagent losses do not occur (41). However, development in the chemical functionalisation of ion exchange resins, required to increase the selectivity of ion exchange resins, has been slow. There are still only two main types of ion exchange resins, acid cationic and basic anionic and their selectivity for the recovery of a particular anion/cation is often hindered by the presence of interfering anions/cations.

2.5 Solvent Impregnated Resins

The physical impregnation of a solvent onto a high surface area polymeric support was first proposed by Abraham Warshawsky in South Africa in the early 1970's (43). The impregnated resins were developed as a technological alternative to ion exchange and solvent extraction processes, for the extraction, separation and recovery of metallic species from solution. Warshawsky named the resins *solvent impregnated resins*, chosen to emphasise the method of extraction (solvent), the method of incorporation (impregnation) and the solid support (resin).

The resins can be described as liquid complexing agents, similar to a solvent in liquid solvent exchange, dispersed homogeneously through solution in a solid polymeric medium (39). The role of the polymeric support in an SIR system is to act as a reservoir, which can be filled to a certain capacity with an extractant. Just as the extractant in a solvent extraction process can be described as a reagent diluted by a diluent, impregnated resins can be regarded as reagents diluted by a resin (40).

The development of solvent impregnated resins arose from the need for ion specific resins, the difficulties in chemical functionalisation of ion exchange resins and from the availability of suitable, high surface area, polymeric supports. Also, the advantages of solvent extraction reagents in terms of selectivity and kinetics were recognised. As such, the resins are a compromise between ion exchange resins and solvent extraction reagents, combining the properties of both techniques with the advantage of compatibility with the equipment and operating facilities of ion exchange. There are two basic types of S.I.R.s depending on the method of solvent impregnation. The methods of impregnation are:

1. Physical impregnation onto a selected polymeric carrier. This type of resin was pioneered by Warshawsky and co-workers and its main advantage is the simplicity of the impregnation step.

2. Copolymerisation of the monomer and crosslinking agent in the presence of the extractants to produce Levextrel® resins. These resins were developed by Kroebel and Meyer and pioneered by Bayer AG. They were named after the resins origin (Leverkusen) and functions (extraction and elution). These resins require a more specific type of impregnation, employing in-situ incorporation of the extractant during the co-polymerisation process. As such, they can only be produced by ion exchange manufacturers, thus limiting their versatility (41).

The resins chosen for this study are physically impregnated with a solvent, in a method similar to Warshawsky's proposed model, since this is by far the simpler of the two methods and does not require any specialised equipment etc..

2.5.1 Physical Properties of Solvent Impregnated Resins

Solvent impregnated resins can be described as bridging the gap between liquid and solid extraction techniques and ideally incorporate the advantages of both techniques. These include:

(a) High mobility of the reagent in the resin phase.
(b) High mass transfer rates.
(c) High selectivity factors.
(d) Low reagent losses.
(e) Good phase separation properties.
(f) High chemical and physical stability (38).

The following set of requirements must also be met by the extractant, the polymeric support and the impregnation method in order for the system to be called a solvent impregnated resin.

1. The extractant must be a liquid or retained in the liquid state by the addition of a diluent.
2. Both the extractant and diluent should have minimal solubility in water or in the aqueous solutions employed.
3. The polymeric support should be fully expanded during the impregnation process and remain so. Macroporous supports which show minimum volume variations during impregnation are preferred.
4. The impregnation method should not destroy the properties of the extractant or the polymer. (39)

2.5.2 Choice of Resin

The development of high surface area, macroreticular resins has been a significant factor in the recent success of S.I.R.s. These resins contain very small microspheres which are fused into a large macrospherical or macroreticular particle. The remaining network space between the agglomerated microspheres in the particle is porous and readily allows for diffusion among the microspheres. Unlike conventional gel type or microreticular resins, the pores are rigid and remain open whether the beads are swollen or not. Solvent uptake is determined by the availability of space in the resin's lattices (i.e. the resin's surface area) and not by their swelling ability, as is the case in microreticular resins (41). The macroporous properties of these resins give them an unusually high surface area making them suitable for impregnation procedures. The macroreticular structure also imparts unusual strength to the beads making them useful under aggressive conditions such as moving bed systems. The resins are effective as ion exchangers and acid-base catalysts in non-polar media where conventional resins had been unsuccessful (41). Also, the partial sulphonation step, which was required for the impregnation of microporous resins is not required for macroporous resins (40). Fig. 2.1 shows the structure of a macroporous resin bead.

2.6 Amberlite Resins

The resins chosen for this study are Amberlite XAD resins which were developed by the Rohm and Haas chemical company. They are produced as insoluble, polymeric beads and are designed for use in columns and in batch operations. The resins are characterised by their high physical porosity, uniform pore size distribution and high surface areas due to their macroporous nature, as well as a chemically homogeneous non-ionic structure which differentiates them from most other adsorbents. Because of their macroporous properties, XAD resins have large internal surface areas and rigid pore structure (44).

Three XAD resins were chosen for impregnation, these were Amberlite XAD 2, XAD 4 and XAD 7. The properties of these resins are given below.

Resin	**Polarity**	**Chemical Nature**	**Porosity Vol %**	**Density (g/cm^3)**	**Area (m^2/g)**	**Average Pore Diameter (Å)**
XAD 2	Non-polar	Polystyrene	42	1.02	330	90
XAD 4	Non-polar	Polystyrene	51	1.02	750	50
XAD 7	Intermediate	Acrylic Ester	55	1.02	450	80

Table 2.2 Physical Properties of XAD 2, XAD 4 and XAD 7 (45).

XAD 2 is a synthetic cross linked polystyrene resin with particle sizes of between 0.30 to 0.78 mm. It has no ionic functional groups attached to it. Applications include the removal of impurities of sugars, meat products and water and the isolation of steroids, carotenoids, toxic drugs and other biologically important compounds from urine or blood (44). XAD 4 is also a polystyrene resin. Its particle size ranges from 0.30 to 1.2mm and it has no ionic groups attached to it. Its surface area is over double that of XAD 2, due to its smaller pore diameter. Its non-ionic nature makes it suitable for the recovery of hydrophobic solutes from polar solvents. It has a high physical durability and can undergo repeated exhaustion and regeneration cycles. Applications include the removal of phenols and chlorophenols (45). XAD 7 is more polar than XAD 2 or XAD 4. It is formed from acrylic ester and has an intermediate polarity, which gives the resin a more hydrophilic structure than either XAD 2 or XAD 4. It can be used to adsorb non-polar solutes from aqueous solutions and can also adsorb certain polar solutes from non-polar solvents. Applications include the recovery of enzymes, polypeptides and proteins of up to Mr = 60,000 (45).

2.6.1 The Application of Amberlite XAD Resins to Hydro-Metallurgical Processes

Amberlite XAD resins have been proposed for the recovery of metals in numerous systems. They are mainly used as supports for solvents in solvent impregnated resin systems, although they have been proposed for recovery as bare resins. The resins are used because their large surface areas give them the high capacity for solvent required for hydrometallurgical recovery applications.

Systems reported include:

Resin	Solvent	Recovery	Refs
XAD 2 / XAD 7	Triisobutyl Phosphine Sulphide (Cyanex 471)	Extraction of Au (III) from chloride media	(46)
XAD 2	Tri n Dodecylammonium Chloride (TLAHCL)	Extraction of Au(III) from chloride media	(47)
XAD 7	Bare Resin	Separation of gold from acidic leach liquors	(48)
XAD 2	Di 2 Ethylhexyl Phosphoric Acid (D2EHPA)	Separation and extraction of Zn^{2+} and Cu^{2+}	(49)
XAD 7	2 Ethylhexylhydrogen 2 Ethylhexylphosphonate (PC - 88A)	Recovery of trace scandium from acid aqueous solutions	(23)
XAD 2	(2 Ethylhexyl) Phosphonic Acid Mono -(2 ethylhexyl ester) (EHPNA)	Separation of Co^{2+} from Co^{2+}/Ni^{2+} solution	(27)
XAD 2	Di-(2,2,4-Trimethylpentyl) Phosphinic Acid (Cyanex 272)	Separation of Zn^{2+} from Cd^{2+} and Cu^{2+}	(50)
XAD 4	Tributylphosphate (TBP)	Extraction of uranium (VI) from 3M Nitric Acid	(41)
XAD 2 / XAD 4	Phenolic Oxime Type Extractants (Lix-64N)	Extraction of Cu^{2+} from sulphate solutions	(51)

Table 2.3 Proposed hydrometallurgical recovery systems using Amberlite XAD resins.

2.7 Methods of Impregnation

Because of the difficulties in the production of Levextrel resins most studies on impregnated resins have concentrated on Warshawsky's model. Very little information on the preparation and application of Levexterel resins is available.

Early methods of impregnation were developed by Warshawsky et al (39). They proposed three different methods of impregnation, these are summarised below.

2.7.1 The Dry Impregnation Method

In this method, the extractant is diluted in an appropriate solvent and the solution is contacted with the polymer. The diluent is removed by slow evaporation under vacuum.

2.7.2 The Wet Impregnation Method

(a) The extractant is dissolved in a pre-calculated amount of diluent and contacted with the polymer, until all the liquid is absorbed by the resin. The polymeric beads are then immersed in an aqueous metal salt solution. After the formation of the metal extractant complex, the impregnated resin is washed by water, the metal is eluted by acid washing and the resin rewashed with water.

(b) Similar to method (a), except that the extractant-metal complex is formed before contact with the polymer.

2.7.3 The Modifier Addition Method

A modifier such as dibutylpolypropylene glycol is added, to promote absorption of water into the polymer. The diluent is then evaporated as in method 1.

2.7.4 Variations to Impregnation Methods

Modifications of Warshawsky's methods have been proposed by others. Villaescusa et al used a variation on the wet method where the resin was filtered from the organic solvent solution after a given period of time. The concentration of solvent remaining in solution after contact was analysed and the mass of solvent impregnated onto the resin was taken as the difference between the initial and final mass of solvent in solution. The resin was washed and stored in deionized water (46).

Cortina et al used the same impregnation method but the final level of impregnation of the resin was determined by washing a given amount of the impregnated resin in ethanol, to completely elute the solvent. From an acid-base titration of the eluted solvent, the level of impregnation of the solvent was calculated (50).

Akita et al evaporated the diluting solvent from the resin after contact and determined the change in weight of the resin after impregnation (27).

For this study, the method of impregnation was similar to Villaecusa's variation on the wet method. To determine the final level of impregnation of the resins, an acid-base titration, similar to Cortina's method was used.

2.8 Extraction Mechanisms for Solvent Impregnated Resins

The mechanism for the extraction of metal ions from solution by S.I.R.s has not been fully rationalised. Researchers have proposed various models based on conventional ion exchange and solvent extraction theories, however no definitive theory on the recovery mechanism has been established.

Studies on the extraction mechanism of S.I.R.s include a comparison by Villaescusa et al between a conventional solvent extraction system and an impregnated resin system, both using tri-n-dodecylammonium chloride for the recovery of Au^{3+}. The study showed that metal extraction efficiency was higher for the SIR system than the solvent extraction system. It was suggested that this was due to the contributory effect of the solid support, which can recover gold as a bare resin (47).

For the liquid-solid extraction of gold using Cyanex 471 impregnated onto XAD 2 and XAD 7 resins, two different approaches were taken (46). In the case of XAD 2, the resin was taken to be a non-active support and extraction governed by a simple solvent extraction type interaction. For XAD 7, it was suggested that the action of the polymer also contributed to the final recovery efficiency of the solvent/resin system. The weak ester groups of the XAD 7 resin can form a hydrolytic product of the type $R\text{-}COOH_2^+$, which extracts Au^{3+} as $Au(Cl_4)^-$ via an ion pair mechanism.

The extraction mechanism for the recovery of scandium using a XAD 7 resin impregnated with (2-ethylhexyl hydrogen 2-ethylhexylphosphonate) was taken to be analogous to a solvent extraction system. While this contradicts other systems using XAD 7 resins, the assumption was consistent with results of distribution experiments for lanthanide metal ions (23).

The mechanism of Zn^{2+} sorption by D2EHPA on XAD 2, proposed by Akita et al (27) was expressed in terms of a simple ion exchange reaction. No solvent extraction analogies were considered.

Warshawsky et al, studying the application of solvent impregnated resins to hydrometallurgical systems, found that their behaviour was similar to solvent extraction systems using equivalent concentrations of the reagents concerned (40).

The varied and often contradictory mechanisms proposed for SIR systems illustrate the complex nature of the recovery systems. Further studies on SIR extraction are needed before any conclusive model of their behaviour in solution can be established.

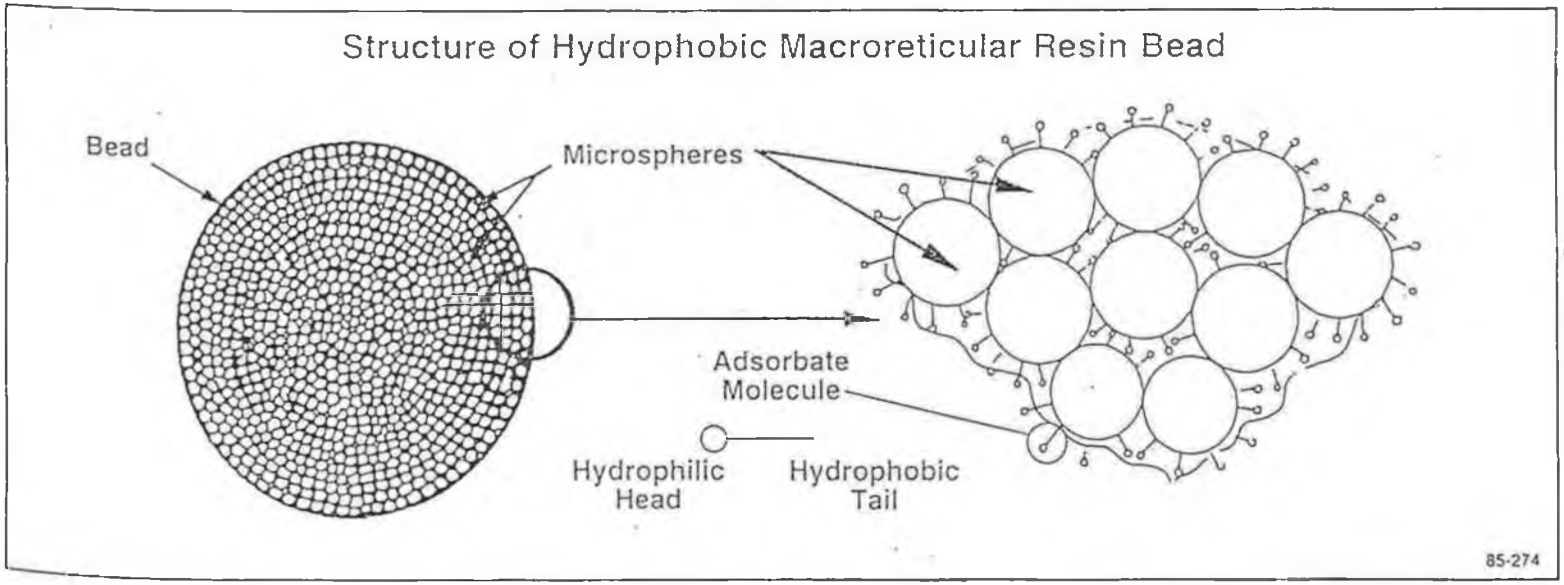


Fig. 2.1 Structure of a macroreticular resin bead

References

1 Ion Exchange and Solvent Extraction of Metal Complexes. Chapter 4. Y. Marcus and A.S. Kertes (Eds.). Wiley Interscience.

2 Vogel's Textbook of Quantitative Chemical Analysis, 5th Edition. Chapter 7. G.H. Jeffery, J. Bassett, J. Mendham and R.C. Denney. Longman Scientific & Technical.

3 A Review of the Application of Ion Exchange Technology for Gold Recovery. V.I. Lakshmanan and P.D. Tackaberry. Advances in Gold and Silver Processing, Proc. Sympgold Tech 4, Chapter 25, pp 257-262, (Sept 10-12, 1990).

4 Recent Developments in Resins for the Extraction of Gold. B.R. Green, A.H. Schwellnus and M.H. Kotze. Gold 100, Proceedings of the International Conference on Gold. Vol. 2: Extractive Metallurgy of Gold, Johannesburg, SAIMM, (1986).

5 M. Matsuda and Y. Yoshida. Japanese Patent 1293139. (1989).

6 CIP and RIP - Where to next? C. A. Flemming. Hydrometallurgy: Fundamentals, Technology and Innovations. Chp 24. J.B. Hiskey and G.B. Warren, (Eds). SME. (1993).

7 A Dedicated Resin for Gold -The Stimulus Needed for Universal Acceptance of a Resin in Pulp Process. B. R. Green, K. G. Ashurst and T. E. Chanston. Gold 89, Gold Forum Tecnol. Proc. World Australasian Inst. Mining & Metall., pp 339-346, Nov 5-8, (1989).

8 Gold and Silver Recovery from Thiourea Leach Solutions. W.W. Simpson, L. Peterson and R.G. Sandberg. Pacific Northwest Metals and Minerals Conference. Portland, Oregon. (April 29-May 2 1984).

9 Investigation on the Potential Techniques to Recover Gold from Thiourea Solution. G. Deschênes. Proc. of Intl. Symp. on Gold Metallurgy. R.S. Salter (Ed.), CIM, Montreal, pp 359-377, (1987).

10 The Loading Capacity of Selected Cation Exchange Resins and Activated Carbons for Gold-Thiourea Complex. R. Mensah-Biney, K.J. Reid and M.T. Hepworth. Minerals Engineering, Vol. 8, Nos1/2, pp 125-146, (1995).

11 The Crystal Structure of Tris(Thiourea) Copper(I) Perchlorate. F. Hanic and E Durcanska. Inorganic Chemica Acta. Vol 3, No.2 (1969).

12 Research and Development Activities for the Recovery of Gold from Non-Cyanide Solutions. R. Y. Wan and M. LeVier. Hydrometallurgy: Fundamentals, Technology and Innovations. Editors: J.B. Hiskey and G.B. Warren, Chapter 27. SME (1993).

13 Vogel's Textbook of Quantitative Chemical Analysis, 5th Edition. Chapter 6. G.H. Jeffery, J. Bassett, J. Mendham, R.C. Denney. Longman Scientific & Technical.

14 The Extraction of Metallic Species by Dialkylphosphoric Acids. C.F. Baes, Jr. J. Inorg. Nucl. Chem., Vol. 24, pp 707-720, (1962).

15 Acidic Esters of Orthophosphoric Acid as Selective Extractants for Metallic Cations - Tracer Studies. D.F. Peppard, G.W. Mason, W.J. Driscoll and R.J. Sironen. J. Inorg. Nucl. Chem., Vol. 7, pp 276-285, (1958).

16 Solvent Extraction of $^{152, 154}$Eu and ^{241}Am by Di-n-butyl Phosphate (DBP) in Different Organic Solvents. D. Dryssen and L. Djiet Hay. Acta Chemica Scandinavia, Vol 14, pp 1100-1111, (1960).

17 Extraction of Thorium(IV) by Di Esters of Orthophosphoric Acid $(GO)_2PO(OH)$. D.F. Peppard, G.W. Mason and S. McCarty. J. Inorg. Nucl. Chem., Vol. 13, pp 138-150 (1960).

18 Studies on Mono- and Di-n-Butyl Phosphoric Acids - II. C.J. Hardy, B.F. Greenfield and D. Scargill. J. Inorg. Nucl. Chem., Vol 11, pp 128-143, (1959).

19 Hydrometallurgical Extraction and Reclamation. E. Jackson. Ellis Horwood Series in Industrial Metals, (1986).

20 Solvent Extraction. Principles and Applications to Process Metallurgy. Part II. G.M. Ritcey and A.W. Ashbrook. Elsevier Scientific Publishing Company, (1979).

21 Design of a Process for the Purification of Cobalt by Means of Di-2-Ethylhexyl Phosphoric Acid. P. Mihalop, C.J. Barton, D.H. Logsdail, H.A.C. McKay and D. Scargill. Proc Int Solvent Extraction Conference, pp 1263-1273, (1974).

22 The Extraction of Zinc(II) from Sulphate and Perchlorate Solutions by Di(2-Ethylhexyl) Phosphoric Acid Dissolved in Isopar-H. A.M. Sastre and M. Muhammed. Hydrometallurgy, Vol 12, pp 177-193, (1984).

23 Selective Recovery of Trace Scandium from Acid Solution with (2-Ethylhexyl Hydrogen 2-Ethylhexyl Phosphonate)-Impregnated Resin. Y. Wakui, H. Matsunaga and T. M. Suzuki. Analytical Sciences, Vol. 5, pp 189-193, (1989).

24 Recovery of Zinc, Cadmium and Mercury (II) from Chloride and Sulphate Media by Solvent Extraction. N.M Rice and M.R. Smith. J. Appl. Chem. Biotecnol, Vol 25, pp 379-402, (1975).

25 Separation of Molybdenum from Tungsten by Di-2-Ethylhexyl Phosphoric Acid Extractant. Q. Zheng and H. Fan. Hydrometallurgy, Vol. 16, pp 263-270, (1986).

26 The Separation of Zinc from Copper by Di-2-Ethylhexyl Phosphoric Acid - An Equilibrium Study. C Forrest and M.A. Hughes. Hydrometallurgy, Vol. 3, pp 327-342, (1978).

27 Sorption and Separation of Divalent Metals by a Macromolecular Resin Containing Organophosphorus Acids. S. Akita and H. Takeuchi. Journal Of Chemical And Engineering Data, Vol. 37, No. 3, pp 303-306, (1992).

28 The Separation of Manganese from Cobalt by D2EHPA. Y.-C. Hoh, W.-S Huang, B.-D Lee and C.-C Chang. Hydrometallurgy, Vol. 12, pp 375-386, (1984).

29 The Extraction of Iron (III) from Aqueous Acid Solutions by Di-2-Ethylhexyl Phosphoric Acid. T. Sato, T Nakamura and M. Ikeno. Hydrometallurgy, Vol. 15, pp 209-218, (1985).

30 Acidic Organophosphorus Extractants-I. Extraction of Lanthanides by Means of Structure and Size of Alkyl Group. Z. Kolarik and H. Pankova. J. Inorg. Nucl. Chem., Vol. 28, pp 2325-2333, (1966).

31 Gold Metallurgy in South Africa. R.J. Adamson (Ed). Chamber of Mines of South Africa, (1972).

32 Mechanism for the Extraction of Amines in an Alkaline System. I.R. Plaskin and G.N. Shivrin. Dokl. Akad. Nauk. SSSR., Vol. 150, No. 3, pp 870-873, (1963).

33 A Modified Diluent for the Solvent Extraction of Gold(I) Cyanide from Alkaline Solution. T. Groenewald. Proceedings of Int. Solvent Extraction Conference, ISEC ’74. Pub. Soc. Chem. Ind., London.

34 The Chemical Treatment of Gold Slime for the Recovery of High Purity Gold and Silver. G.A. Walker. Proceedings of the Aus. I.M.M., No. 180, pp 45-54, (1956).

35 Literature Survey on the Recovery of Gold from Thiourea Solutions and the Comparison with Cyanidation. G. Deschênes. C.I.M. Bulletin, Vol. 79, pp 895, (1986).

36 Solvent Extraction of Gold with Di-2-Ethyl Hexyl Phosphoric Acid. N.A. Balakireva, L. A. Novosel'Tseva and I.S. Levin. Zh. Anal. Khim., Vol. 30, pp 684-688, (1975).

37 Stoichiometric Relation for the Extraction of the Gold-Thiourea complex with D2EHPA. K. Sun-Gyu, L. Hwa-Young, O. Jong-Kee and L. Eung-Cho. Hydrometallurgy, Vol 38, pp 7-13, (1995).

38 Solvent Impregnated Resins: Bridging the Gap Between Liquid And Solid Extraction. A. Warshawsky. Proc. Int. Solvent Extraction Conf. Toronto, ISEC-77. Paper 20A, pp 127-130, (1977).

39 Ion Exchange and Solvent Extraction Vol. 8. Chapter 3, Extraction with Solvent Impregnated Resins. A. Warshawsky. J. A. Marinsky and Y. Marcus (Eds).

40 Solvent-Impregnated-Resins in Hydrometallurgical Applications. A. Warshawsky. Trans Inst Min Metall, Vol. 83, pp 101-104, (1974).

41 Solvent Impregnated Resins Incorporating Phosphoric Acid Compounds. A. Warshawsky, R. Kalir and H. Berkovitz. Trans Inst in Metall, Vol. 88, Part C, pp 31-35, (1979).

42 Ion Exchange Resins in Non Aqueous Solvents-III. Solvent Uptake Properties of Ion Exchange Resins and Related Adsorbents. D.J. Pietrzyk. Talanta, Vol. 16, pp 169-179, (1969).

43 A. Warshawsky. South African Patent Application, 71/5637 (1971).

44 Amberlite XAD Copolymers in Reversed Phase Gravity Flow and High Pressure Liquid Chromatography. D. J. Pietrzyk and C. H. Chu. Analytical Chemistry. Vol. 49, No. 6, pp 757-764, (1977).

45 Amberlite XAD Polymeric Adsorbents. Information Booklet. Rohm and Haas Company, (1995).

46 Liquid-Solid Extraction of Gold(III) from Aqueous Chloride Solutions by Macroporous Resins Impregnated with Triisobutyl Phosphine Sulphide (Cyanex 471). I. Villaescusa, V. Salvadó, J. De Pablo, M. Valiente and M. Aguilar. Reactive Polymers, Vol. 17, pp 69-73, (1992).

48 Comparison Between Liquid-Liquid Extraction and Impregnated Resin Systems. The Extraction of Au(III) From Chloride Media By Tri-n-Dodecylammonium Chloride. I. Villaescusa, M. Aguilar, J. de Pablo, M. Valiente and V. Salvado. Proceedings of the International Solvent Extraction Conference. T. Sekine (Ed), pp 171-176, (1990).

48 The Separation of Gold from Acidic Leach Liquors with Amberlite XAD 7. R.I. Edwards, A.K. Haines and W.A.M. Te Riele. The Theory and Practice of Ion Exchange. M. Streat (Ed) (1976), SCI, London.

49 Preparation and Characterisation of Macroporus Resins Impregnated with Organophosphorus Compounds. J.L. Cortina, N. Miralles, M. Aguilar and A. Sastre. Solvent Extraction (1990), T. Sekine(Ed).

50 Solvent Impregnated Resins Containing Di- (2-Ethylhexyl) Phosphoric Acid. I. Preparation and Study of the Retention and Distribution of the Extractant on the Resin. J.L. Cortina, N. Miralles, M. Aguilar and A.M. Sastre. Solvent Extraction and Ion Exchange, Vol. 12, No 2, pp 349-369 (1994).

51 Recent Developments in Metal Extraction by Solvent Impregnated Resins. A. Warshawsky and A. Patchornik. The Theory and Practice of Ion Exchange. M. Streat (Editor), SCI, London, (1976)

Chapter 3

Impregnation of Amberlite XAD 2, XAD 4 and XAD 7 Resins

3.1 Preparation of the Resins for Use

Amberlite XAD 2, XAD 4 and XAD 7 resins, supplied by Rohm and Haas, were washed overnight in a 50% methanol/4M hydrochloric acid solution, to remove monomeric material and inorganic impurities from the resin beads (1). The resins were then washed free of acid with deionised water. The filtrate was periodically tested for chloride ions using silver nitrate, which forms an insoluble silver chloride precipitate when chloride ions are present in solution. Once the filtrate was free of chloride ions, the resins were stored in deionised water. Before use, the resins were filtered from solution and dried in air.

3.2 Impregnation of the Resins

The method of impregnation chosen was similar to the method used by Villaescusa et al (2). A summary of this method is given in section 2.7.4.

The solvent chosen for impregnation was Di-2-ethylhexyl phosphoric acid (D2EHPA), supplied by BDH. It was used as supplied, without any further purification. A known mass of D2EHPA was dissolved in methanol (15ml) and the solution was contacted with a known mass of each of the three resins, Amberlite XAD 2, XAD 4 and XAD 7. The mixtures were stirred overnight, using a magnetic stirrer.

3.3 Determination of the Level of Impregnation of the Resins

After impregnation, the resins were filtered and the D2EHPA/CH_3OH filtrate was made up to 100ml with methanol. The final concentration of D2EHPA in solution was determined by an acid/base titration with sodium hydroxide (NaOH) (0.1M), using phenolphthalein as an indicator (3).

From the difference between initial and final masses of D2EHPA in solution, the mass of D2EHPA retained by the resin was determined. The mass of solvent retained per gram of resin was calculated.

Note:

A series of blank titrations of methanol (10ml) with NaOH (0.0108M) gave an acid blank of 7.5×10^{-5} moles/25ml or 0.003M. For all work involving the volumetric analysis of D2EHPA in methanol, 0.003M was subtracted from the calculated concentration of acid remaining in solution, in order to obtain a true concentration of D2EHPA remaining in solution.

3.3.1 Validation of D2EHPA Analysis Method

The determination of the level of D2EHPA remaining in the methanol solution by titration with NaOH was validated by titrating a standard D2EHPA/methanol solution with a standardised NaOH solution. The concentration of the two standard solutions are given below.

Concentration of NaOH (mol.dm^{-3})	Concentration of D2EHPA (mol.dm^{-3})
0.083	0.101

Table 3.1 Concentration of standard acid/base solutions.

Results

Volume of D2EHPA solution (cm^3)	Volume of NaOH required (cm^3)	Indicator	Calculated Molarity of D2EHPA solution (mol.dm^{-3})
10ml	12.2ml	phenolphthalein	0.101mol.dm^{-3} ± 0.005 mol.dm^{-3} (burette error)
10ml	12.2ml		
10ml	12.2ml		

Table 3.2 Validation of volumetric analysis of D2EHPA in methanol by titration with NaOH.

The reaction between D2EHPA and NaOH is:

$$NaOH + RO\text{-}POOH\text{-}OR \longrightarrow RO\text{-}POONa\text{-}OR + H_2O.$$

Where R is the 2-ethyl hexyl group

3.3.2 Calculated Impregnation Levels of the Resin

Resin	Mass of Resin (g)	Initial Mass of D2EHPA in Solution (g)	Mean Titre (cm^3)	Moles of Acid (D2EHPA) remaining in Solution (mol)	Mass of D2EHPA remaining in solution (g)
XAD 2	5	4.999	13.2	1.39×10^{-2}	4.500
XAD 4	5	5.000	10.80	1.14×10^{-2}	3.676
XAD 7	5	4.999	12.84	1.33×10^{-2}	4.288

Table 3.3 – Analysis of Filtrate After Impregnation of Resins.

Resin	Mass of D2EHPA retained by resin (g/5g resin)	Mass of D2EHPA retained by 1g resin
XAD 2	0.499	0.100
XAD 4	1.324	0.265
XAD 7	0.714	0.143

Table 3.4 - Level of Impregnation of the Resins.

The final level of impregnation of the resins appears, as expected, to be dependent on the surface area of the resins. The highest level achieved was for XAD 4, with a reported surface area of $750m^2/g$. XAD 2 ($330m^2/g$) gave a much lower level of impregnation under the same set of conditions. XAD 2 also became significantly more hydrophobic on impregnation. It floated on the surface of the aqueous solution and adhered to the side of the containing vessel, it also adhered to pipettes etc. which were used to take samples from solution. This resulted in loss of resin with each sample taken. It is likely that the hydrophobicity exhibited by the impregnated XAD 2 resin would cause problems for any large scale use of impregnated XAD 2 since adhesion of the resin onto the recovery vessel out of solution may inhibit recovery rates. Loss of resin would also increase recovery costs. Satisfactory dispersion of the resin through the solution is also more difficult using XAD 2 because of its hydrophobicity.

XAD 4 and XAD 7 resins did not become hydrophobic upon impregnation. They mixed well upon agitation and quickly settled to the bottom of the container after mixing. Resin losses for these resins were kept to a minimum by allowing the resins to fully settle before sampling. The resin did not adhere to the containing vessel and homogeneous dispersion of the resins was also easier.

3.4 Mass Balance of D2EHPA on Resins at pH 3.5.

The mass of solvent impregnated onto the resin was determined by calculating the difference between the mass of solvent in solution before and after impregnation. In order to fully validate this method, it was necessary to establish the mass balance of solvent by directly determining the mass of solvent on the resin. For this, a known mass of the impregnated resin was washed in methanol. Any D2EHPA retained by the resin was re-dissolved into the methanol and the acid concentration of the methanol solution was determined by titration as before.

Results:

Resin	Calculated Level of Impregnation of Resins (g D2EHPA/g resin)	Mass of D2EHPA washed off Resin (per g of resin)	% Variation
XAD 2	0.100	0.116	+13.8
XAD 4	0.265	0.253	-4.5
XAD 7	0.143	0.137	-4.2

Table 3.5 - Mass balance of D2EHPA on impregnated resins (average of three determinations in each case).

The difference in the initial calculation for the level of impregnation of the resins and the mass of D2EHPA washed off the resins ranged between 6mg for XAD 7 and 16 mg for XAD 2. The difference between the levels gives an indication of the experimental error involved in this method of D2EHPA analysis. While some error is inevitable in volumetric analysis, it was kept to a minimum by ensuring no acidic or basic contaminants came into contact with the resin/solvent impregnation system and by careful titration.

3.5 Stability of D2EHPA on the Resin in Acidic Solution

The stability of D2EHPA on the resins is very important since any loss of the solvent to the aqueous solution would result in decreased efficiency and capacity of the resins, loss of any gold complexed to the redissolved solvent and an overall increase in the cost of recovery.

In order to determine the effect of acid on the stability of the impregnated resins, a comparison between the level of impregnation of each of the three resins before and after contact with an acidic solution was made. The level of acidity of the aqueous solution was chosen to be similar to the working pH of the recovery solution (sec. 4.6.1).

The resins were analysed for D2EHPA, before and after contact with acidic solution, by contacting a known mass (1g) of resin in acidic solution (pH 3.5). Subsequent washing in methanol and an acid/base titration of the washings determined the level of impregnation after acid contact (3). The bare resins were also treated in the same manner so that any acid adhering to the resins, other than D2EHPA, could be accounted for.

A comparison was then made between the level of impregnation of the resins contacted with acidic solution, with resins of the same batch which had not had any contact with an acidic solution.

3.5.1 Bare Resins - Analysis of Methanol Wash Solution

Analysis of *acid* washed off resins into methanol (no D2EHPA).

Resin	**Mass of Resin Washed (g)**	**Average Titre (cm^3)**	**Acid Concentration ($mol.dm^{-3}$)**	**After Subtraction of Acid Blank (0.003 $mol.dm^{-3}$)**	**Moles of H^+/25ml (per g of resin)**
XAD 2	0.679	3.83	0.004	0.001	3.7 x 10-5
XAD 4	0.749	3.81	0.004	0.001	3.3 x 10-5
XAD 7	0.900	2.67	0.003	0.000	-

Table 3.6 Concentration of acid washed off bare resins.

The concentration of acid remaining on the *bare* resins after contact in acidic solution is small, since the resins were rinsed with deionised water. However, the concentration of *solvent* on the *impregnated* resins is also small. Therefore, when calculating the mass of solvent remaining on the resin it is necessary to take into account any acid on the resin due to contact with the aqueous solution, rather than impregnation of the acidic solvent.

3.5.2 Impregnated Resins - Analysis of Methanol Wash Solution

Resin	Level of Impregnation (g/g)	Average Titre (cm^3)	Acid Concentration ($mol.dm^{-3}$)	Moles of H+/25ml	Corresponding Mass of D2EHPA (g)
XAD 2	0.100	10.2	0.011	2.8×10^{-4}	0.089
XAD 4	0.265	29.6	0.032	8.0×10^{-4}	0.258
XAD 7	0.143	14.81	0.016	4.2×10^{-4}	0.136

Table 3.7 Mass of D2EHPA washed off resins (no contact with acid solution).

3.5.3 Impregnated Resins Contacted with Acid Solution - Analysis of Methanol Wash Solution

Resin	Level of Impregnation g/g	Average Titre cm3	Acid Concentration (mol.dm^{-3})	Moles of H+/25ml (mol)	Corresponding Mass of D2EHPA (g)
XAD 2	0.100	9.9	0.011	2.7×10^{-4}	0.086
XAD 4	0.265	31.1	0.033	8.4×10^{-4}	0.271
XAD 7	0.143	15.9	0.017	4.3×10^{-4}	0.137

Table 3.8 The mass of D2EHPA washed off resins (after contact in a pH 3.5 acid solution).

A comparison between the initial acid/base analysis of the resins, with the mass of D2EHPA washed off the resin before and after acid contact was then made in order to note the variation in the calculated level of impregnation of the resins in each case.

Resin	Level of Impregnation (g/g)	Mass of D2EHPA washed off resin (no acid contact) (g)	Mass of D2EHPA washed off resin (Acid contact) (g)
XAD 2	0.100	0.089	0.086
XAD 4	0.265	0.258	0.271
XAD 7	0.143	0.136	0.137

Table 3.9 Comparison of results.

The effect of acid on the stability of the solvent on the resin appears to be small. While some variation is seen between the initial calculated level of impregnation of the resins and the mass of D2EHPA on the resins before and after contact with acid solution, the decrease is small and is within the limits of experimental error. Losses of solvent by this manner are expected to be minimal and should not significantly affect impregnation levels. The effect of acid on solvent stability is therefore taken to be negligible.

3.6 Ability of Resins to Retain D2EHPA.

Because of the different properties of each of the three resins (surface area, porosity, etc.), the final level of impregnation of the resins under similar conditions of impregnation is not comparable. To compare the ability of each of the resins to adsorb the solvent, a series of solutions of different concentrations of D2EHPA were contacted with each of the resins, XAD 2, XAD 4 and XAD 7. The level of impregnation in each case was calculated by titration with NaOH (0.1M). In this case, the initial mass of D2EHPA in methanol was varied between approx. 0.080g and 5.1g.

1.XAD 2

Resin No.	Concentration of D2EHPA (mol/dm^3)	Mass of Resin (g)	Final Level of Impregnation (g/g)
1	0.016	4.559	0.002
2	0.047	4.794	0.015
3	0.108	4.642	0.037
4	0.207	4.950	0.062
5	0.423	4.913	0.089
6	0.634	4.934	0.091

Table 3.10 The impregnation of XAD 2 at varying initial concentrations of D2EHPA.

2. XAD 4

Resin No.	Concentration of D2EHPA (mol/dm^3)	Mass of Resin (g)	Final Level of Impregnation (g/g)
1	0.022	4.979	0.019
2	0.053	5.019	0.041
3	0.115	5.096	0.077
4	0.213	5.010	0.122
5	0.420	5.052	0.218
6	0.832	5.106	0.302

Table 3.11 The impregnation of XAD 4 at varying initial concentrations of D2EHPA.

3. XAD 7

Resin No.	Concentration of D2EHPA (mol/dm^3)	Mass of Resin (g)	Final Level of Impregnation (g/g)
1	0.021	4.779	0.002
2	0.053	5.108	0.021
3	0.116	5.152	0.051
4	0.208	5.198	0.084
5	0.416	5.108	0.125
6	0.833	5.017	0.175

Table 3.12 The impregnation of XAD 7 at varying initial concentrations of D2EHPA.

Graphs 3.1 to 3.3 show the change in the level of impregnation of each of the resin with increasing concentration of solvent. The level of impregnation of each of the three resins rises steadily with the initial mass of solvent in the impregnation solution. However, the *rate of increase of impregnation*, depends on the physical properties of the resin, as well as the initial concentration of solvent. Graph 3.4 is an overlay of the three graphs showing a comparison of the levels of impregnation achieved by each set of resins at increasing levels of impregnation.

A comparison of resin no. 4 in each case illustrates the ability of the resin to adsorb solvent. The initial mass of solvent is approx. 1g, the initial mass of solvent is approx. 5g. The final level of impregnation for the resins are 0.062g/g, 0.122g/g and 0.084g/g for XAD 2, 4 and 7 respectively. XAD 4 resins are the most efficient and adsorb the highest level of solvent at a given initial concentration. XAD 7 resins adsorb at a moderate rate, although the final level is significantly lower than for XAD 4. XAD 2 resins have the lowest final level of impregnation at a given initial concentration of D2EHPA.

3.7 Scanning Electron Microscopy

Electron microscopy is a technique used to magnify objects many thousands of times. It uses beams of electrons to form images, in a manner identical to the formation of images by light for optical microscopy. The difference between optical and electron microscopy comes from the limits of resolution of the two techniques. The resolution of a microscope is related to the wavelength of the magnifying beam. The wavelength of a beam of electrons is thousands of times smaller than that of visible light, therefore its resolution is thousands of times larger. Scanning electron microscopy (SEM) is a variation of electron microscopy where the electron beam is focused into a very fine line and is swept across the object. SEMs appear more three-dimensional than conventional electron micrographs, however, resolution of the images is not as great (4).

Scanning electron micrographs of the resins were obtained using a Leica Stereoscan 440 SEM system. Micrographs of the bare resins and the resins at two different levels of impregnation are discussed.

3.7.1 Preparation of the Resins

The resins were vacuum dried to remove any volatile solvents and were mounted onto a level plane for scanning. They were then coated with either a carbon or a gold coating in order to make them conducting. For work on the internal surface of the resins, the beads were fractured by immersing in liquid nitrogen and then scraping away the surface of the resin using tweezers under an optical microscope (5).

3.7.2 SEM Analysis of Bare Resins

Figs 3.1 to 3.3 show the resin beads at 25X magnification. The general external appearance of the resins is no different to any other ion exchange resins. The beads are perfectly spherical although they do not have a uniform size. Point to point analysis gives a typical range of diameters for each of the three resins:

Resin	**Diameter Range (µm)**	
XAD 2	297.92	577.50
XAD 4	256.67	774.58
XAD 7	444.58	705.83

Table 3.13 Typical diameter ranges for the resins.

These values compare with values quoted by the manufacturer (6).

Figs 3.4 to 3.9 show the same resins as fractured beads at 500X magnification and their internal surface at 30,000X magnification. At 500X magnification, the internal structure of the bare resins appears to be quite similar to the external surface. However on increasing magnification to 30,000X, the macroreticular nature of the resins becomes apparent. The 30,000X micrographs show the internal network of spherical particles, fused into the large macrosphere and the porous area surrounding the microspheres. It is these tiny microspheres which give macroporous resins their characteristically high surface area. A point to point analysis of the microspheres gives their typical diameter ranges.

Resin	**Diameter (nm)**
XAD 2	253.62
XAD 4	296.70
XAD 7	340.78

Table 3.14 Typical diameters of the resins microspheres.

3.7.3 SEM Analysis of Impregnated Resins

For each resin, two different levels of impregnation were viewed They were chosen so that the effect of both high and low levels of solvent on the resin could be seen. The levels of impregnation of the resins are given below.

Resin	**Levels of Impregnation (g D2EHPA/g)**	
XAD 2	0.003	0.285
XAD 4	0.041	0.302
XAD 7	0.021	0.224

Table 3.15 Level of impregnation of resins.

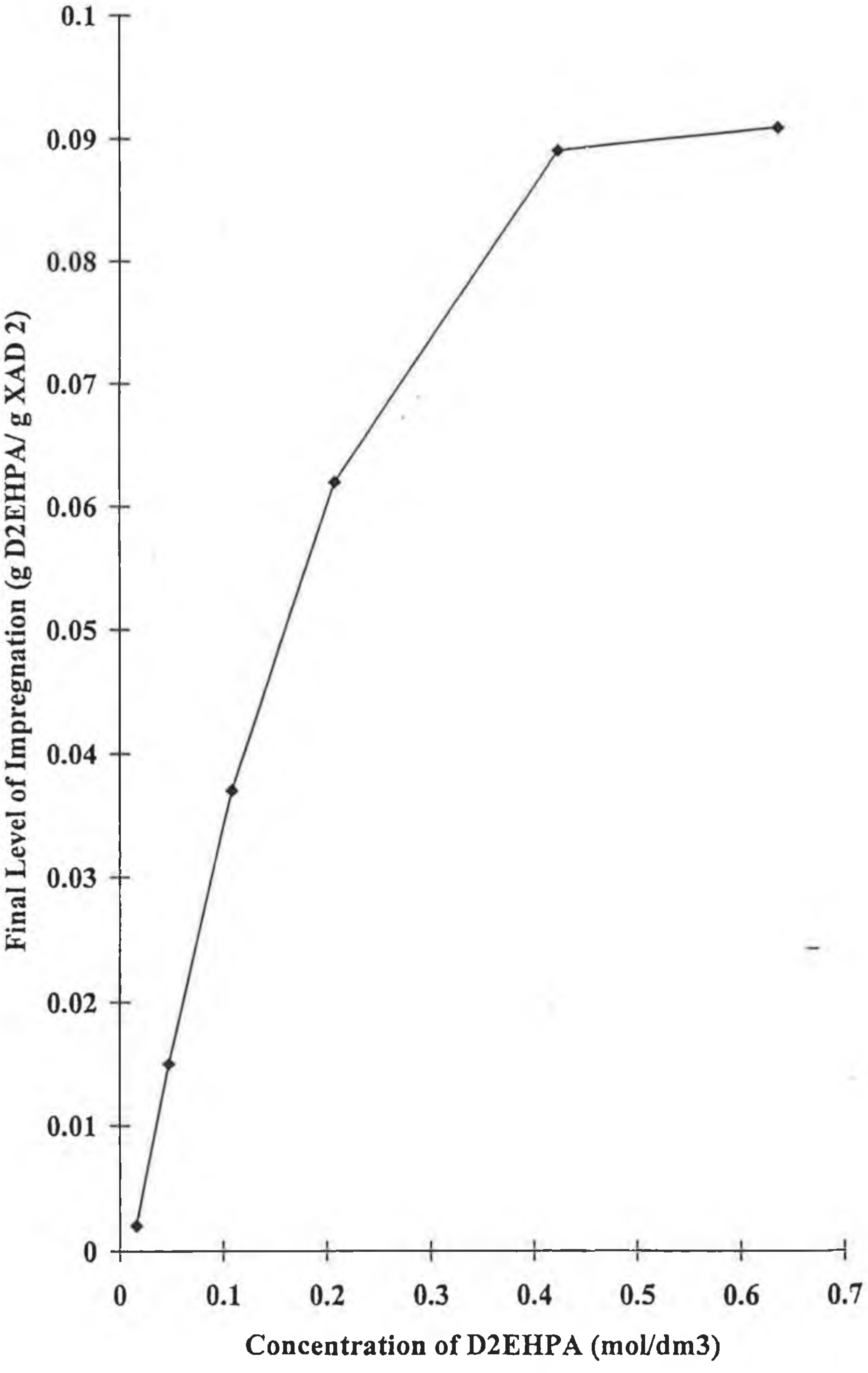
3.7.4 The Change in the Structure of the Resins after Impregnation

The structure of an impregnated polymeric support can only change if the support allows considerable expansion and contraction during the impregnation process. Since macroporous resins are rigid supports, they should not be structurally modified during impregnation and significant changes in the resin's appearance should not be seen (7).

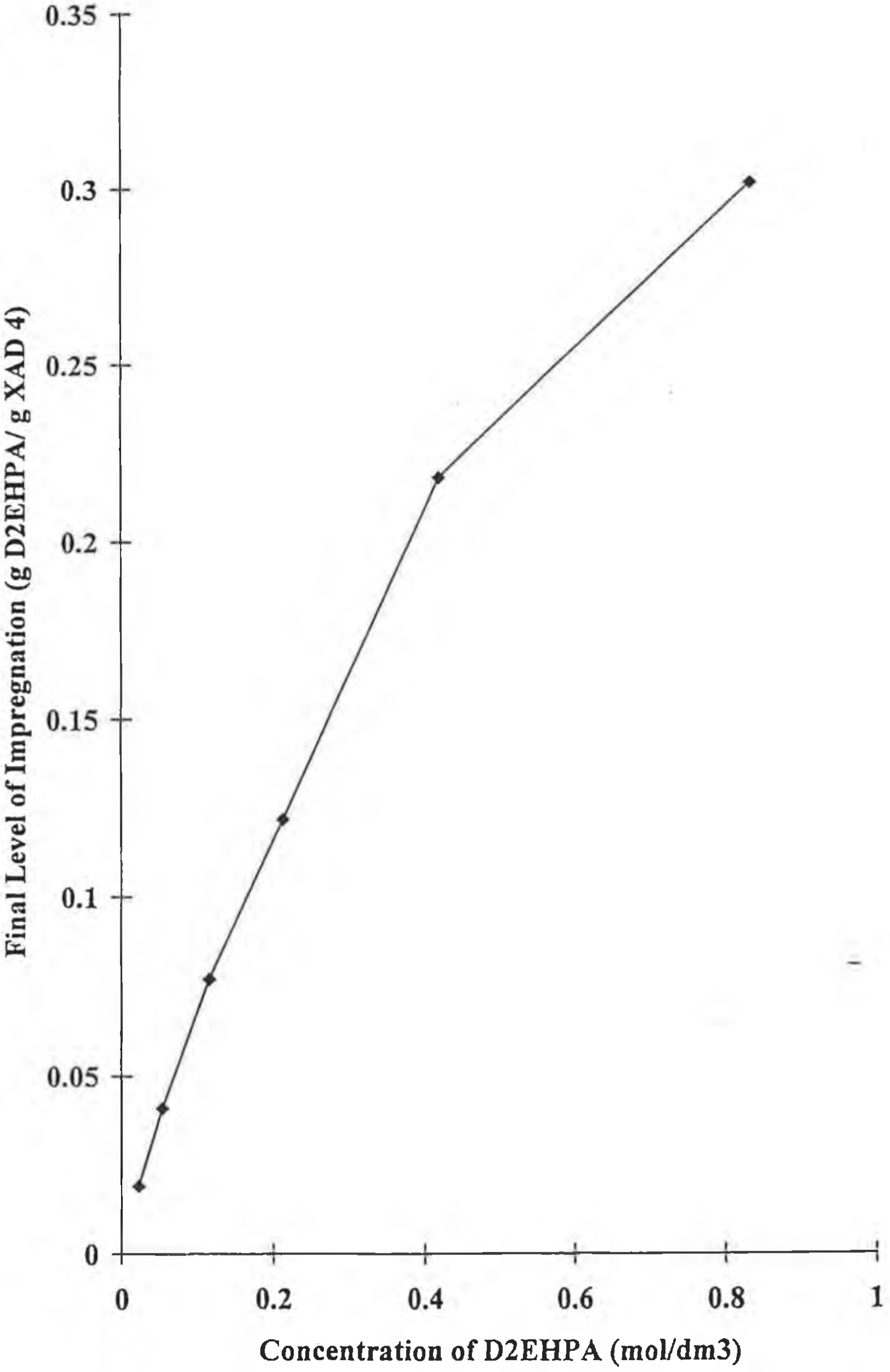
Figs. 3.10 to 3.12 show the external surface of the higher level impregnated resins at 500X magnification. No apparent change in the resin's external surface after impregnation can be seen, except in the case of XAD 2 (at 5K X mag.) (Fig. 3.13), which shows a speckled surface coverage of solvent at the higher level of impregnation. This type of speckling was not seen on the lower level XAD 2 resin or on any of the other impregnated resins. Warshawsky suggests that solvent clusters on the surface of the resin is an indication of imperfect impregnation (5).

The internal surface of the impregnated resins was viewed at 30,000X magnification. Fig. 3.14 to 3.19 show the three resins at both the low and high impregnation levels. The internal structure of the low level impregnated resins is quite similar to the bare resins although some coverage of the microspheres is apparent and the pore volume of the internal network appears to have decreased, due to the partial blocking of the pores by the impregnation process. For the resins impregnated to a higher level, the change in the internal surface of the resins after impregnation is more clearly seen. More of the microspheres are now coated with solvent and they now appear larger and more clustered. The internal pore volume of the resins also appears to have decreased significantly, since more of the microspheres are now coated with D2EHPA.

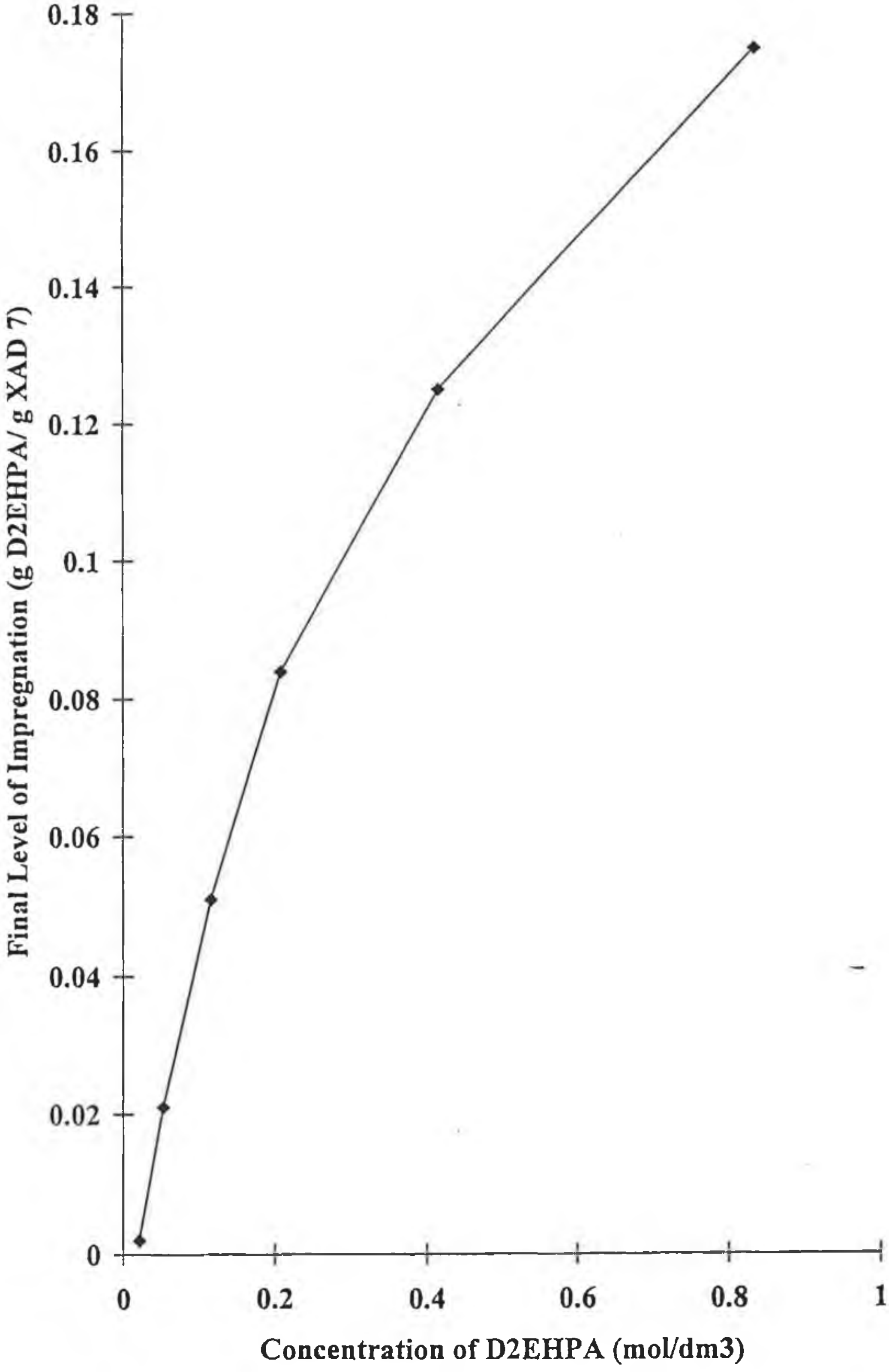
Graph 3.1 Impregnation of XAD 2 at Increasing Concentrations of D2EHPA



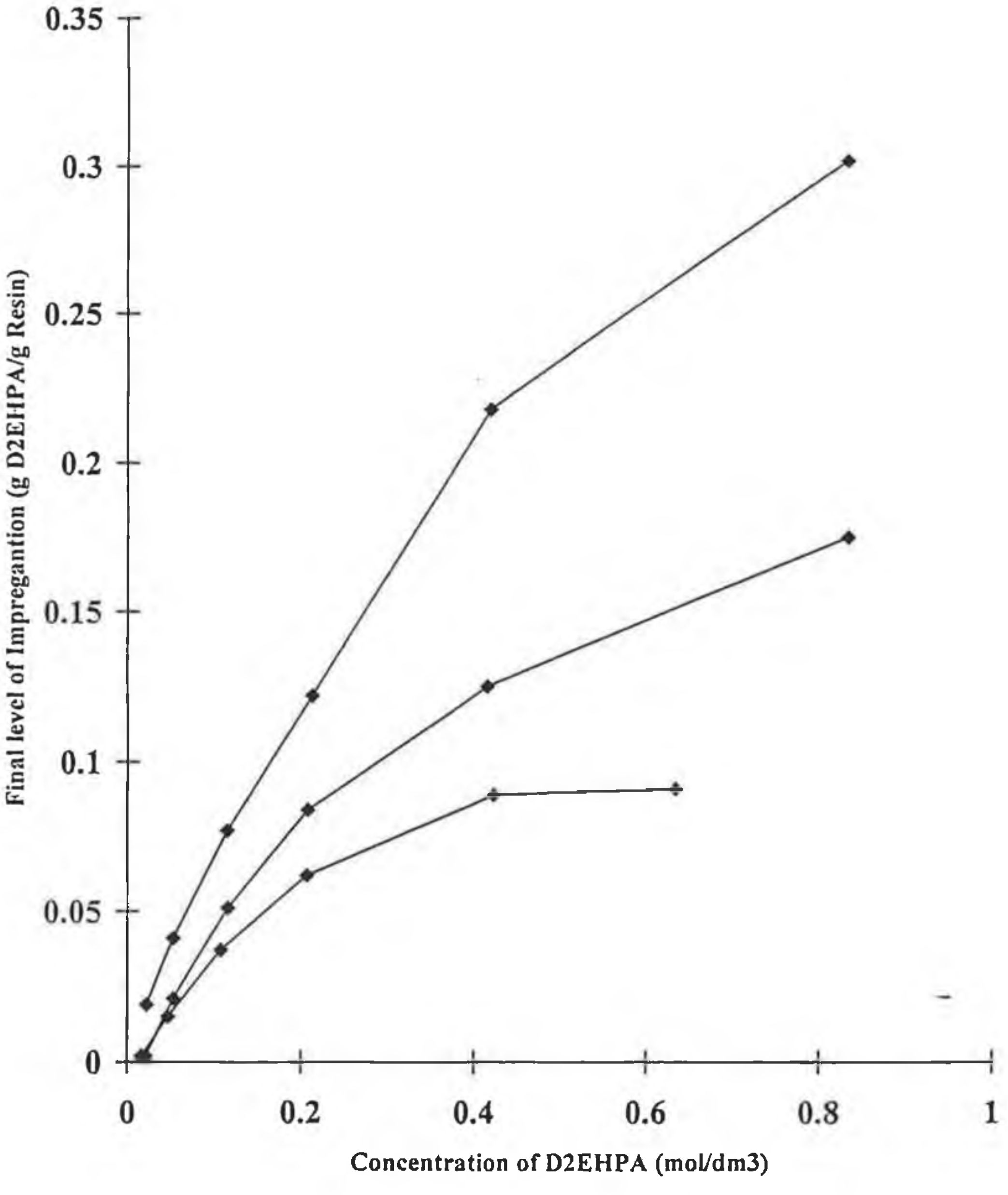
Graph 3.2 Impregnation of XAD 4 at Increasing Concentrations of D2EHPA



Graph 3.3 Impregnation of XAD 7 at Increasing Concentrations of D2EHPA



Graph 3.4 A Comparison of the Impregnation of XAD 2, XAD 4 and XAD 7 at Increasing Concentrations



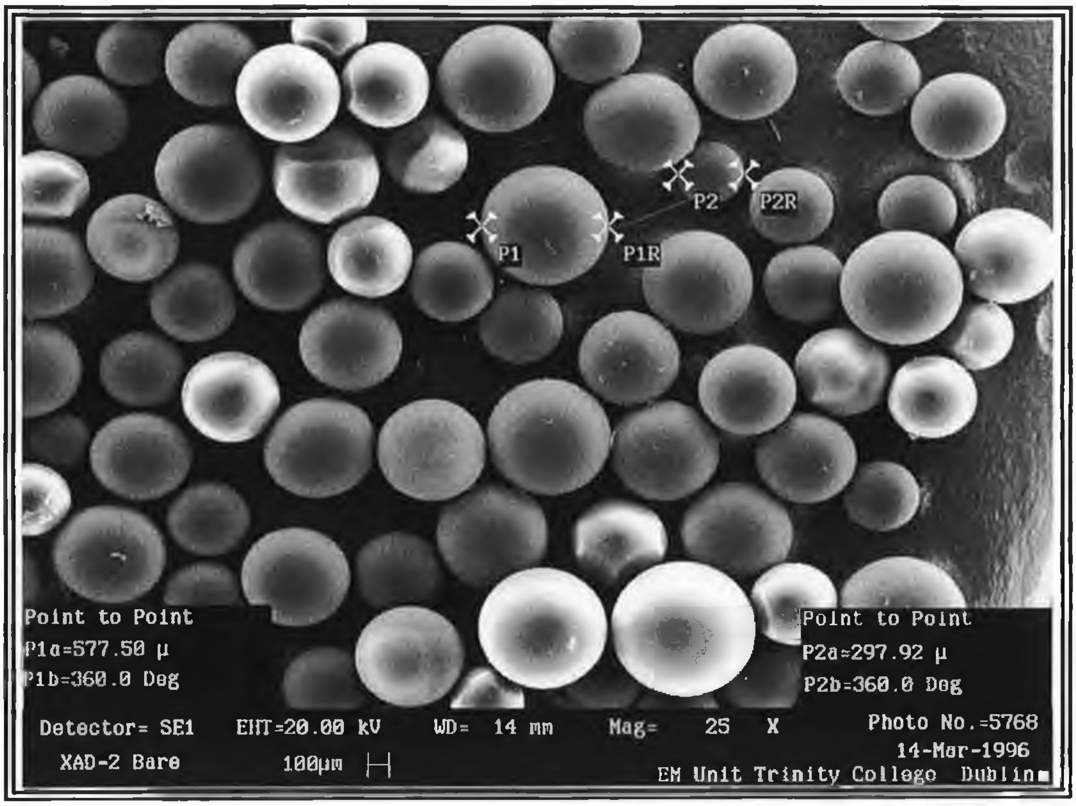


Fig. 3.1 Scanning electron micrograph of XAD 2 bare resin. Magnification: 25X

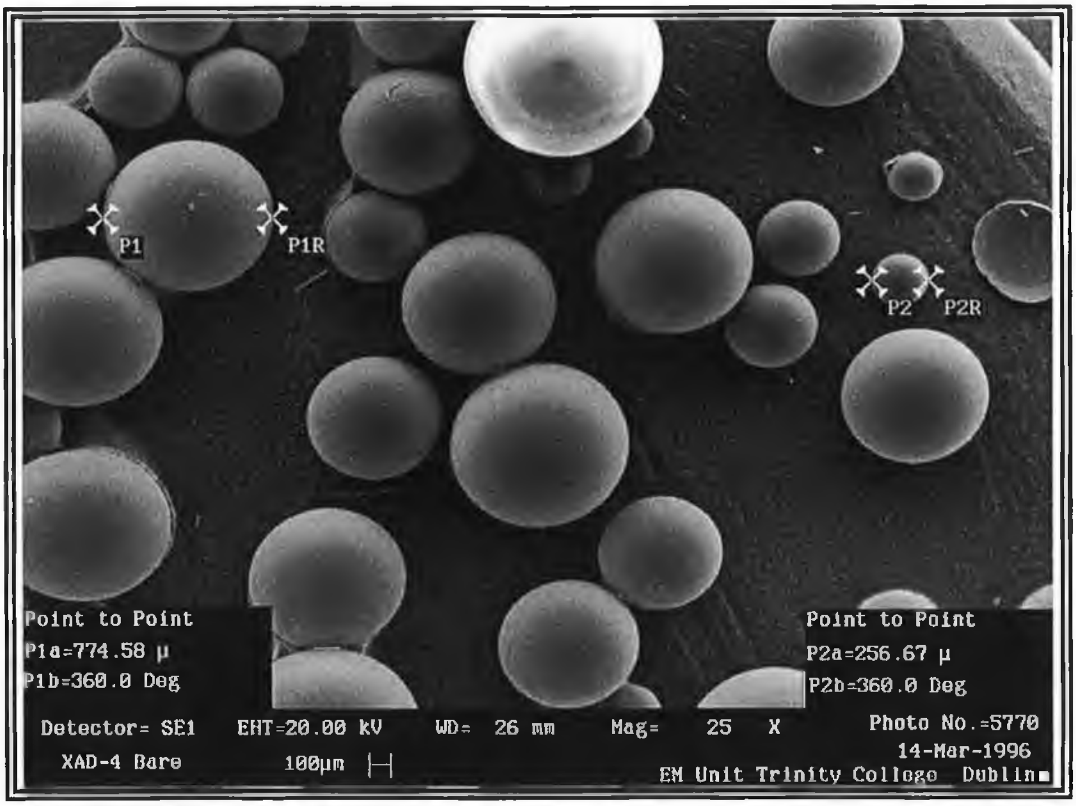


Fig. 3.2 Scanning electron micrograph of XAD 4 bare resin. Magnification: 25X

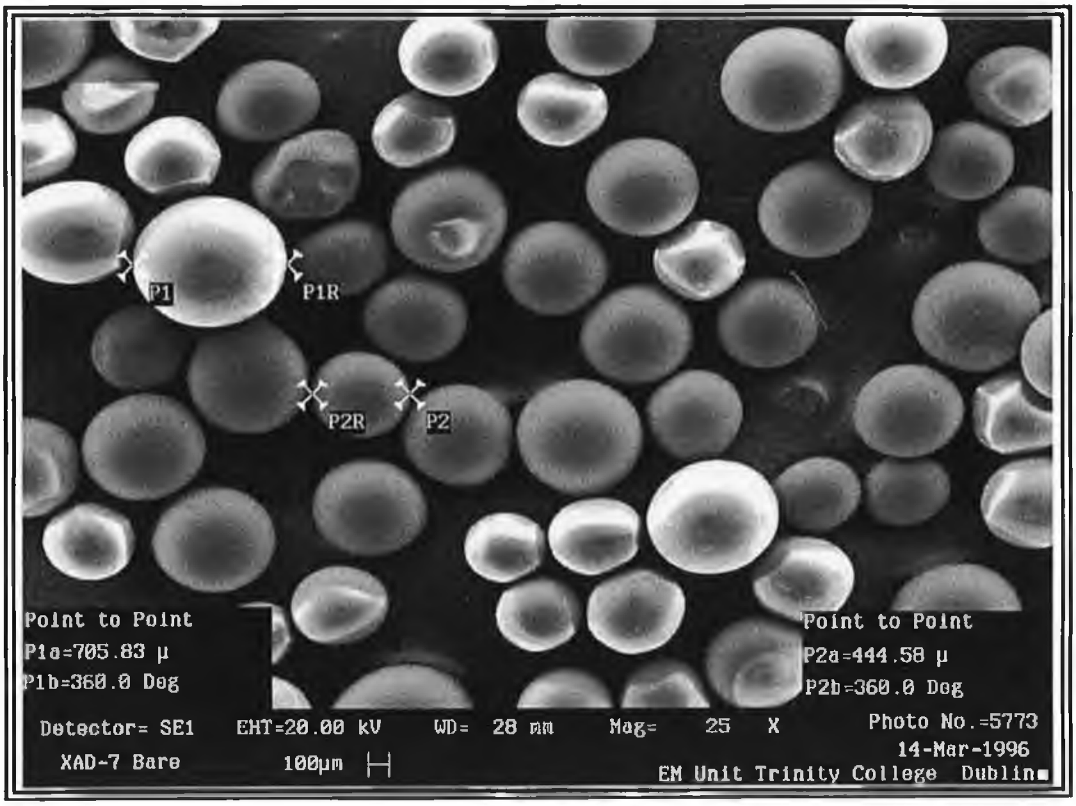


Fig. 3.3 Scanning electron micrograph of XAD 7 bare resin. Magnification: 25X

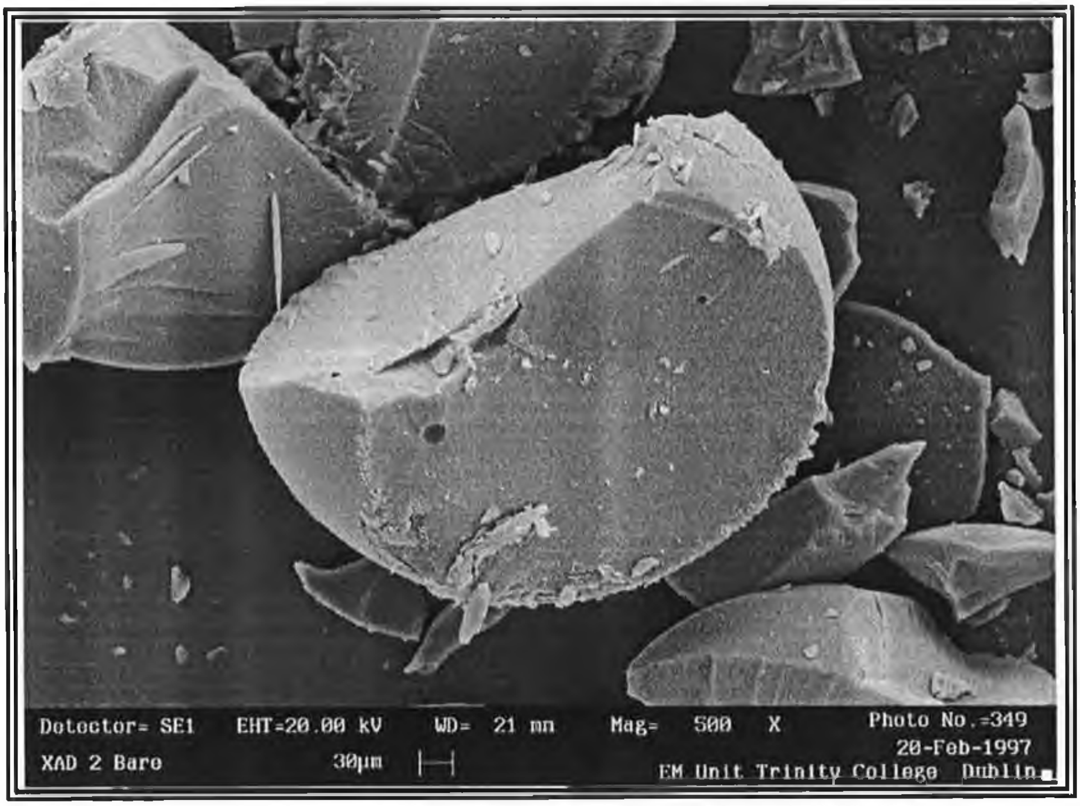


Fig. 3.4 SEM of fractured XAD 2 bare resin. Magnification: 500X.

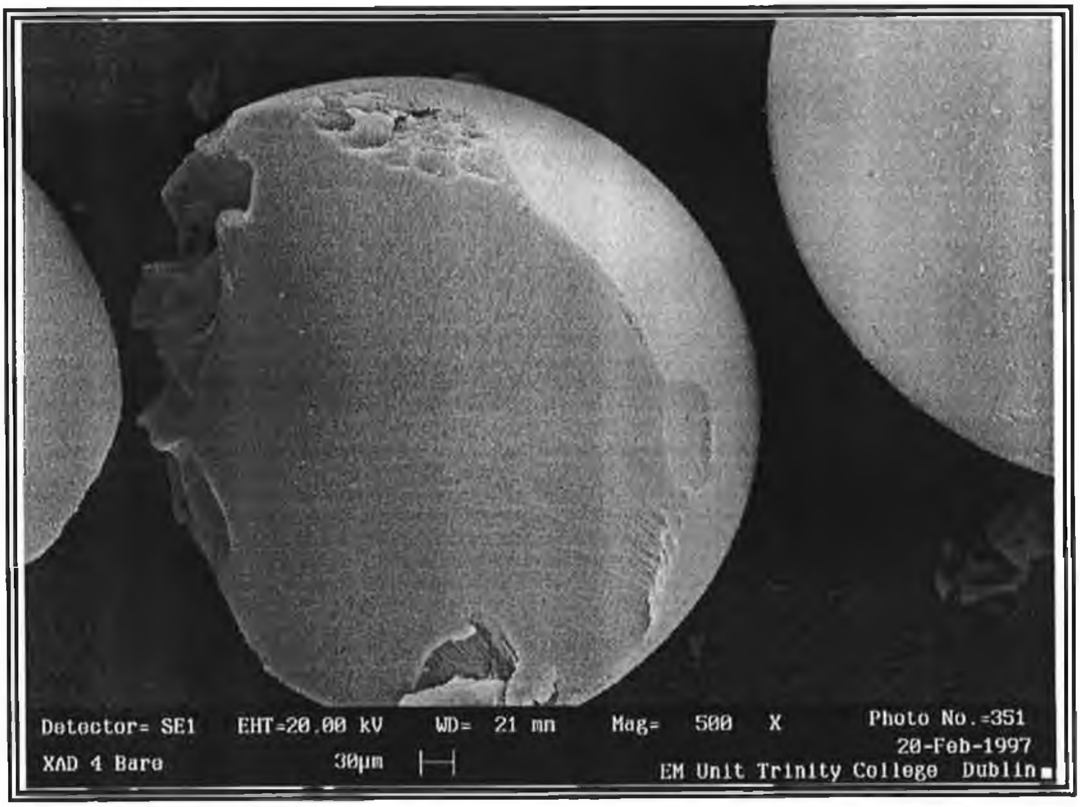


Fig. 3.5 SEM of fractured XAD 4 bare resin. Magnification: 500X.

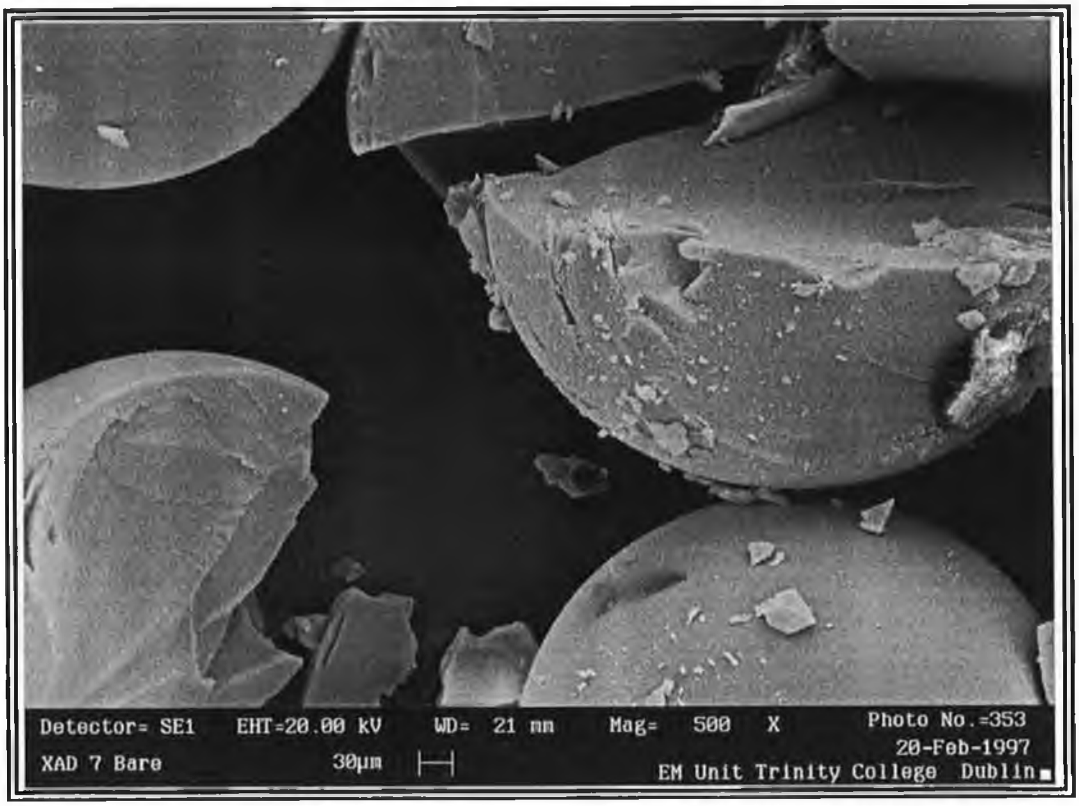


Fig. 3.6 SEM of fractured XAD 7 bare resin. Magnification: 500X

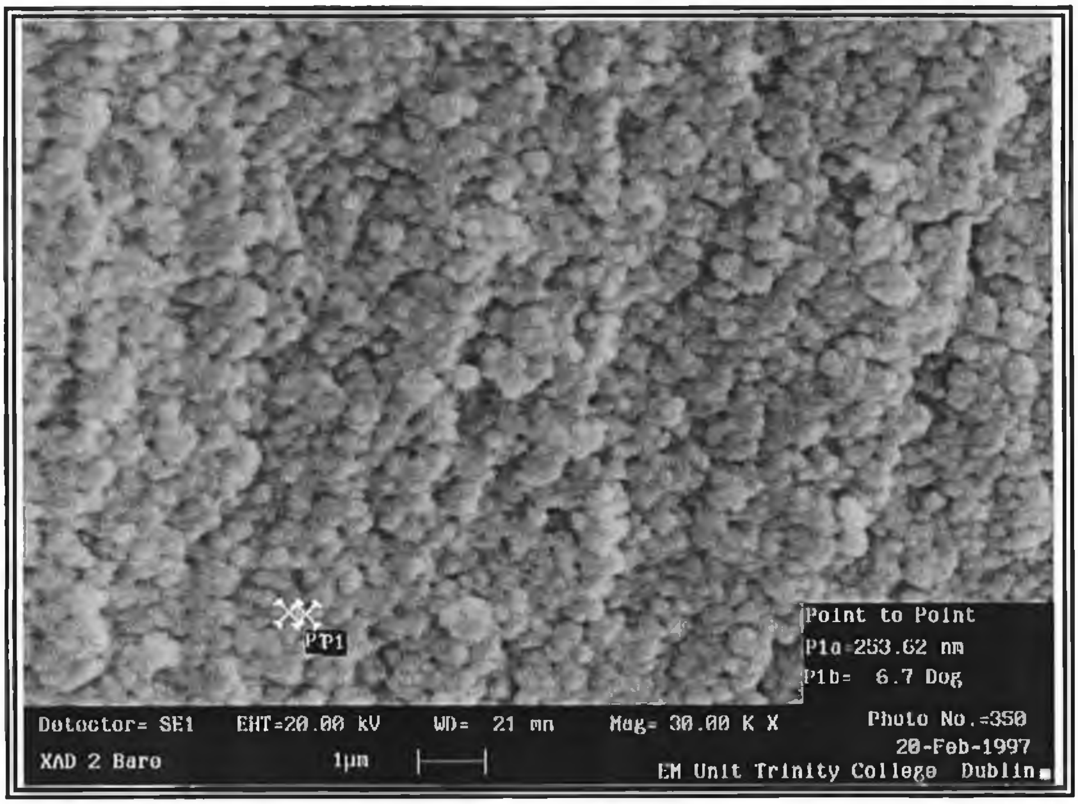


Fig. 3.7 SEM of fractured XAD 2 bare resin. Magnification: 30,000X.

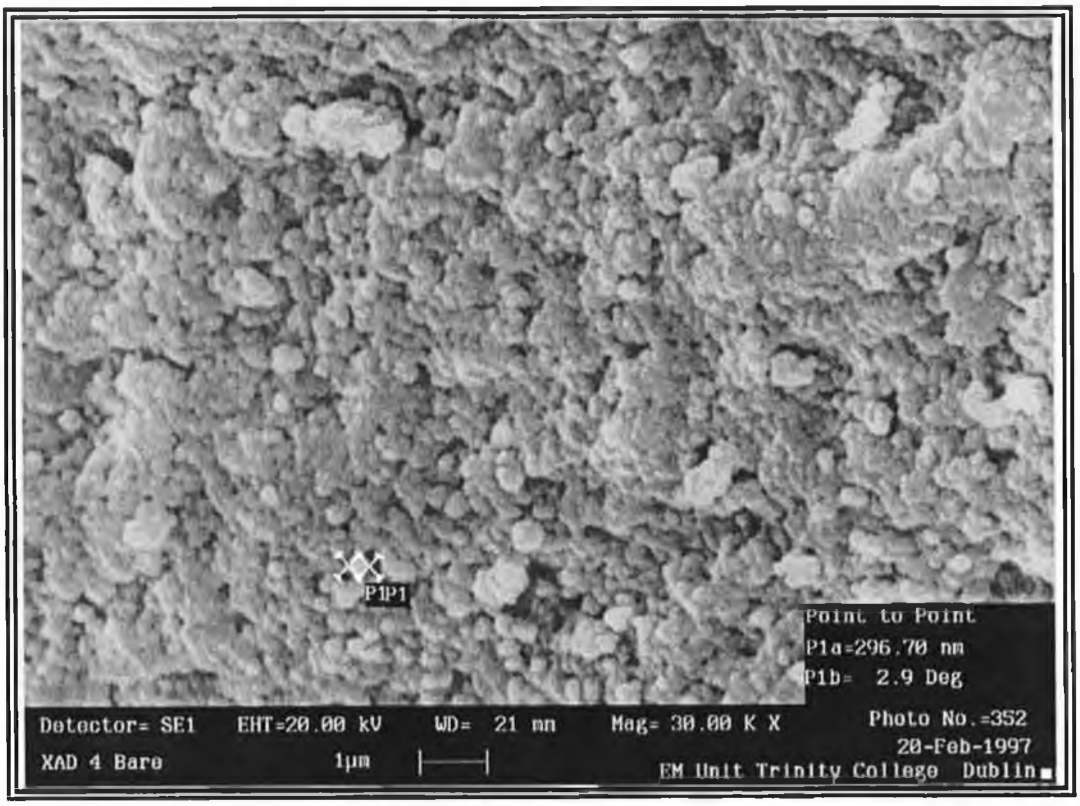


Fig. 3.8 SEM of fractured XAD 4 bare resin. Magnification: 30,000X.

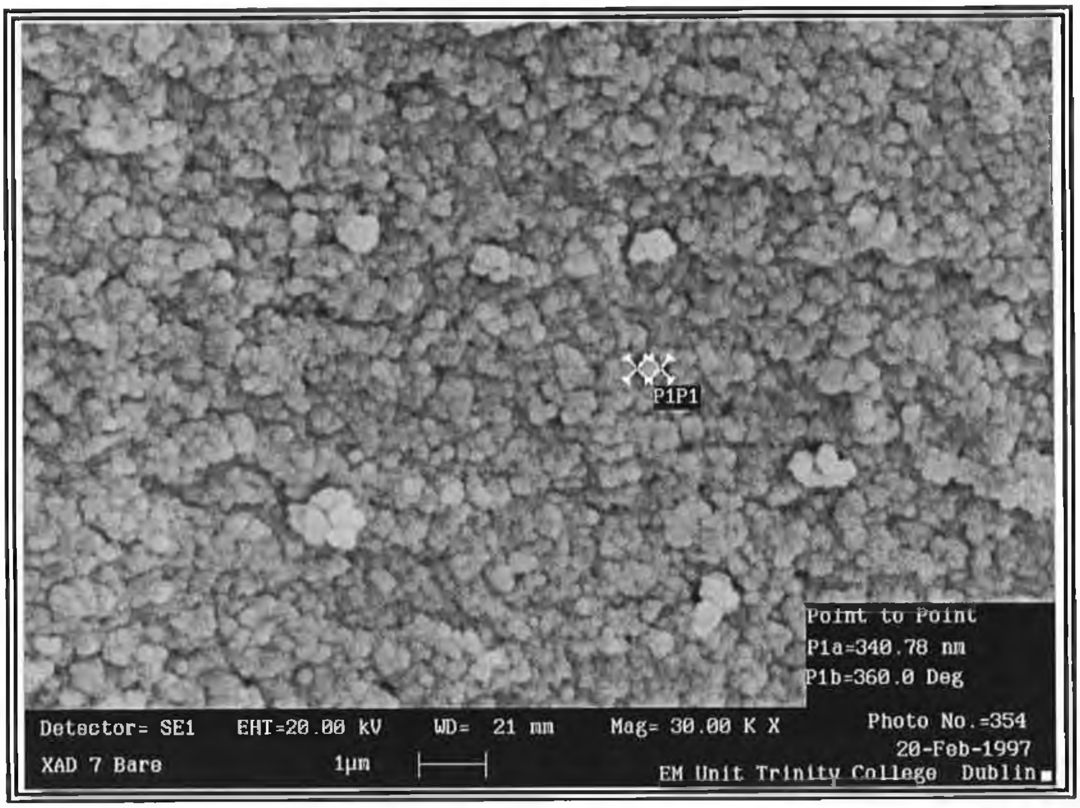


Fig. 3.9 SEM of fractured XAD 7 bare resin. Magnification: 30,000X.

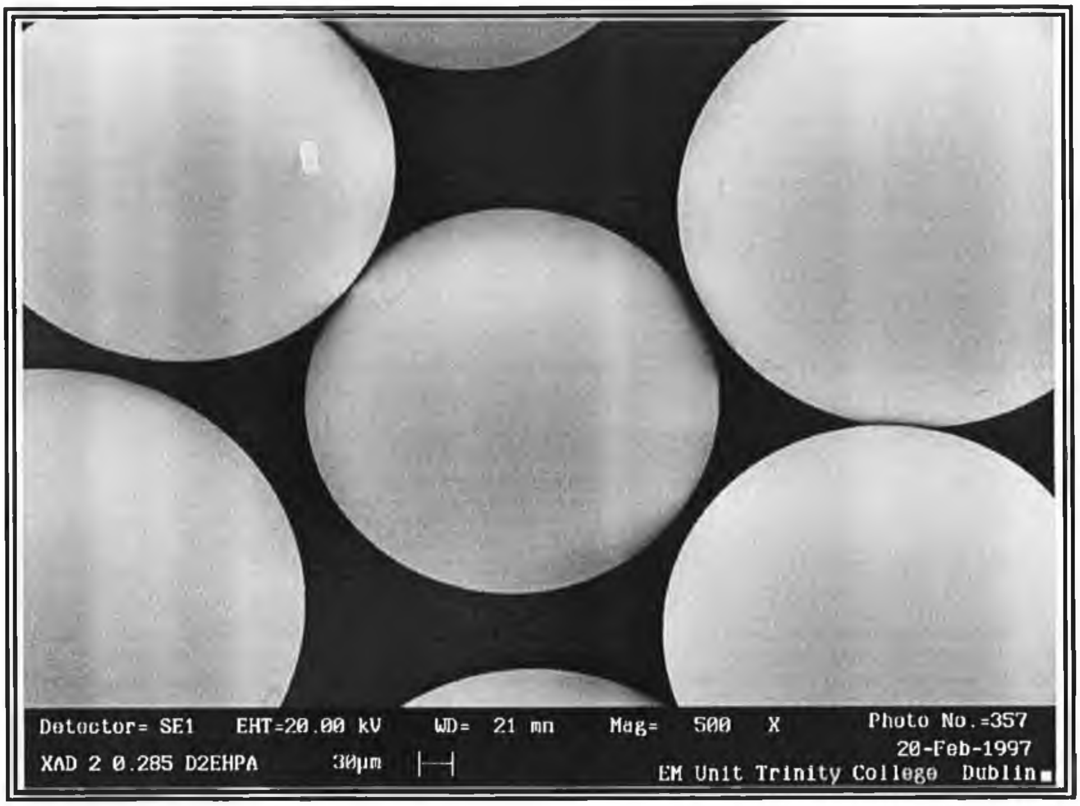


Fig 3.10 XAD 2 impregnated resin (0.285g D2EHPA/g). Magnification: 500X.

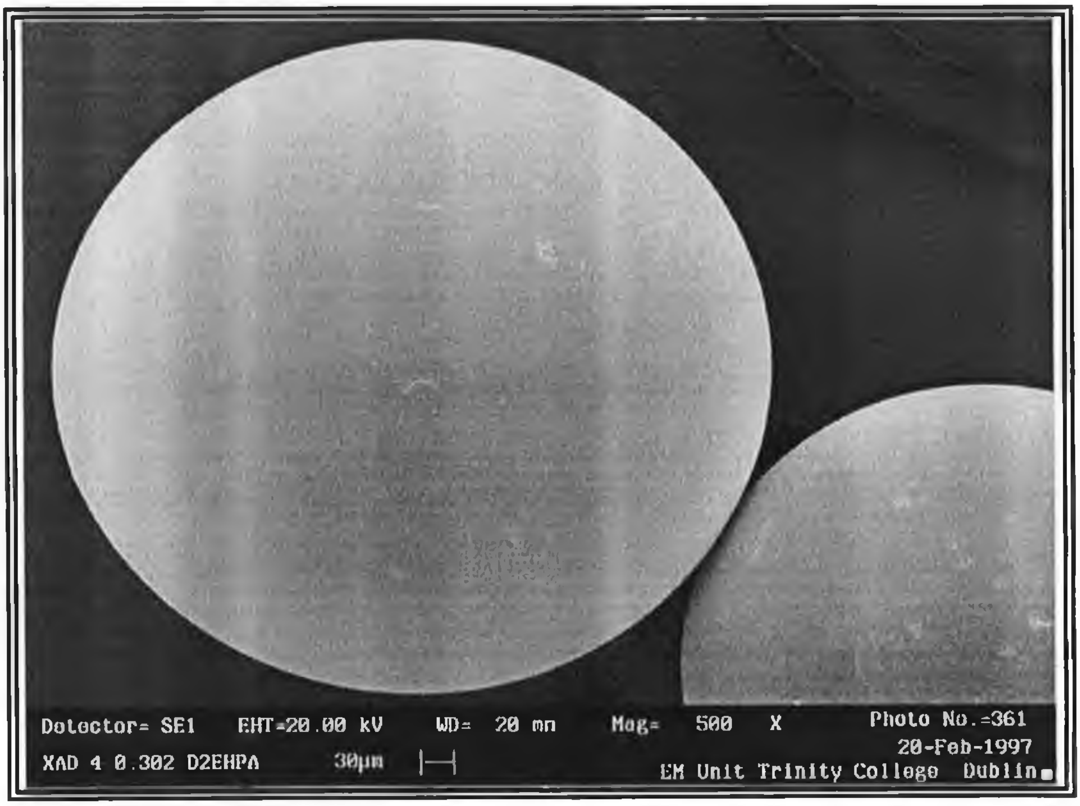


Fig 3.11 XAD 4 impregnated resin (0.302g D2EHPA/g). Magnification: 500X.

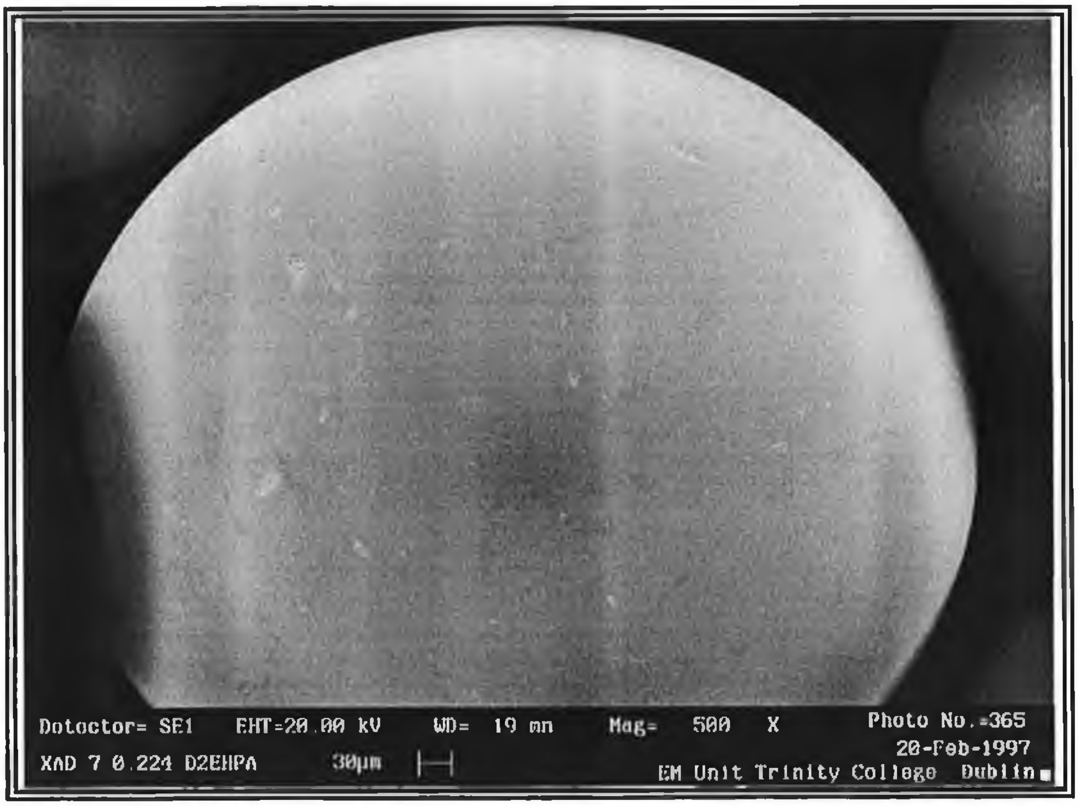


Fig 3.12 XAD 7 impregnated resin (0.224g D2EHPA/g). Magnification: 500X.

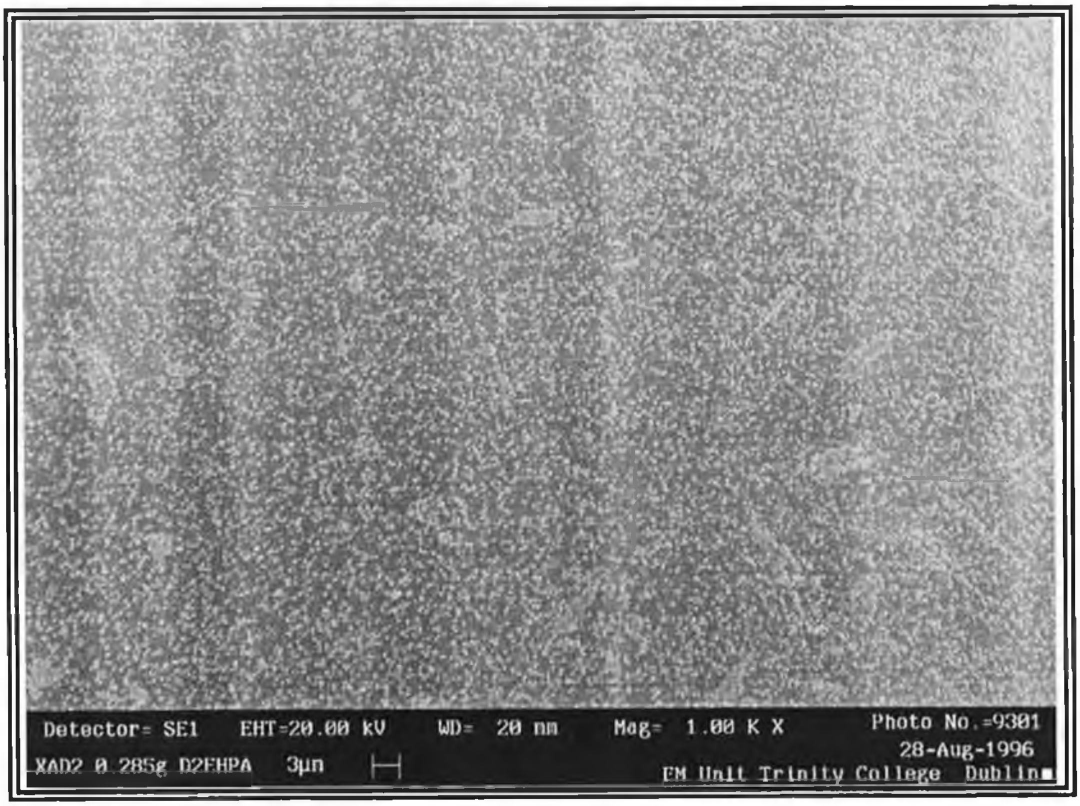


Fig 3.13 XAD 2 impregnated resin (0.285g D2EHPA/g). Magnification: 1,000X.

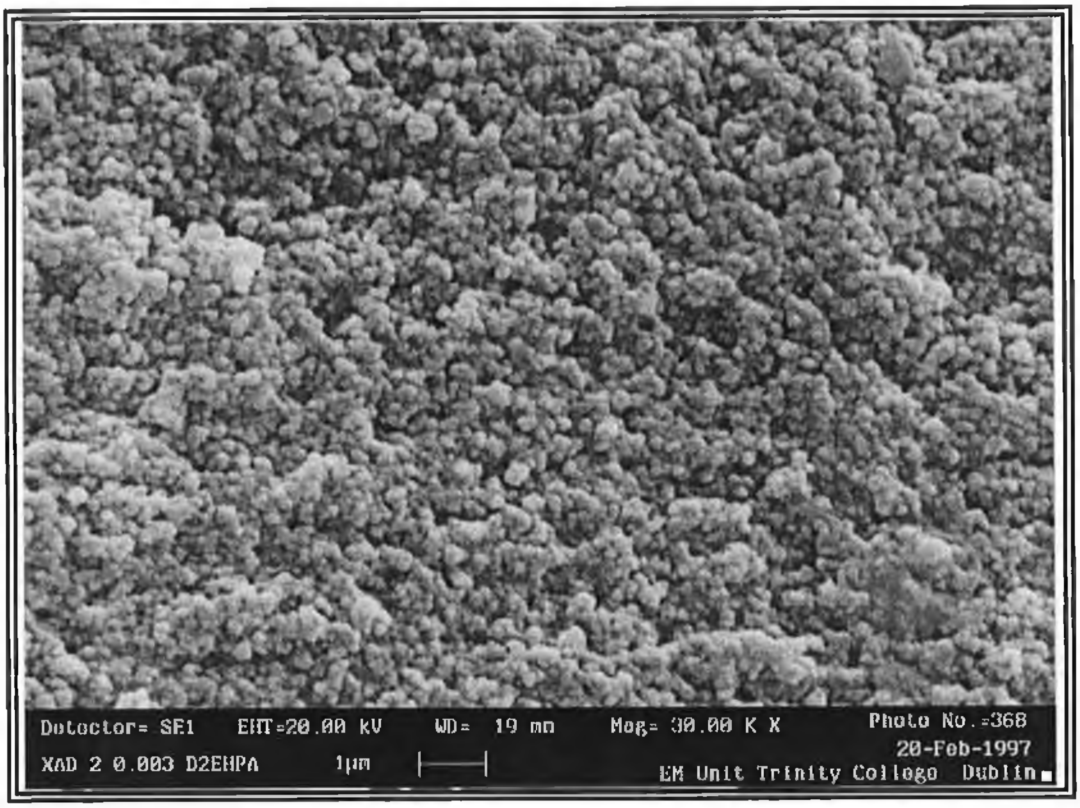


Fig 3.14 Fractured XAD 2 impregnated resin (0.003g D2EHPA/g). Magnification: 30,000X.

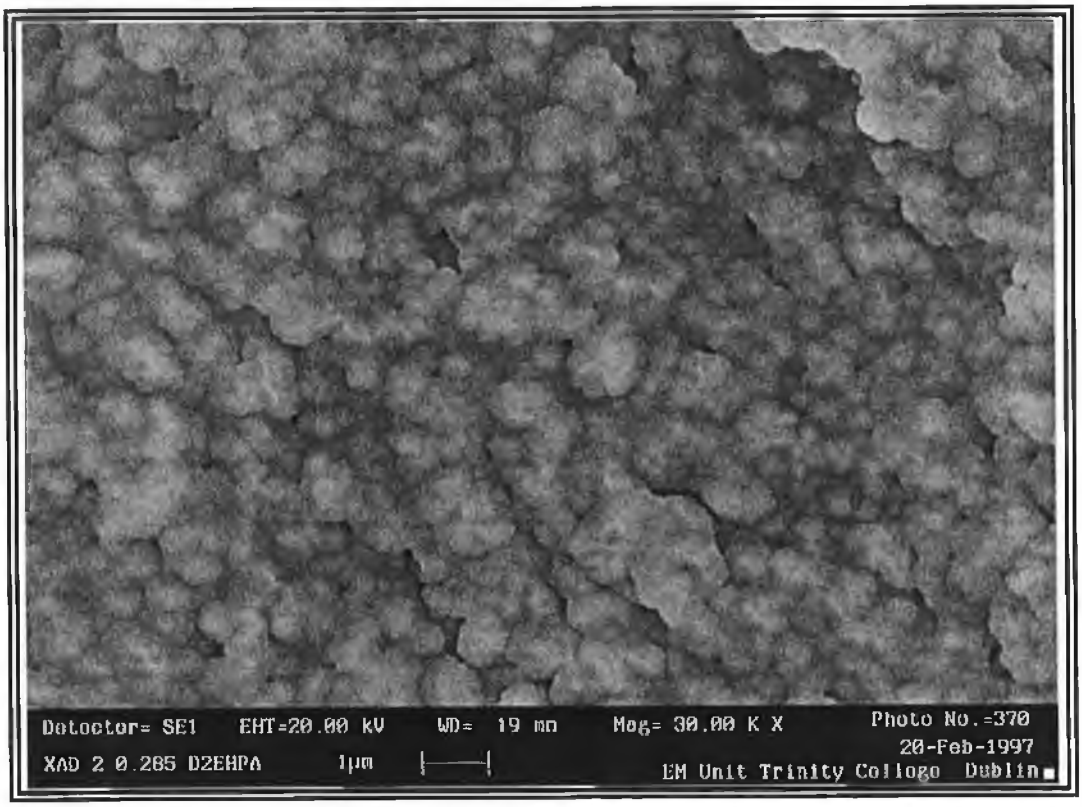


Fig 3.15 Fractured XAD 2 impregnated resin (0.285g D2EHPA/g). Magnification: 30,000X.

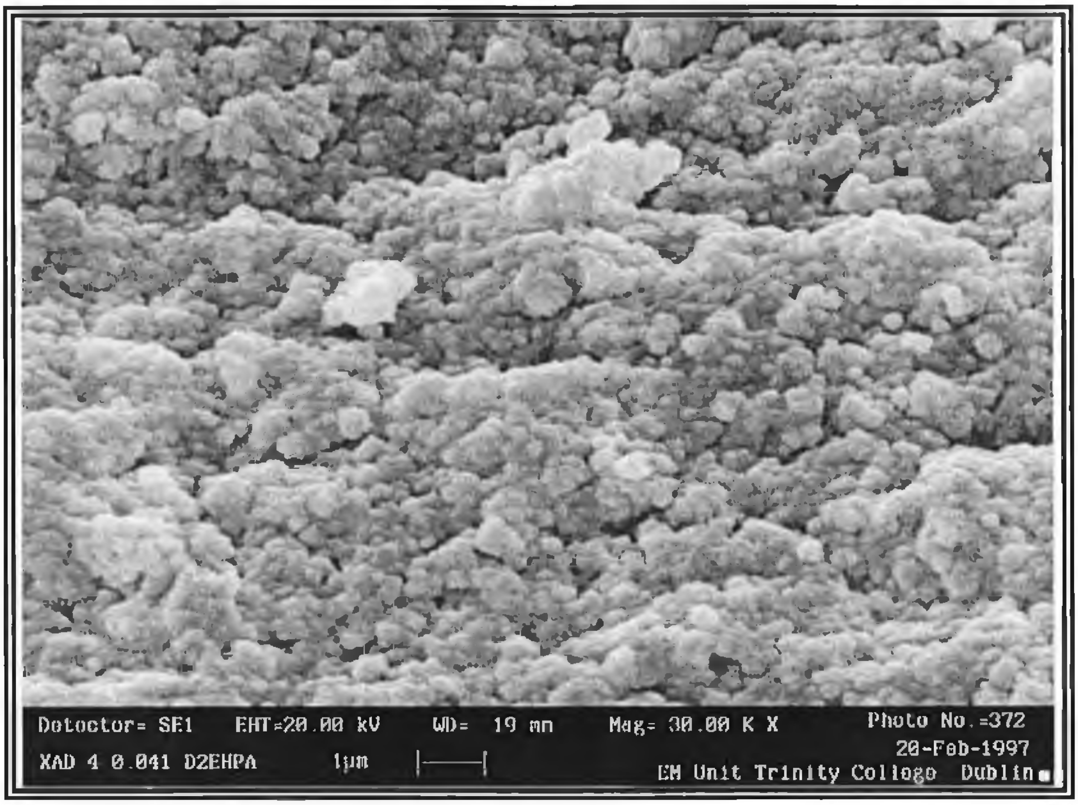


Fig. 3.16 Fractured XAD 4 impregnated resin (0.041g D2EHPA/g)
Magnification: 30,000X

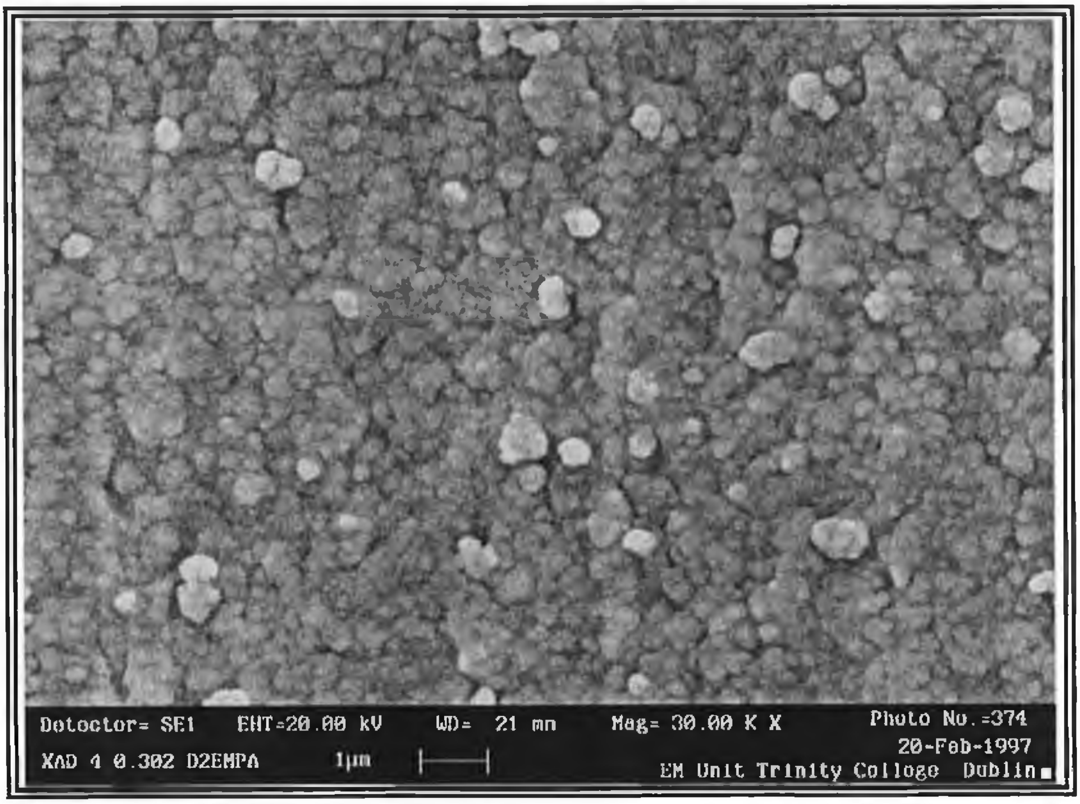


Fig. 3.17 Fractured XAD 4 impregnated resin (0.302g D2EHPA/g)
Magnification: 30,000X

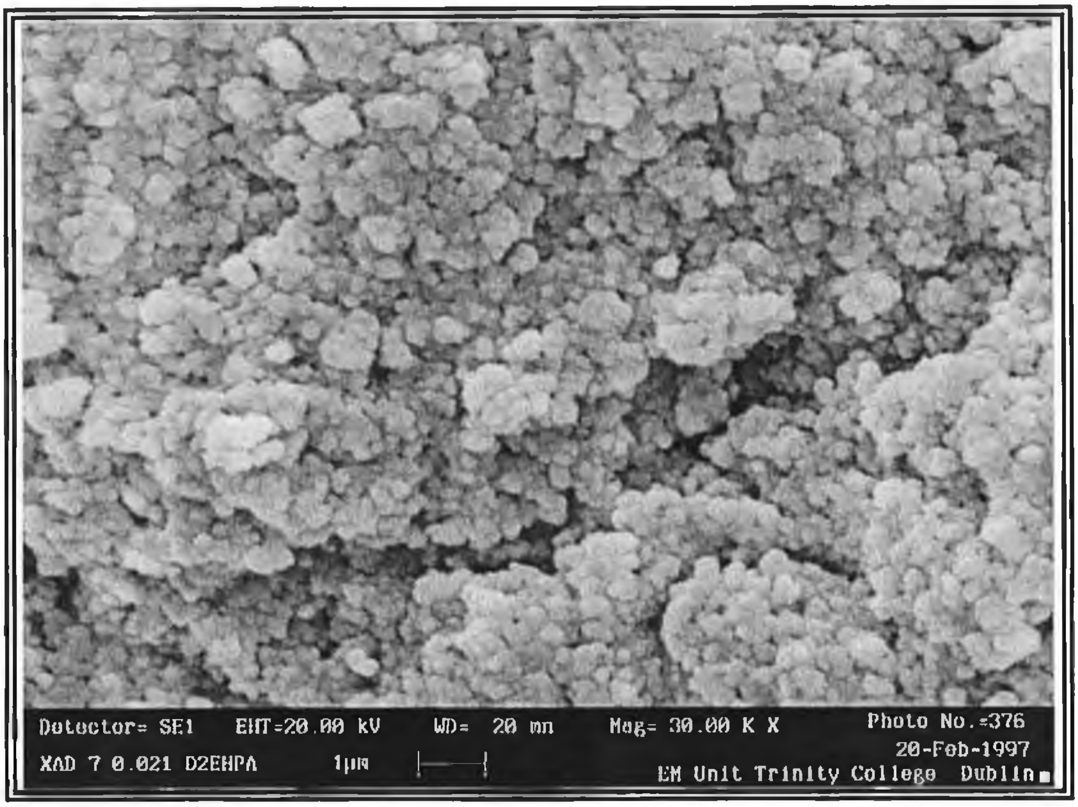


Fig. 3.18 Fractured XAD 7 impregnated resin (0.021g D2EHPA/g)
Magnification: 30,000X

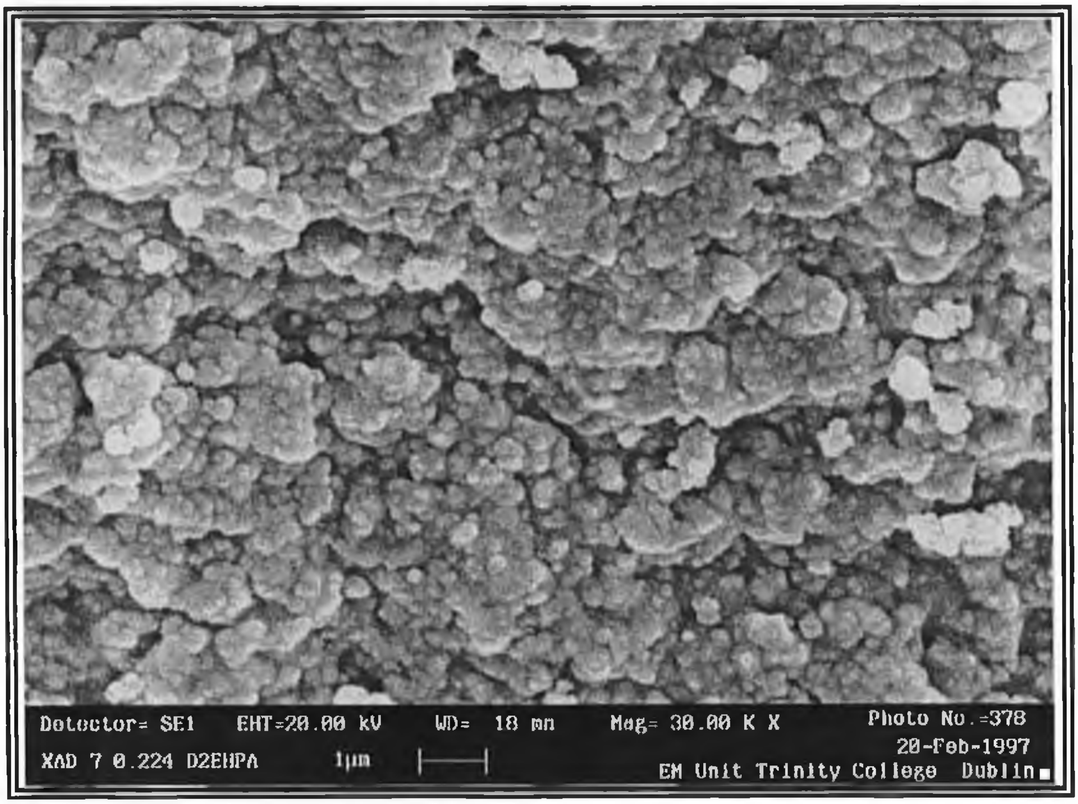


Fig. 3.19 Fractured XAD 7 impregnated resin (0.224g D2EHPA/g)
Magnification: 30,000X

References

1 Comparison Between Liquid-Liquid Extraction and Impregnated Resin Systems. The Extraction of Au(III) From Chloride Media By Tri-n-Dodecylammonium Chloride. I. Villaescusa, M. Aguilar, J. de Pablo, M. Valiente and V. Salvado. Proceedings of the International Solvent Extraction Conference. T. Sekine (Ed), pp 171-176, (1990).

2 Liquid-Solid Extraction of Gold(III) from Aqueous Chloride Solutions by Macroporous Resins Impregnated with Triisobutyl Phosphine Sulphide (Cyanex 471). I. Villaescusa, V. Salvadó, J. De Pablo, M. Valiente and M. Aguilar. Reactive Polymers, Vol. 17 , pp 69-73, (1992).

3 Solvent Impregnated Resins Containing Di- (2-Ethylhexyl) Phosphoric Acid. I. Preparation and Study of the Retention and Distribution of the Extractant on the Resin. J.L. Cortina, N. Miralles, M. Aguilar and A.M. Sastre. Solvent Extraction and Ion Exchange, Vol. 12, Part 2, pp 349-369 (1994).

4 University Physics, 7th Edition. F. W. Sears, M.W. Zemansky and H. D. Young. Addison-Wesley Publishing Company.

5 Extraction with Solvent Impregnated Resins. A. Warshawsky. Ion Exchange and Solvent Extraction Vol. 8, Chapter 3. J. A. Marinsky and Y. Marcus (Eds), Marcel Dekker (1981).

6 Amberlite XAD Polymeric Adsorbents. Information Booklet. Rohm and Haas Company, (1995).

7 Dissolution Chemistry of Gold and Silver in Different Lixiviants. J. Brent Hiskey and V.P. Atluri. Mineral Processing and Extractive Metallurgy Review. Vol. 4, pp 95-134, (1988).

Chapter 4

The Recovery of Bis-Thiourea Gold Perchlorate Using Solvent Impregnated Resins

4.1 Preparation of Gold Solutions for Recovery from Solution

Gold solutions were prepared by the dissolution of solid bis-thiourea gold(I) perchlorate ($[AuTu_2]ClO_4$). $[AuTu_2]ClO_4$ was prepared by reacting thiourea perchlorate with tetrachloroauric acid. The procedure was taken from Kazakov (1), as modified by Bowden (2). This reaction is given below:

$$Tu_2HClO_4 + HAuCl_4 \longrightarrow Cl_2 + 2HCl + [AuTu_2]ClO_4$$

4.1.1 Preparation of Thiourea Perchlorate

Thiourea (9g) was dissolved in perchloric acid ($HClO_4$) (50ml), with gentle heating (caution: $HClO_4$ can react violently with organic compounds). Cold deionised water was added and the solution was cooled on ice. After about 10 minutes, white needle-like crystals of thiourea perchlorate (Tu_2HClO_4) were formed. These were filtered on a büchner funnel and dried in a desiccator overnight. The crystals were stored in a refrigerator to prevent decomposition.

4.1.2 Preparation of Bis-Thiourea Gold(I) Perchlorate

Thiourea perchlorate (Tu_2HClO_4) (0.8g) was dissolved in 15ml of deionised water; tetrachloroauric acid ($HAuCl_4$) (0.4g) was dissolved in 20ml of deionised water. The Tu_2HClO_4 solution was slowly added to the $HAuCl_4$ solution to form the $[AuTu_2]ClO_4$ complex and the solution cooled on ice. The fine crystalline precipitate formed was filtered and dried in a desiccator prior to use.

4.1.3 Confirmatory Analysis

Atomic absorption spectrophotometry analysis of the synthesised bis-thiourea gold(I) perchlorate showed that the complex contained 39.70% gold. The stoichiometric concentration of gold in bis-thiourea gold(I) perchlorate is 43.9%. The lower value in this case may have been due to the recrystallisation of thiourea perchlorate or thiourea during synthesis of the complex. The melting point of the complex was 201.9°C, which is slightly below the previously reported value of 203.2°C (3).

Infra-red spectra for thiourea and bis-thiourea gold(I)perchlorate are given in Figs. 4.1 and 4.2. The main ir vibrational bands for thiourea and bis-thiourea gold(I)perchlorate are given in Table 4.1 below. The changes in the vibrational bands of thiourea perchlorate after complexation with Au are outlined briefly.

Vibrational Mode	**Thiourea**	**Thiourea Gold Perchlorate**	**Changes in Thiourea Vibrational Bands on Complexation**
	Wavenumber (cm^{-1})		
N-H Stretching	Broad band between 3500 and 3000	Broad band between 3500 & 3000	No significant change.
N-H Bending	1618.5	1618.1	No significant change.
N-C-N Stretching	1470.3	1495.9	C-N bond becomes more like double bonds, energy and therefore frequency increases.
N-C-S Stretching	1414.3	1394.3	Decrease in C-S stretching frequency due to decrease in bond order from double to single.
NH Rocking	1085.0	1086.8	No significant change.
C=S Stretching	730.8	709.3	Decrease in C-S stretching frequency due to decrease in bond order from double to single.

Table 4.1 Infra red vibrational bands for thiourea and gold(I)thiourea perchlorate.

The N-H absorption bands in the thiourea spectrum were not shifted to lower frequencies on the formation of the gold-thiourea complex. This indicates that nitrogen to metal bonds are not present and that bonding in the complex must therefore be between the sulphur and gold atoms. The formation of a S→Au bond increases the polarity of the thiourea molecule, resulting in a greater double bond character for the nitrogen to carbon bond and a greater single bond character for the carbon to sulphur bond (3). See Fig. 4.3.

4.2 Analysis of Gold in Solution

The concentration of gold in solution was determined by atomic absorption spectrophotometry (AAS). AAS is a method of elemental analysis, based on the absorption, by atoms, of electromagnetic radiation. If a solution containing a metallic compound is aspirated into a flame, a vapour which contains atoms of the metal may be formed. These atoms are capable of absorbing radiant energy of their own specific resonance wavelength, which will promote the atoms from their ground state level to an excited energy state. If electromagnetic radiation of the atoms particular resonance wavelength is shone through the flame, then part of the light will be absorbed by the atoms. The portion of the electromagnetic radiation which is absorbed by the free atoms is recorded by the instrument. The extent to which absorption occurs is proportional to the concentration of atoms in the flame (4).

Two instruments were used for this work; these were a Shimadzu 670AA and a Varian Spectra AA-200. Conditions for analysis are given below.

4.2.1 Instrument Conditions:

Element:	Au
Slit width:	0.5 nm
Wavelength:	242.8 nm

4.2.2 Flame Conditions:

Flame:	Air-C_2H_2
Oxidant:	8.0 $dm^3\ min^{-1}$
Fuel:	1.6 $dm^3\ min^{-1}$
Burner:	10 cm
Height:	6 mm

4.2.1 Preparation of Gold Standards for AAS Analysis

Gold standards of concentrations ranging between 2ppm and 20ppm were prepared using a stock solution of Spectrosol® grade gold chloride (1,000ppm) (supplied by BDH). The standards were reduced from gold(III) to gold(I) by the addition of excess thiourea (25 times excess). The effect on absorbance of the addition of excess thiourea was determined by comparing two sets of standard calibration curves; the first curve is for Au^{3+}standards i.e. no thiourea was added, the second curve is for Au^{+} i.e. excess thiourea was added. Absorbance values for both sets of standards are given in Table 4.2 below. A calibration curve for AAS analysis of gold, taken from a Varian Spectra AA 200 is given in Fig. 4.4.

SET 1: Au^{3+} (no excess thiourea)		**SET 2: Au^{+}(25X excess thiourea)**	
Standard concentration (ppm)	**Absorbance Values**	**Standard concentration (ppm)**	**Absorbance Values**
Cal Zero	-0.0003	Cal Zero	-0.0013
2	0.0728	2	0.0730
5	0.1701	5	0.1741
7	0.2358	7	0.2409
10	0.3171	10	0.3230
15	0.4426	15	0.4510
20	0.5438	20	0.5394
Characteristic Concentration = 0.12mg/L		Characteristic Concentration = 0.12mg/L	

Table 4.2 AAS absorbance values for Au^{3+} and Au^{+}.

The concentration of gold in all cases is quoted as ppm or parts per million. A one part per million solution of gold is equivalent to 1mg of gold per litre of solution. Cal zero is the absorbance value measured when deionised water is aspirated through the AAS.

The characteristic concentration of the standard calibration curve is the concentration of an analyte that would normally give an absorbance of 0.0044 or 1% absorbance (5). It is calculated from the linear portion of the graph (based on absorbances < 0.2), using the equation:

$$\text{Characteristic Concentration} = \frac{\text{Standard concentration x 0.0044}}{\text{Mean Absorbance}}$$

The characteristic concentration of a calibration curve is a convenient way to compare two sets of standard calibration curves. If the characteristic concentration of the curves is the same, then it is possible to compare the two calibration curves. In this case, agreement between the two sets of data indicates that excess thiourea does not affect absorbance values.

4.3 Initial Tests on the Recovery of Gold by the Resins

Initial tests on the bare resins were carried out in order to establish the optimum conditions for gold recovery.

4.3.1 Experimental Conditions

The resins used for all experiments were XAD 2, XAD 4 and XAD 7 Amberlite resins (supplied by Rohm & Haas). Their recovery properties were studied as bare resins and when impregnated with di-2-ethylhexyl phosphoric acid (D2EHPA) (supplied by BDH). In each case, 1g of resin was contacted with 100ml of gold solution. All chemicals used were reagent grade and all experiments were carried out at ambient temperature and pressure.

4.4 Study of the Effect of pH on the Recovery of Gold by the Bare Resins

The effect of pH on the efficiency of the resins was tested by contacting the resin (1g) with gold solutions (100ml) of pH values ranging from 1.5 to 4.5. The resins were shaken for three hours in a sealed polypropylene container on a Stuart Scientific Flask Shaker. The study was limited to acidic solutions since the gold(I)thiourea complex is only stable in an acidic solution (6).

Results

1. XAD 2

pH	Initial Concentration (ppm)	Final Concentration (ppm)	% Gold Recovered by Resin
1.5	14.58	13.44	7.75
2.5	13.39	11.02	17.68
3.5	14.76	10.78	26.94
4.5	13.87	9.70	30.07

Table 4.3 The recovery of gold by XAD 2 bare resin at varying pH.

2. XAD 4

pH	Initial Concentration (ppm)	Final Concentration (ppm)	% Gold Recovered by Resin
1.5	17.30	13.52	21.85
2.5	17.30	12.32	28.78
3.5	17.30	11.77	31.97
4.5	17.30	10.71	38.09

Table 4.4 The recovery of gold by XAD 4 bare resin at varying pH.

3. XAD 7

pH	Initial Concentration (ppm)	Final Concentration (ppm)	% Gold Recovered by Resin
1.5	21.83	16.29	25.38
2.5	23.06	17.27	25.11
3.5	22.13	15.95	27.93
4.5	23.66	14.98	36.69

Table 4.5 The recovery of gold by XAD 7 bare resin at varying pH.

The pH of the aqueous solution significantly affects the recovery efficiency of the resins. The percentage recovery increases from 7.7% to 30.1% for XAD 2 resins, 28.9% to 38.1% for XAD 4 and from 25.6% to 36.7% for XAD 7 as the pH increases from pH 1.5 to pH 4.5. However, the recovery of gold from solution in all cases is low.

4.5 Study of the Kinetics of Recovery of Gold onto the Bare Resins

The three bare resins (1g) were contacted with a bis-thiourea gold solution (100ml). The resins were shaken in a sealed polypropylene container. Samples for analysis (5ml) were taken at 1, 3, 6 and 24 hours and the gold remaining in solution was analysed by Atomic Absorption Spectrophotometry. The mass recovered by the resin was taken as the difference between the initial and final concentration of gold in solution, after subtracting the mass of gold taken from solution during sampling. The pH of the solution was 3.5.

Results

1. XAD 2

Time (Hours)	Concentration of Au Remaining (ppm)	Mass of Au Adsorbed (mg)	% Gold Recovered
1	11.97	0.41	25.57
3	11.72	0.43	26.82
6	11.88	0.42	26.20
12	11.87	0.42	26.20
24	11.03	0.50	31.19

Table 4.6 The recovery of gold by XAD 2 bare resin over time. $[Au^+]_0$= 16.03ppm.

2. XAD 4

Time (Hours)	Concentration of Au Remaining (ppm)	Mass of Au Adsorbed (mg)	% Gold Recovered
1	10.87	0.52	32.44
3	10.60	0.54	33.69
6	10.90	0.51	31.82
12	10.81	0.52	32.44
24	10.56	0.55	34.31

Table 4.7 The recovery of gold by XAD 4 bare resin over time. $[Au]_0 = 16.03$ppm

3. XAD 7

Time (Hours)	Concentration of Au Remaining (ppm)	Mass of Au Adsorbed (mg)	% Gold Recovered
1	11.74	0.43	26.82
3	11.68	0.44	27.45
6	11.81	0.42	26.20
12	11.66	0.44	27.45
24	11.49	0.45	28.07

Table 4.8 The recovery of gold by XAD 7 Bare resin over time. $[Au]_0 = 16.03$ppm.

The mass of gold recovered by the bare resins after one hour was low, between 0.4mg and 0.5 mg. Recovery does not improve significantly after the first hour and even after 24 hours gold recovery remains at approximately 0.5mg. It would appear that equilibrium loading of the bare resins has occurred within the first hour. Although the rate of loading is relatively fast, the extent of loading is quite low.

4.6 Initial Tests on the Adsorption of Gold by Solvent Impregnated Resins

Initial tests on the efficiency of XAD 2, XAD 4 and XAD 7, as solvent impregnated resins, for the recovery of bis-thiourea gold, were similar to the tests on the bare resins and the experimental procedures are the same in both cases.

4.6.1 Study of the Effect of pH on the Recovery of Gold by the Impregnated Resins

Results

1. **XAD 2**

pH	Initial Concentration of Au^+ (ppm)	Final concentration of Au^+ (ppm)	% Gold Recovered
1.5	19.31	18.33	5.1
2.5	21.62	9.63	55.48
3.5	18.75	3.68	80.39
4.5	19.21	3.60	81.26

Table 4.9 The recovery of gold by XAD 2 impregnated resin at varying pH. XAD 2: 0.124g D2EHPA/g.

2. **XAD 4**

pH	Initial Concentration of Au^+ (ppm)	Final concentration of Au^+ (ppm)	% Gold Recovered
1.5	20.70	17.60	14.98
2.5	18.26	1.88	90.46
3.5	21.15	0.34	98.41
4.5	20.49	0.38	98.16

Table 4.10 The recovery of gold by XAD 4 impregnated resin at varying pH. XAD 4: 0.381gD2EHPA/g.

3. XAD 7

pH	Initial Concentration of Au^+ (ppm)	Final concentration of Au^+ (ppm)	% Gold Recovered
1.5	21.83	16.27	25.47
2.5	23.06	7.43	67.78
3.5	22.13	1.50	93.21
4.5	23.66	0.62	97.37

Table 4.11 The recovery of gold by XAD 7 impregnated resin at varying pH. XAD 7: 0.344g D2EHPA/g.

The effect of pH on the impregnated resins is more apparent for the impregnated resins than for the bare resins. XAD 2 impregnated resin recovered over 80% of gold in solution at a pH of 3.5, this compares very favourably with a recovery rate of 26.94% for the bare resin under similar conditions. For XAD 4 and XAD 7 resins, the recovery efficiency had increased to over 90% at a pH of 3.5, again comparing very favourably with their bare counterparts.

The pH dependence of the impregnated resins is related to the distribution ratio of D2EHPA (the distribution ratio, for a given metal, is the ratio of the total metal concentration in the organic solvent phase to the total metal concentration in the aqueous phase). The distribution ratio for systems involving D2EHPA in sulphuric acid decreases rapidly at H_2SO_4 concentrations higher than 0.1M. This is due to the enhanced stability of the anionic sulphato-D2EHPA complexes at higher concentrations, which inhibits the extraction of gold by D2EHPA (8).

For all subsequent work, the pH of the aqueous bis-thiourea gold solution was adjusted to pH 3.5 so that optimal gold recovery could be achieved without affecting the stability of the gold thiourea complex in solution (since previous work has indicated that the complex may be unstable above a pH of approx. 4 (7)).

Although the level of impregnation of the resins is not exactly the same for each of the three resins and in the case of XAD 2 is significantly lower, it is still possible to compare the initial recovery levels, since it is the resins *capacity*, rather than its efficiency which is dictated by the level of impregnation of the resins. This is dealt with in more detail in section 4.7.

4.6.2 Study of the Recovery of Gold by the Impregnated Resins over Time

In this case, 5ml samples were taken every 10 minutes for the first hour and again at 2 hours.

Results

1. XAD 2 Impregnated

Time (minutes)	Concentration of Au remaining (ppm)	Mass of Au Adsorbed (mg)	% Gold Recovered
10	16.27	0.57	25.93
20	10.62	1.05	49.80
30	6.61	1.40	67.96
40	6.03	1.43	70.31
50	4.15	1.58	79.21
60	3.80	1.60	80.76
120	3.64	1.59	81.39

Table 4.12 The recovery of gold by XAD 2 impregnated resin over time. XAD 2 resin 0.124g D2EHPA/g, $[Au^+]_0$= 19.90ppm.

2. XAD 4 Impregnated

Time (minutes)	Concentration of Au remaining (ppm)	Mass of Au Adsorbed (mg)	% Gold Recovered
10	10.53	1.10	51.00
20	5.68	1.50	71.47
35	3.58	1.67	80.75
45	2.55	1.75	85.35
55	1.91	1.80	88.27
120	1.49	1.83	90.19

Table 4.13 The recovery of gold by XAD 4 impregnated resin over time. XAD 4 resin 0.126g D2EHPA/g, $[Au^+]_0$=21.49ppm.

3. XAD 7 Impregnated

Time (minutes)	Concentration of Au remaining (ppm)	Mass of Au Adsorbed (mg)	% Gold Recovered
10	14.42	0.55	27.54
20	10.73	0.91	45.84
30	6.76	1.30	65.81
40	3.81	1.59	80.70
50	2.10	1.76	89.36
60	1.77	2.20	89.16
120	1.51	1.82	92.34

Table 4.14 The recovery of gold by XAD 7 impregnated resin over time. XAD 7 resin 0.106g D2EHPA/g, $[Au^+]_0$= 19.90ppm.

In comparison with the bare resins, recovery efficiency of the impregnated resins has increased significantly. Within 1 hour of agitation, each of the three impregnated resins had recovered between 80% and 90% of all gold in solutions. Graphs 4.1, 4.2 and 4.3 show the recovery of gold by the three resins over time. Again XAD 2 had the lowest level of recovery at 80.16% after 1 hour, XAD 4 recovered 88.3% of gold after 55 minutes and XAD 7 recovered 89.2% after 1 hour.

4.7 Effect of the Level of Impregnation on the Recovery of Gold

The mass of solvent impregnated onto the resins can be controlled, to some extent, by varying the concentration of solvent in the initial D2EHPA/CH_3OH impregnation solution (Sec. 3.6). The mass of gold recovered from solution at equilibrium, by resins at increasing levels of impregnation, was studied by contacting a series of resins (1g), impregnated to varying levels of D2EHPA, with a gold solution (100ml). The percentage recovery at equilibrium was determined by AAS.

Results

1. XAD 2

Level of Impregnation of resin (g/g)	Mass of Gold Recovered after 1 hour (mg)	% Gold Recovered
0.003	0.53	25.37
0.029	0.82	39.12
0.074	1.19	56.99
0.124	1.68	80.73
0.285	1.67	80.25

Table 4.15 The recovery of gold by XAD 2 impregnated resins at varying levels of impregnation. $[Au^{+}]_0 = 20.81$ppm.

2. XAD 4

Level of Impregnation of Resin (g/g)	Mass of Gold Recovered after 1 hour (mg)	% Gold Recovered
0.019	1.47	68.55
0.042	1.73	80.62
0.075	0.83	85.09
0.107	1.95	91.05
0.126	0.96	91.10

Table 4.16 The recovery of gold by XAD 4 impregnated resins at varying levels of impregnation. $[Au^{+}]_0 = 21.46$ppm.

3. XAD 7

Level of Impregnation of Resin (g/g)	Mass of Gold Recovered after 1 hour (mg)	% Gold Recovered
0.001	0.96	45.13
0.002	1.12	52.25
0.010	1.42	66.38
0.109	1.89	88.65
0.137	1.91	89.21

Table 4.17 The recovery of gold by XAD 7 impregnated resins at varying levels of impregnation. $[Au^+]_0$= 21.36ppm.

Graphs 4.4, 4.5 and 4.6 show the change in the efficiency of the resins with the change in the level of impregnation of the resin. The graphs illustrate the gradual increase in the recovery efficiency of the resins with increasing levels of impregnation.

XAD 2 efficiency increases steadily with D2EHPA impregnation, to a maximum of over 80% for XAD 2, 0.124g D2EHPA/g. The percentage recovery by the resins at lower levels of impregnation is low and would not be sufficient for the efficient recovery of gold from solution. Once the impregnation level reaches a certain level, the recovery remains at its maximum for the particular system studied.

For XAD 4 resins, recovery is much more efficient. The level of impregnation of the resins was kept low so that the gradual increase in gold recovery with increasing impregnation could be seen. However, even at low levels of impregnation, the recovery efficiency of the XAD 4 impregnated resins is much better than the XAD 2 impregnated resins. At an impregnation level of 0.042g D2EHPA/g XAD 4 the recovery efficiency of the resin is 80.62%. The recovery of gold by the resin increases to over 90% for resins impregnated with 0.107g of D2EHPA or higher.

For XAD 7 resins, recovery is again much better than recovery by the XAD 2 impregnated resins, although they are not as good as the XAD 4 resins. The recovery of gold by the resins is again seen to gradually increase with the increase in the level of solvent impregnated onto the resin.

Graphs 4.4, 4.5 and 4.6, show the gradual increase in the efficiency of the resins with increased impregnation. They also indicate the minimum level of impregnation necessary to ensure each of the three resins will initially recover gold at its maximum level of efficiency, under the given set of conditions. Resins which are impregnated to this level or higher, should initially recover gold at a similar level of efficiency. The distinction between resins at higher levels of impregnation should only become apparent when the *total mass of gold added to solution* is increased. In this case the level of impregnation should influence the *final capacity* of the resin for gold and it would be expected that resins at higher levels of impregnation should remain efficient over a longer period of time and should eventually recover a higher mass of gold. This is discussed in more detail in Chapter 5.

It should be noted that it is possible to compare the *initial* recovery rates of resins at different levels of impregnation, once the levels are higher than the minimum level required for maximum recovery (indicated on the graphs). The minimum level of impregnation for each of the resins, for the efficient recovery of gold under the given set of conditions is given in Table 4.18.

Resin	**Minimum Required Level of Impregnation (g D2EHPA/g resin)**
XAD 2	0.124
XAD 4	0.107
XAD 7	0.109

Table 4.18 The minimum required level of impregnation for each resin.

4.8 Determination of the Theoretical Capacity of the Resins for Gold by the Application of Adsorption Isotherms.

The resins used in this study are described as 'polymeric adsorbent resins' (10). They are highly porous structures whose internal surfaces can adsorb and then desorb a variety of species in solution. They are non-ionic and so no exchange of ions between the resin and the solution should take place. The bare resins are therefore assumed to recover gold from solution purely by simple adsorption.

4.8.1 Adsorption of Gold by the Resins

Adsorption is a term used to describe the existence of a higher concentration of any particular substance at the surface of a liquid or solid than is present in the bulk of the medium (usually liquid or gas) (11). It can be categorised into two main types, physisorption and chemisorption.

Physisorption, or physical adsorption involves weak Van der Waals forces between the adsorbate (i.e. the substance that is adsorbed) and the adsorbent (i.e. the material that adsorbs). It is characterised by relatively low heats of adsorption and ease of desorption.

Chemisorption or chemical adsorption involves chemical forces of interaction between the adsorbent and adsorbate. Heats of adsorption are much higher than for physisorption. Chemisorption is not reversible.

4.8.2 Adsorption from Solutions

Most studies carried out on adsorption refer to the adsorption of gases onto solids. The adsorption of particles from *solution* was first studied by J. Willard Gibbs (11). Gibbs noted that the concentration of a solution on the interfacial surface often differed to the bulk solution concentration. A thermodynamic relationship expressing this phenomena was formulated for dilute solutions having a concentration C:

$$S = -(C/RT)\, d\chi/dc \qquad (11)$$

where: S = Excess concentration of solute per cm^2 of surface (as compared to the bulk solution concentration).
$d\chi/dc$ = Rate of increase of the surface tension of the solution with the concentration of the solute.
R = Ideal gas constant ($J.mol^{-1}.K^{-1}$).
and T = Temperature (Kelvin).

From the equation, any solute which causes the surface tension of the solvent to decrease (making $d\chi/dc$ negative), will have a higher concentration on the surface than in the bulk solution, since S will become positive.

When a porous substance such as charcoal or a high surface area resin is added to the solution, the area of the solid/liquid phase interface becomes much larger, thus considerably increasing the extent of adsorption.

From Gibbs equation, it may be generally supposed that a particular particle will be adsorbed from solution by a solid adsorbent, if that particle reduces the surface tension of the solvent. Water has a high surface tension and most solutes reduce its value, therefore many substances are adsorbed from aqueous solution.

4.8.3 Adsorption Isotherms

Adsorption isotherms relate the dependence of the rate of adsorption on the concentration of the adsorbate at a constant temperature. Two of the simplest of these isotherms are the Langmuir and Freundlich isotherms. Both of these isotherms can be related to the adsorption of particles from solution. The Langmuir isotherm is based on the assumption that every adsorption site is equivalent and that the ability of a particle to bind there is independent of whether or not neighbouring sites are occupied (12). The Freundlich isotherm is a logarithmic isotherm, based on the physisorption of particles. The isotherm is empirical, that is, it has no theoretical basis but can successfully relate the rate of adsorption to solution concentration nonetheless.

The mathematical formulae used to graph these isotherms are given below:

4.8.4 Langmuir Isotherm

The Langmuir isotherm can be expressed as:

$$\frac{Q.a.C_e}{(1 + a.C_e)}$$

Where: q_e = Equilibrium solid phase solute concentration (mg/g).
x = Mass of solute adsorbed by adsorbent (mg).
m = Mass of adsorbent (g).
Q = Langmuir Monolayer Capacity (mg/g).
a = Langmuir Isotherm constant (dm^3/mg).
and C_e = Equilibrium liquid phase solute concentration (mg/dm^3).

This rearranges to the linear expression:

$$C_e/q_e = 1/K + a/K\ C_e$$

Where:
K = Langmuir Isotherm Constant (dm^3/g) = Q.a.

K and a are Langmuir isotherm constants for a particular solute/solvent system. Since Q = K/a, plotting Ce/qe vs Ce should give a linear graph whose slope corresponds to 1/Q or 1/capacity (mg/g).

The Langmuir isotherm assumes coverage of the solid is limited to a monomolecular layer. Equilibrium is reached when every site on the surface of the resin is occupied by a molecule from solution. Some evidence of this type of behaviour has been found, particularly when chemisorption is the relevant adsorption process (12). The relationship between monomolecular coverage and chemisorption can be explained to some extent by the very rapid decrease in chemical interactions with distance. Since chemical forces are required for chemisorption and the attraction between the surface of the solid and the molecules in solution decrease rapidly after one layer of coverage, adsorption is limited to only one layer.

When Van der Waals forces are involved in the adsorption process e.g. physisorption, the forces of attraction can extend beyond one layer of molecules and can adsorb up to several layers of molecules. In this type of adsorption, equilibrium goes beyond monomolecular coverage.

4.8.5 Freundlich Isotherm

The linear form of this isotherm can be given as:

$$\mathbf{Log}\ q_e = \mathbf{Log}\ K + n\ \mathbf{Log}\ C_e$$

Where:

K = Freundlich Constant

and **n** = Freundlich Exponent

The Freundlich isotherm is often in close agreement with the Langmuir isotherm (12). It is however an empirical adsorption isotherm i.e. its validation comes from experimental agreement rather than any theoretical reasoning. As such, very little practical information can be obtained from the isotherm, in particular, no value for the theoretical capacity of the resins can be deduced from agreement with the isotherm.

4.9 Adsorption Study of Resins

The resins (1g) were contacted with gold solutions of varying concentrations (10ppm-50ppm) and the level of gold recovery at equilibrium was determined. From the results, Langmuir and Freundlich isotherms were constructed to establish whether there was any agreement between experimental recovery and the theoretical isotherms applied to that recovery.

Results

4.9.1 Adsorption of Gold by Bare Resins

1. XAD 2

Initial Concentration (ppm)	Final Concentration (ppm)	Mass Adsorbed (mg)	% Adsorbed
15.40	11.24	0.42	27.01
22.66	17.70	0.49	21.89
30.92	24.53	0.64	20.66
44.87	37.57	0.73	16.27
48.04	40.24	0.79	16.38

Table 4.19 The adsorption of gold by XAD 2 bare resin at varying concentration.

2. XAD 4

Initial Concentration (ppm)	Final Concentration (ppm)	Mass Adsorbed (mg)	% Adsorbed
14.25	9.027	0.52	36.65
23.45	15.54	0.79	33.75
36.64	25.39	1.13	30.75
42.93	30.25	1.27	29.54
57.43	41.50	1.59	27.73

Table 4.20 The adsorption of gold by XAD 4 bare resin at varying concentration

3. XAD 7

Initial Concentration (ppm)	Final Concentration (ppm)	Mass Adsorbed (mg)	% Adsorbed
12.52	8.54	0.34	31.79
21.95	16.52	0.54	24.74
32.83	25.80	0.70	21.41
45.33	37.13	0.82	18.09
50.56	41.45	0.91	18.02

Table 4.21 The adsorption of gold by XAD 7 bare resin at varying concentration.

Plotting the relevant data for both the Langmuir and Freundlich isotherms, gives an indication of that particular recovery system's agreement with the isotherms. Straight line graphs were obtained for plots of both Langmuir and Freundlich isotherms. It can, therefore, be assumed that the bare resins recover gold through an adsorption process which can be described by these isotherms. The graphs also illustrate the close agreement often seen between these two isotherms.

4.9.2 Determination of the Capacity of the Bare Resins

The theoretical monolayer capacity of an adsorption system can be calculated from the Langmuir isotherm, since the Langmuir isotherm constants, a and k are related to capacity. The capacity is calculated from the graph as the inverse of the slope of that graph. The results and calculations for the three bare resins are given in Table 4.22 below.

Resin	Correlation Co-efficient (R^2)	Intercept (= 1/k)	Slope (=a/K=1/Q)	Monolayer Capacity (mg Au /g Resin)
XAD 2	0.980	18.72	0.842	1.19
XAD 4	0.984	15.29	0.271	3.69
XAD 7	0.988	16.84	0.703	1.422

Table 4.22 Theoretical monolayer capacities of the bare resins, calculated from Langmuir isotherms.

The monolayer capacities of the bare resins is very low. It is anticipated that impregnated resins should have a much more satisfactory capacity for gold.

4.9.3 Adsorption Isotherms and Solvent Impregnated Resins

The application of adsorption isotherms to the recovery of gold by solvent impregnated resins is not relevant, since recovery is not exclusively by adsorption. Although it is likely that adsorption is part of the recovery process to some extent, solvent extraction is also involved, therefore, adsorption isotherms cannot be used to calculate the monolayer capacity of the impregnated resins. Data for the adsorption of gold onto the impregnated resins was fitted to both isotherms and as expected, no significant correlation with either isotherm was seen. No experimental data for the application of adsorption isotherms to the recovery of gold by the impregnated resins is given.

4.10 Solvent Extraction of Gold From Aqueous Solution by Liquid/Liquid Extraction

Solvent extraction is a process in which a substance is transferred from one liquid phase into another immiscible liquid phase. The solvent is usually organic and the most common systems involve the extraction of metallic species from the aqueous phase into the organic phase. A more detailed account of solvent extraction is given in section 2.4.

4.10.1 A Comparison of the Recovery Efficiency of D2EHPA in Kerosene with D2EHPA Impregnated Resins

An initial test of the solvent extraction efficiency of D2EHPA in a liq/liq extraction system was performed by adding D2EHPA to kerosene (1g), similar to the system used by Simpson et al (13). The mass added ranged from between 0.019g D2EHPA per g of kerosene to 0.165g D2EHPA per g of kerosene, which are typical masses impregnated onto 1g of resin. A solution of gold (19.12ppm) (100ml) was shaken with the solvent solution for one hour on a shaker. The aqueous solution was separated in a separating funnel and analysed for gold content using AAS. Analysis showed that no gold was removed from the aqueous phase.

That no gold was recovered from the aqueous solution indicates that there was inadequate dispersal of the solvent through the aqueous phase. The small volume of organic solvent, in comparison to the volume of aqueous solution, is the most likely explanation for the failure of the solvent to recover any gold from solution. This illustrates the importance and advantages of a recovery medium which can be easily dispersed homogeneously through solution, such as S.I.R.s.

4.10.2 Study of the Recovery Efficiency of D2EHPA in Kerosene

The efficiency of D2EHPA in kerosene at percentage concentrations of 1 to 25 (% vol/vol) was studied. The initial concentration of gold in solution was 23.63ppm. A 1:1 ratio of aqueous to organic solution (50ml of each) was used.

Results

% D2EHPA	Concentration of Gold remaining in aqueous solution (ppm)	Mass of gold recovered from aqueous solution. (mg)	% Gold Recovered
1	23.19	0.022	1.86
3	20.99	0.132	11.17
5	17.30	0.317	26.83
7	13.16	0.524	44.35
10	8.49	0.759	64.24
15	4.309	0.926	81.12
20	2.187	1.032	91.42
25	1.327	1.075	94.18

Table 4.23 The recovery of gold by D2EHPA in kerosene at varying concentrations of D2EHPA. $[Au^+] = 23.63$ppm.

Graph 4.13 shows the increase in gold recovery with increasing concentration of D2EHPA. For higher concentrations of D2EHPA in kerosene, the percentage efficiency rises steadily to nearly 95% at 25% D2EHPA. The actual mass of D2EHPA needed for recovery of 90-95% is 10g to 12g D2EHPA in 50ml of kerosene. Since the same levels of recovery were achieved using resins impregnated with only 0.15g D2EHPA, S.I.R.s mark a very significant improvement in the efficient use of solvents. This has many potential advantages for industries where solvent extraction processes are used, most importantly, the decrease in the mass of solvent used by the system allows for more cost effective use of the solvent. From an environmental point of view, more efficient use of organic solvents in extraction systems, means less solvent disposal problems.

4.11 Recovery Mechanism of Solvent Impregnated Resins

The recovery of gold by solvent impregnated resins is much more efficient than recovery by the bare resins. The impregnated resins recovered between 80% and 94% of gold in solution after 1 hour, in comparison to the bare resins which only recovered between 25% and 32.15%. It is clear that the impregnation of the resins greatly enhances that resin's ability to recover gold efficiently. This indicates that solvent extraction of gold by the impregnated solvent plays a very important role in the recovery process of solvent impregnated resins. However, since the resins also recover some gold as bare resins, adsorption is also a significant mechanism. In the case of the impregnated resin, it is proposed that two separate processes are involved in the recovery of gold from solution:

1. Adsorption of gold onto the resin surface in a manner similar to recovery by the bare resins. Adsorption of particles from liquid onto solid supports is discussed in Sec. 4.8.

2. Solvent extraction of gold by the impregnated solvent (Sec. 2.4).

Since the efficiency of recovery increases so significantly upon impregnation of the resins with D2EHPA, it appears that solvent extraction is the dominant process for the recovery of gold by the S.I.R.s. The mechanism for solvent extraction by D2EHPA is cationic exchange (8). This involves the exchange of metal cations with the hydrogen ions of the reagent dissolved in the organic phase. The gold(I)thiourea complex is reported to be solvated with five molecules of the D2EHPA monomer (9). The extraction is given as:

$$[Au(CS(NH_2)_2)_2{}^+]_{aq} + 3[R_2H_2]_{org} \longrightarrow [Au(CS(NH_2)_2)_2R.5RH]_{org} + [H^+]_{aq}$$

The equilibrium constant was calculated as 0.398.

However, it is unlikely that solvent extraction is the exclusive method of extraction by a solvent impregnated resin but more likely that the overall process is a combination of both adsorption and solvent extraction. The extent to which each process contributes in the overall extraction of gold from solution has not been quantified, however the level of impregnation of the resin will affect the level to which solvent extraction contributes to the overall recovery of gold by the impregnated resin. In the case of a highly impregnated resin, more solvent is in contact with the gold solution and less sites available for bare adsorption, it therefore follows that solvent extraction will be a more significant process in this case. For a similar resin impregnated to a lesser extent, where less solvent is in contact with the gold solution and more sites are available for bare adsorption it is likely that solvent extraction will not contribute as significantly to overall recovery.

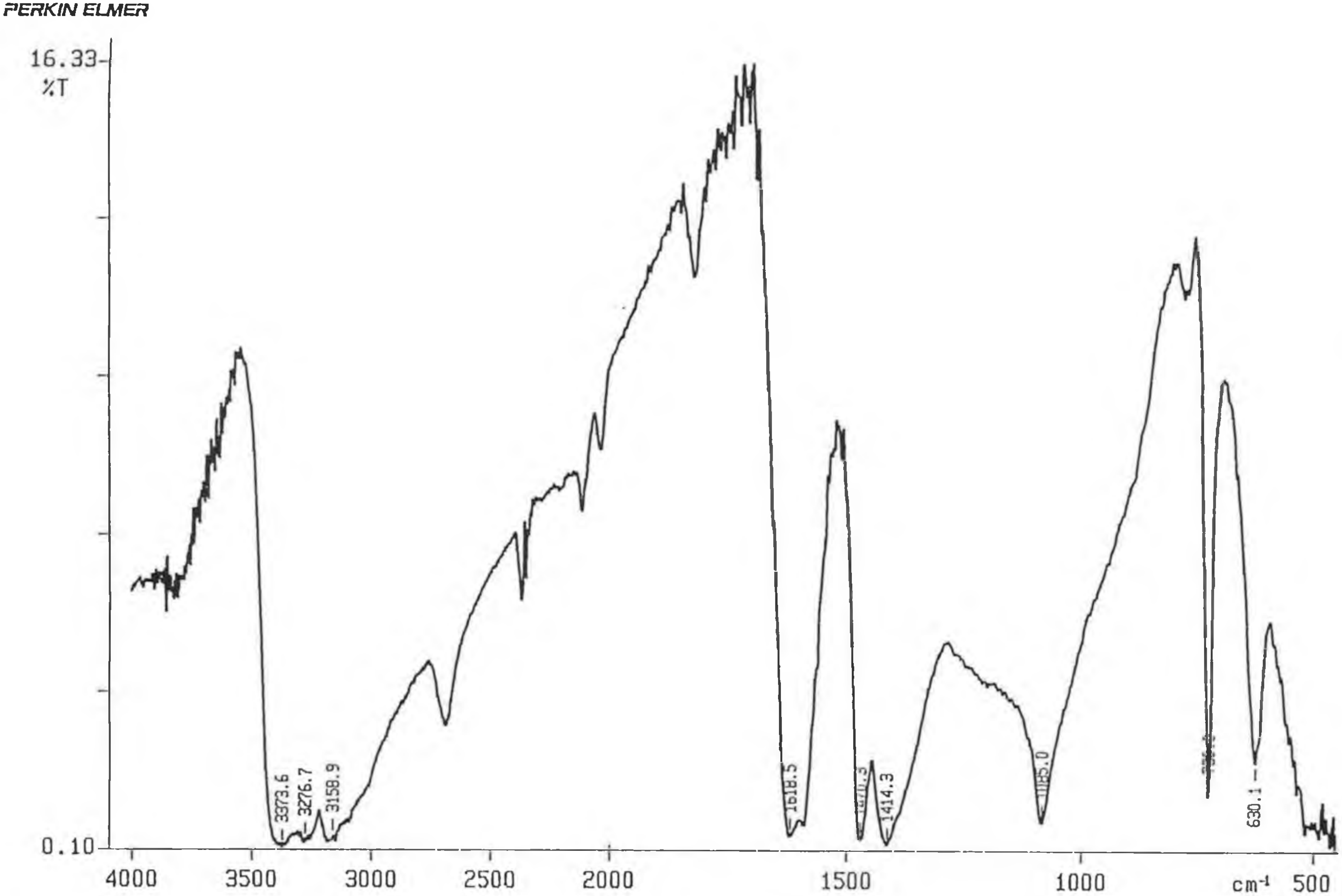


Fig. 4.1 FT-IR Spectrum of Thiourea.

97/03/26 15:24 F. FITZPATRICK
fional: 1 scan, 4.0cm-1
FT-IR THIOUREA (KBR DISC)

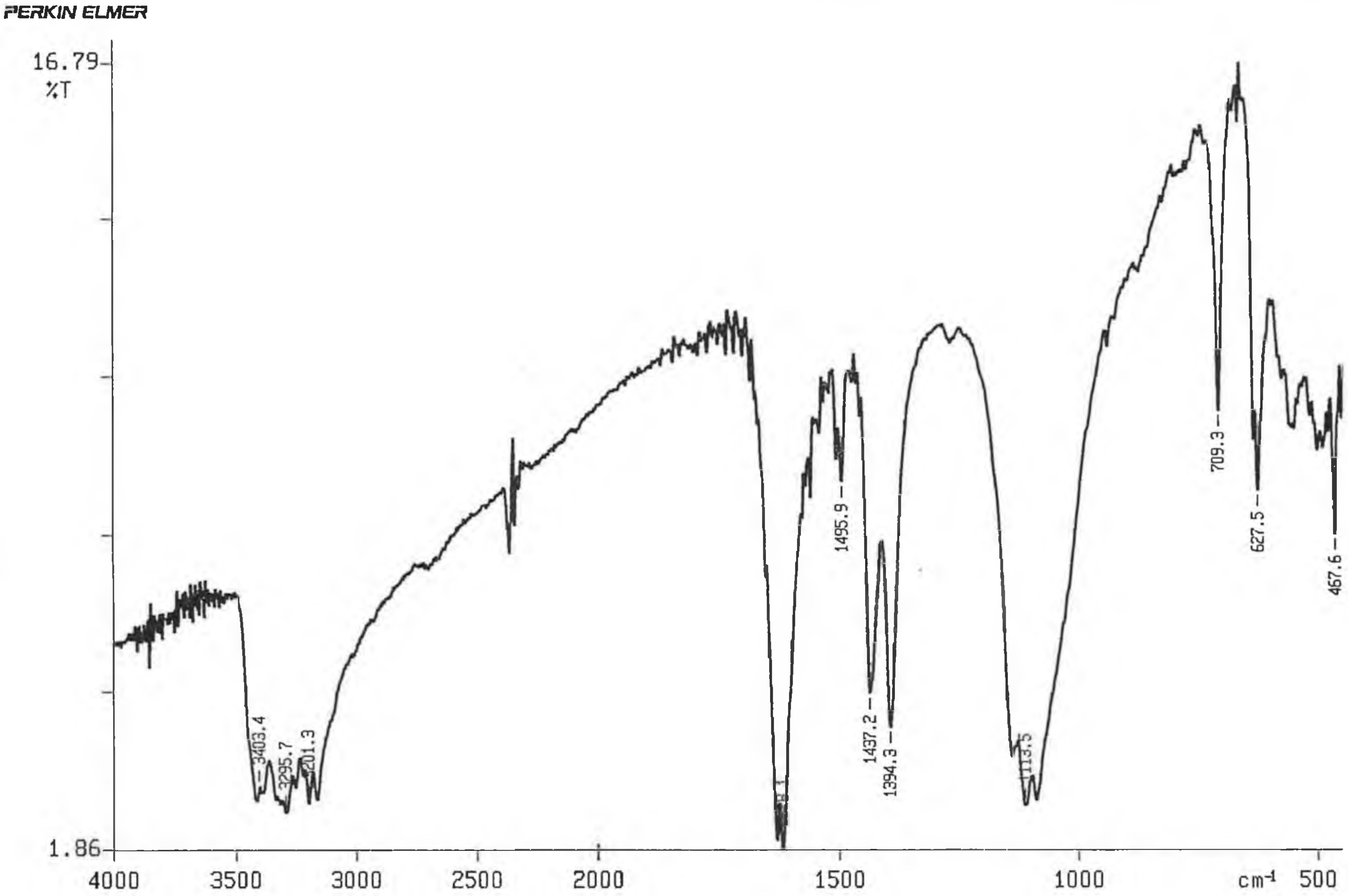


Fig. 4.2 FT-IR Spectrum of BisThiourea Gold(I) Perchlorate.

97/03/26 15:58 F. FITZPATRICK
fiona2: 1 scan, 4.0cm-1
FT-IR BIS-THIOUREA GOLD PERCHLORAATE (KBR DISC)

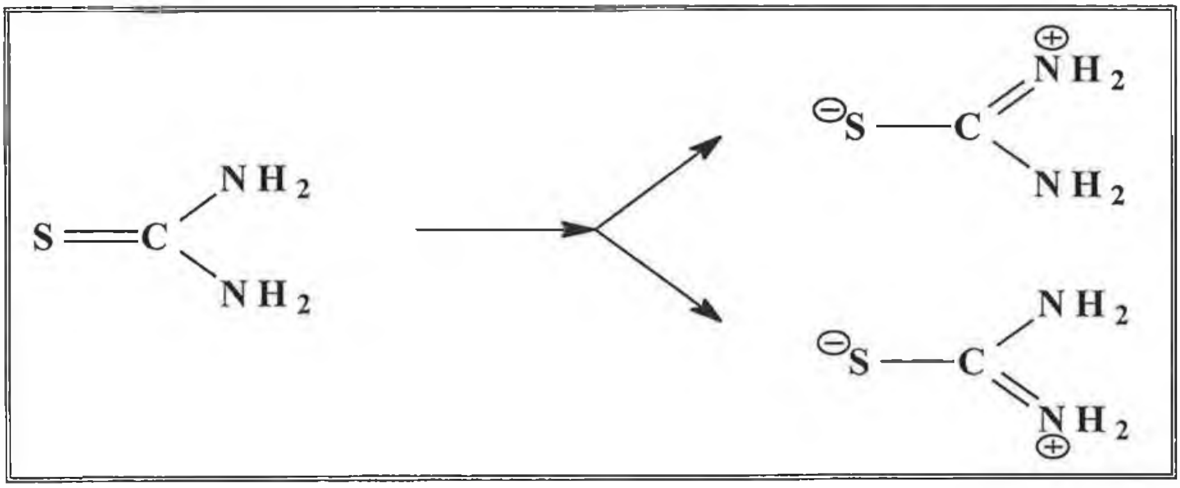


Fig. 4.3 Resonance structures of thiourea.

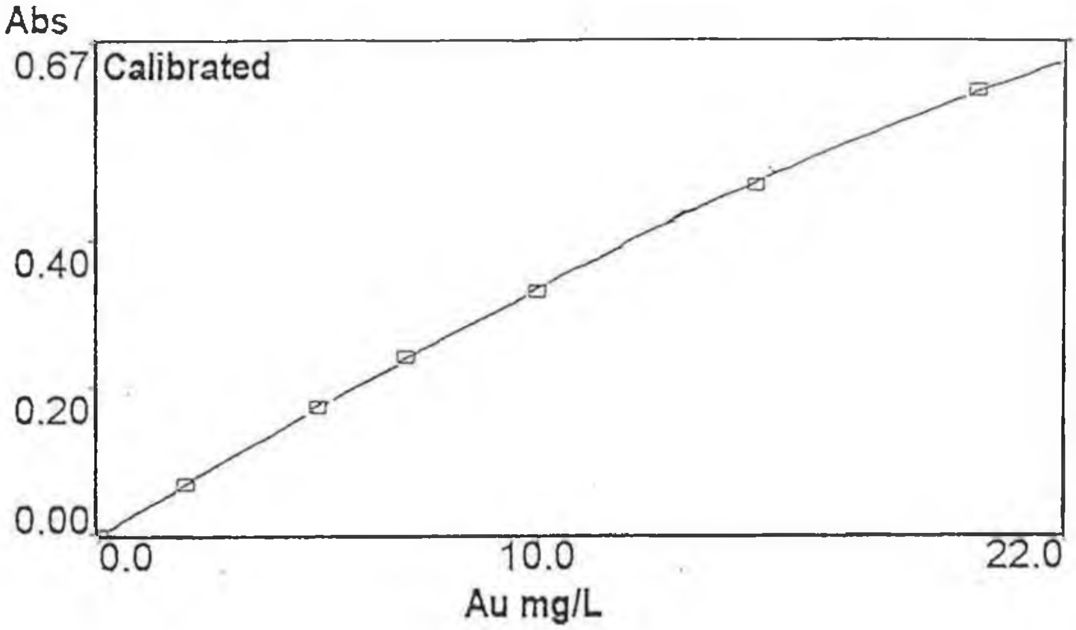
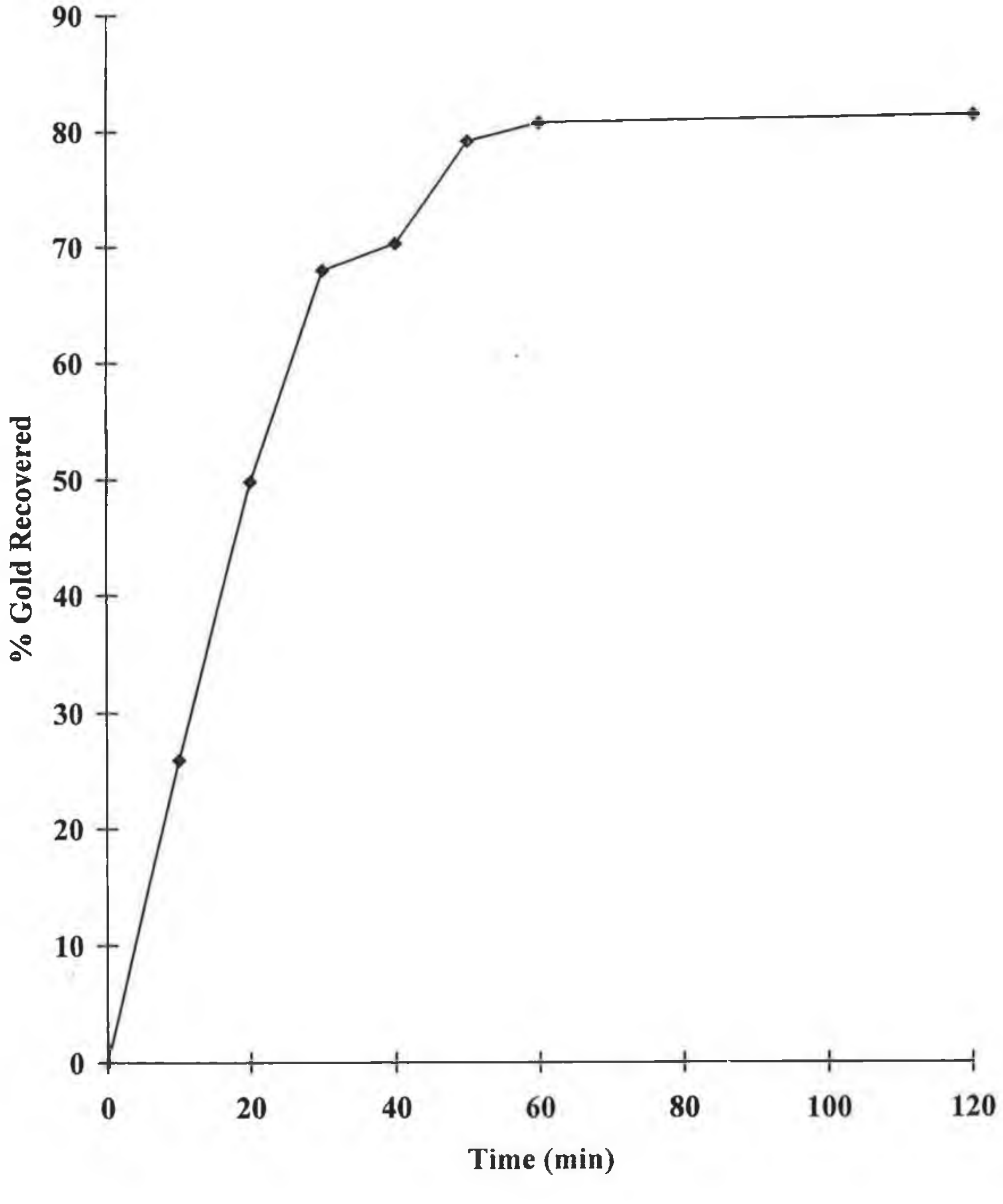
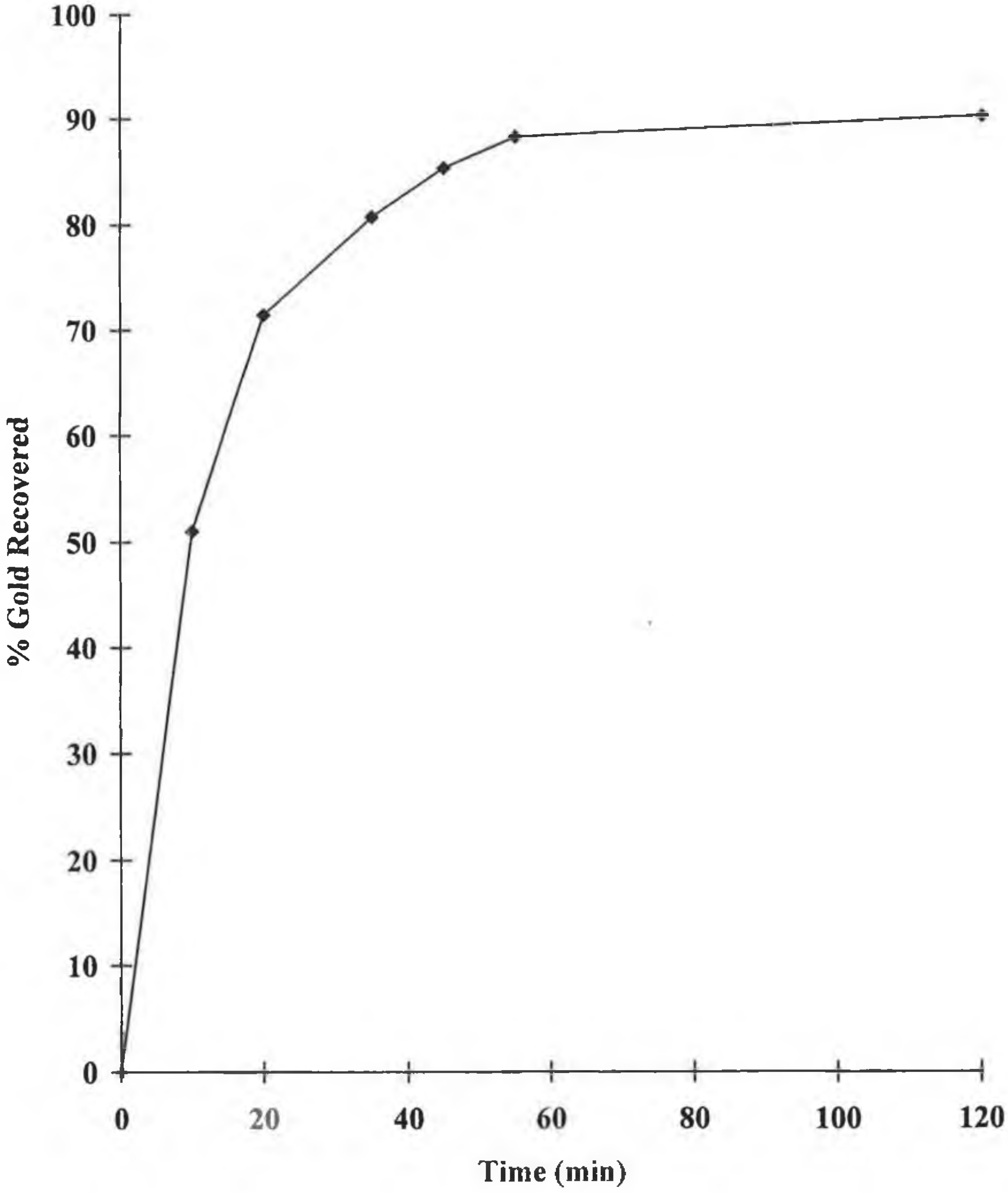


Fig. 4.4 AAS calibration curve for gold in aqueous solution, taken from a Varian Spectra AA 200.

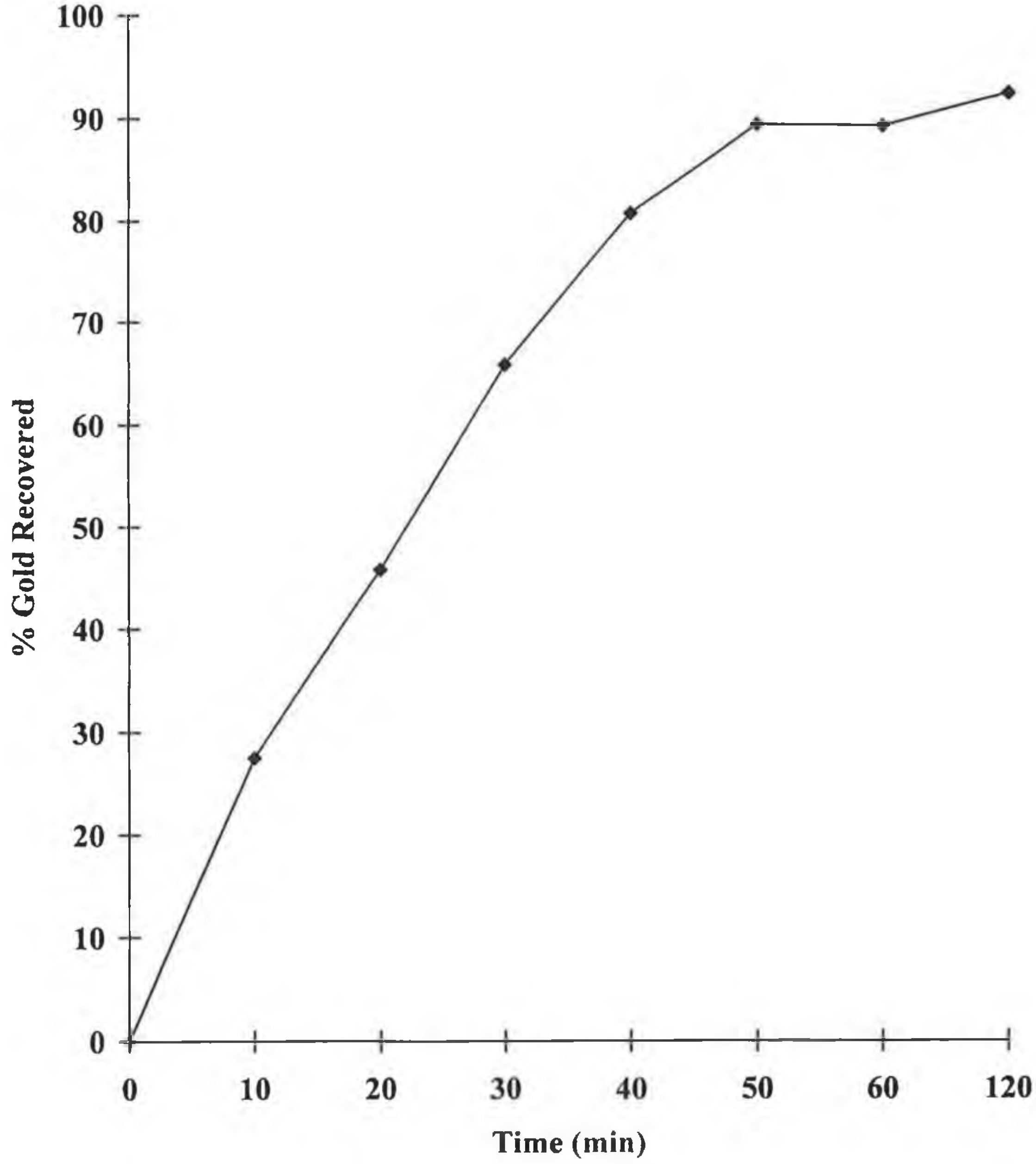
Graph 4.1 The Recovery of Gold by Impregnated XAD 2 Resin Over Time



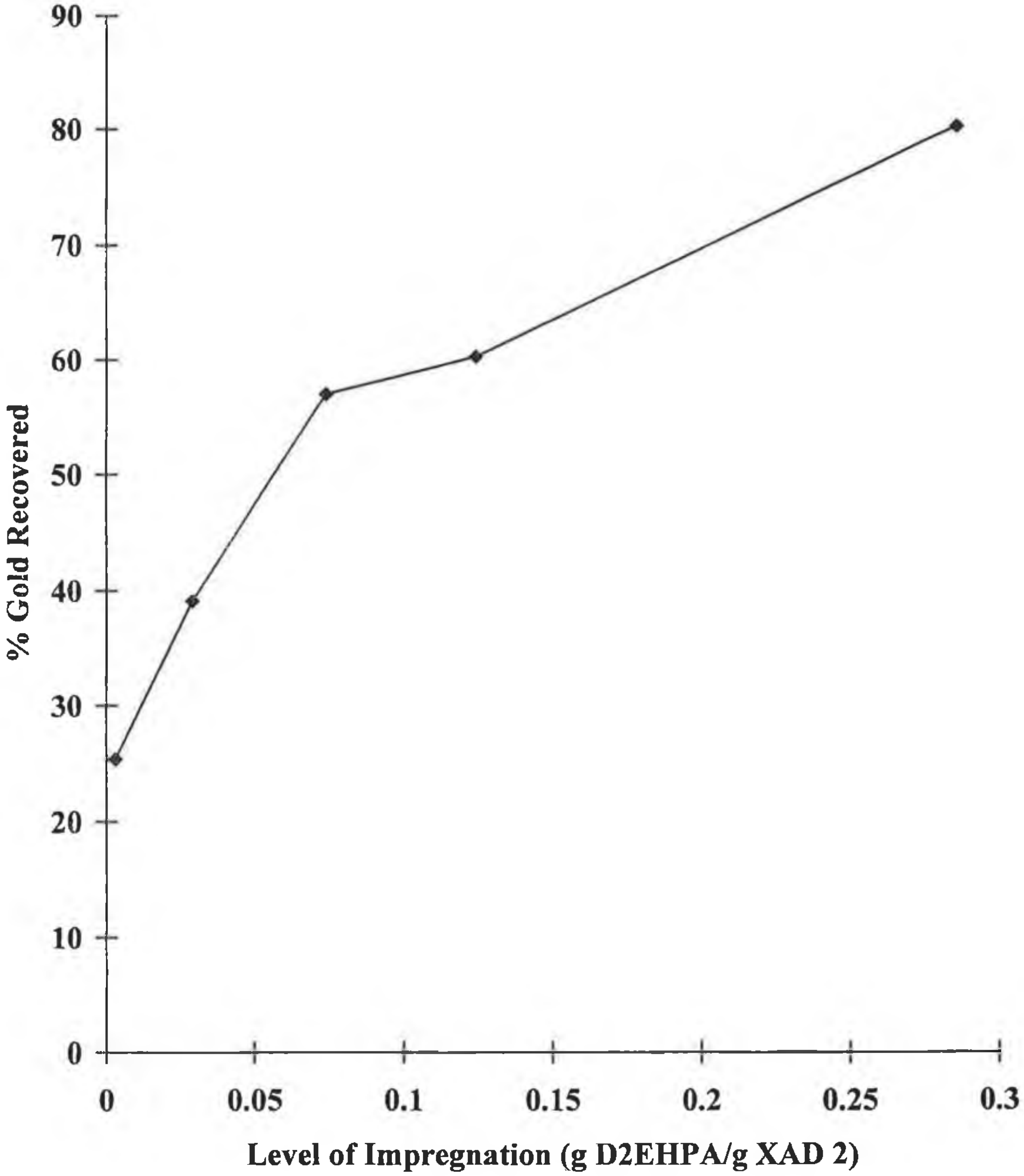
Graph 4.2 The Recovery of Gold by Impregnated XAD 4 Resin Over Time



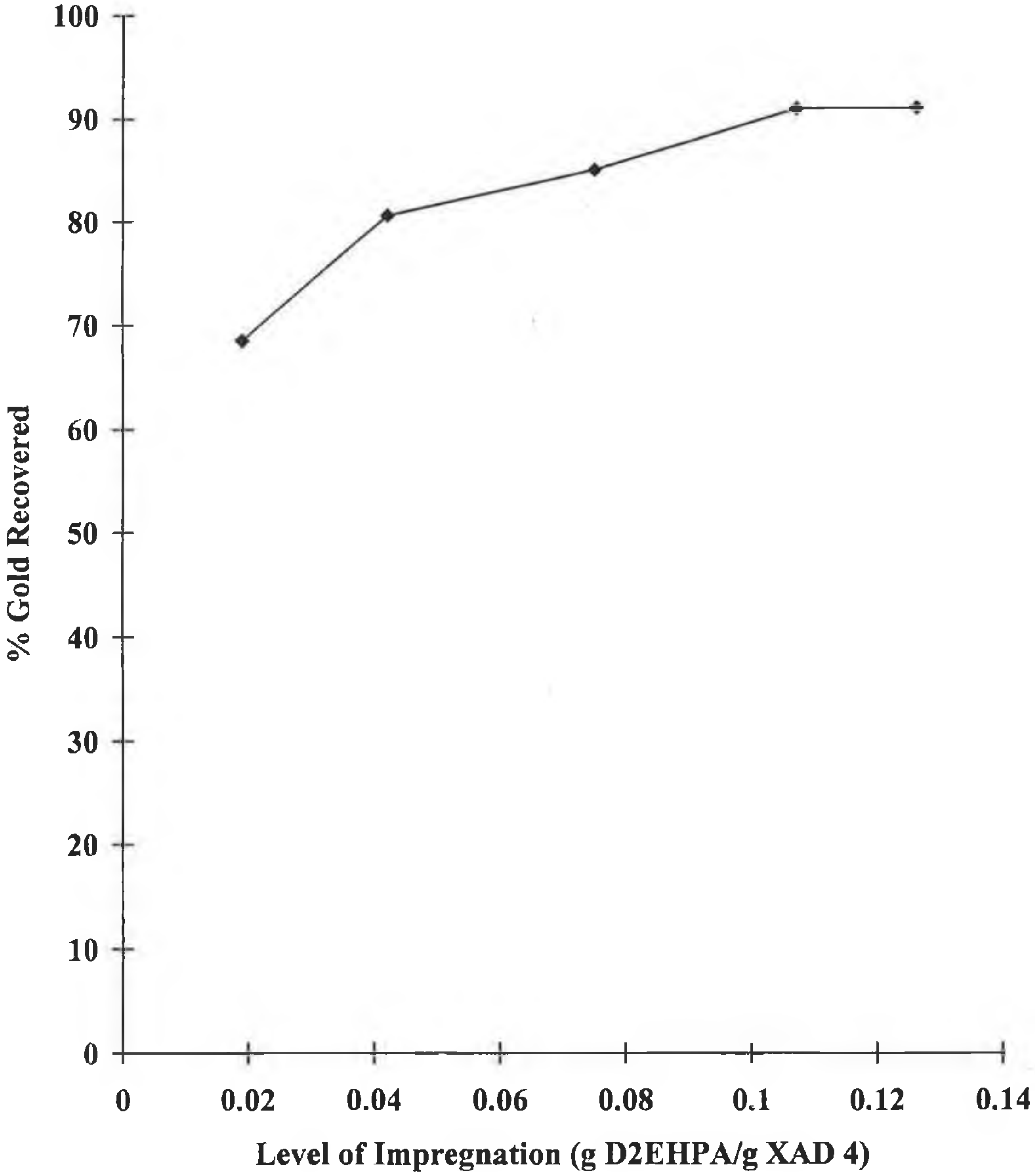
Graph 4.3 The Recovery of Gold by Impregnated XAD 7 Resin Over Time



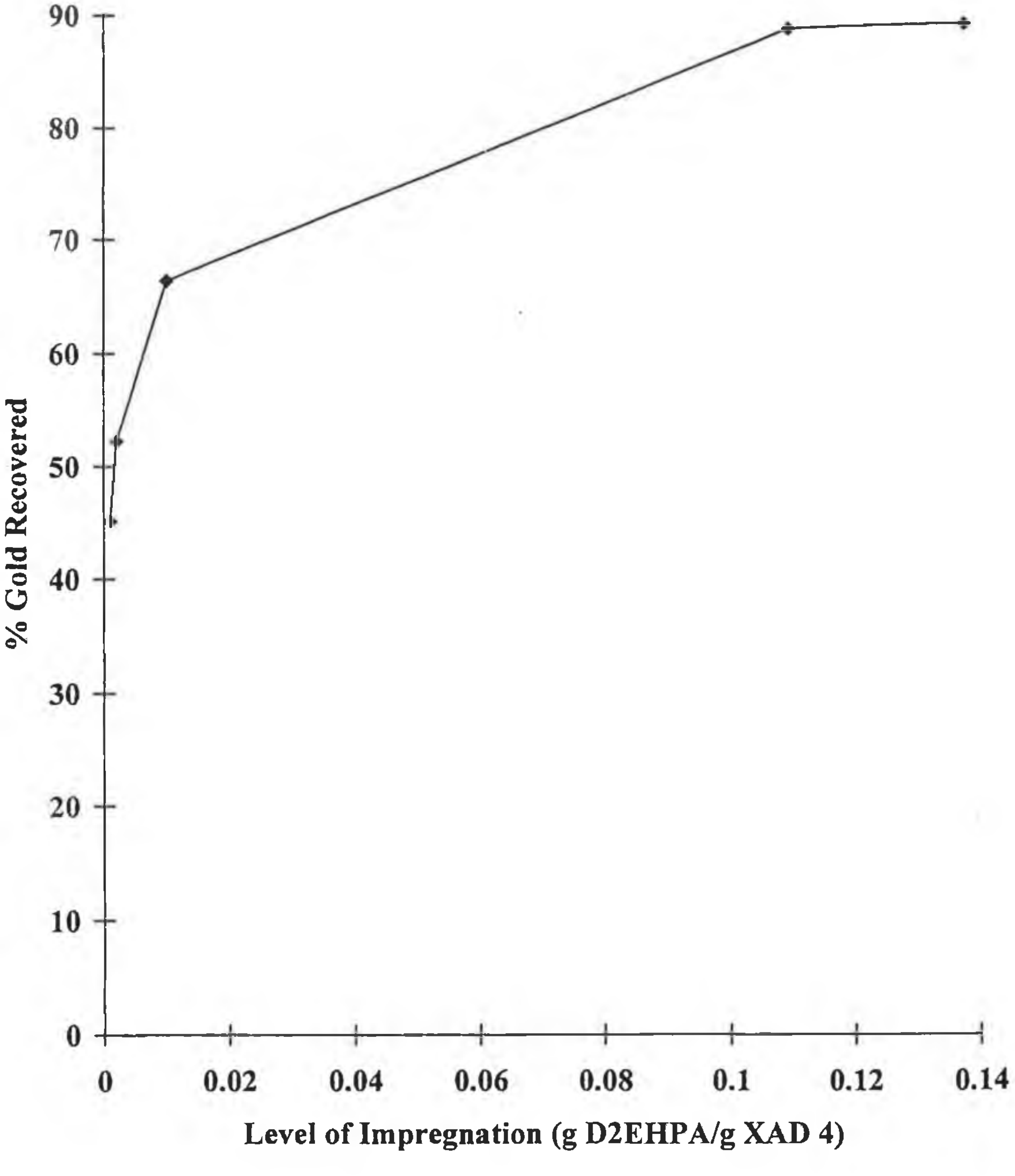
Graph 4.4 The Recovery of Gold By XAD 2 Impregnated Resins



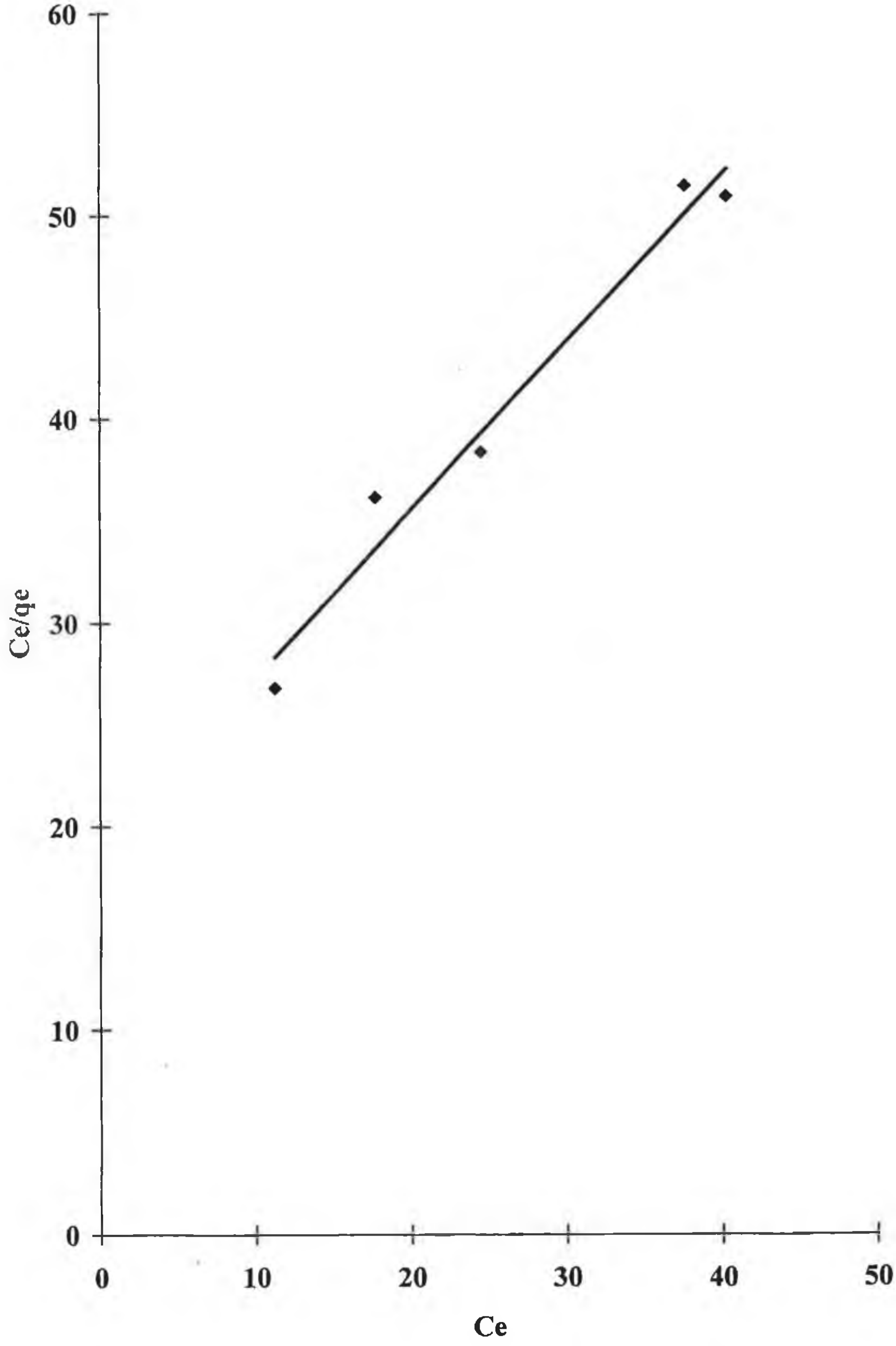
Graph 4.5 The Recovery of Gold By XAD 4 Impregnated Resins



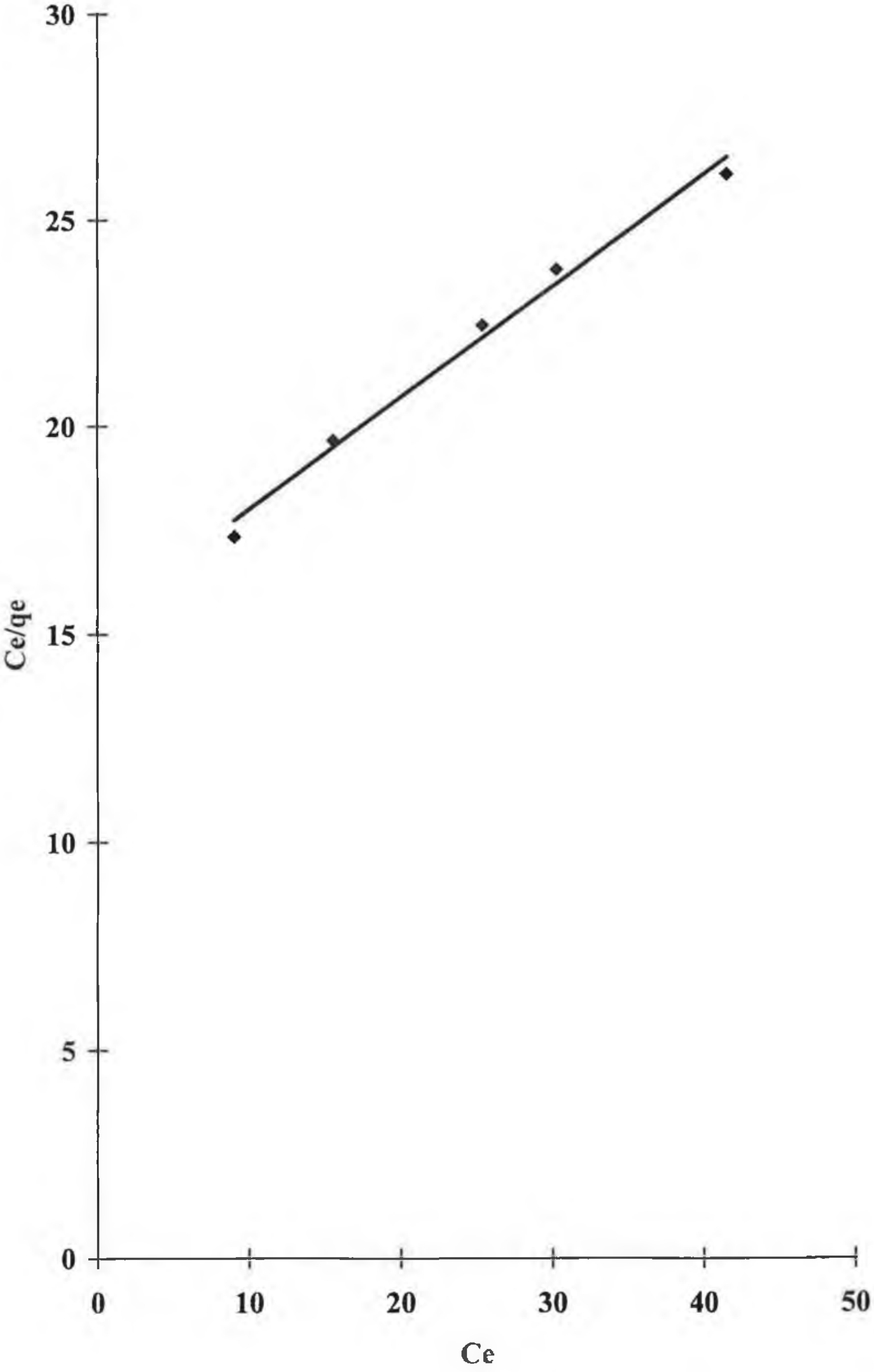
Graph 4.6 The Recovery of Gold By XAD 7 Impregnated Resins



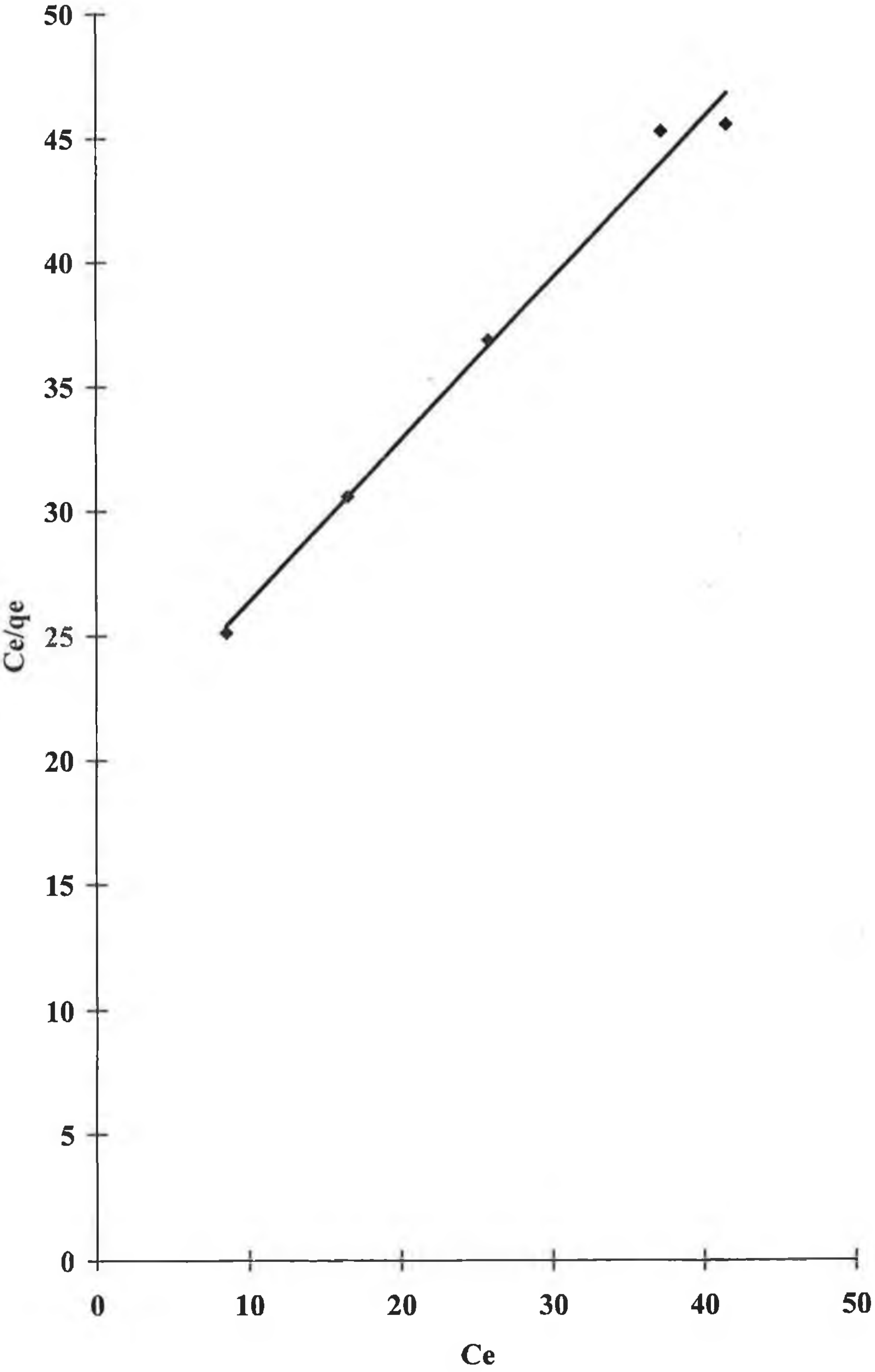
Graph 4.7 Langmuir Isotherm for the Adsorption of Gold onto Bare XAD 2 Resin



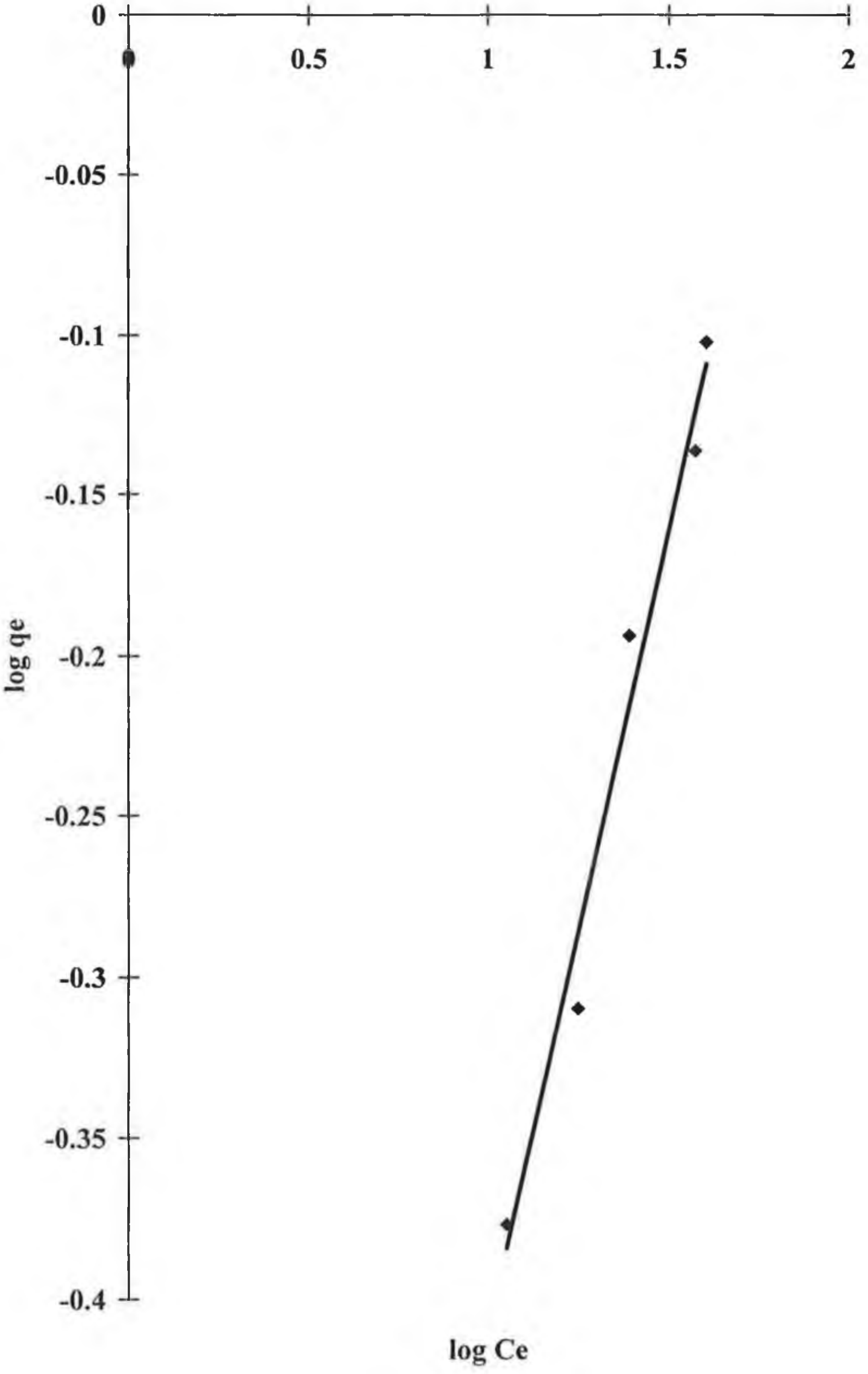
Graph 4.8 Langmuir Isotherm for the Adsorption of Gold onto Bare XAD 4 Resin



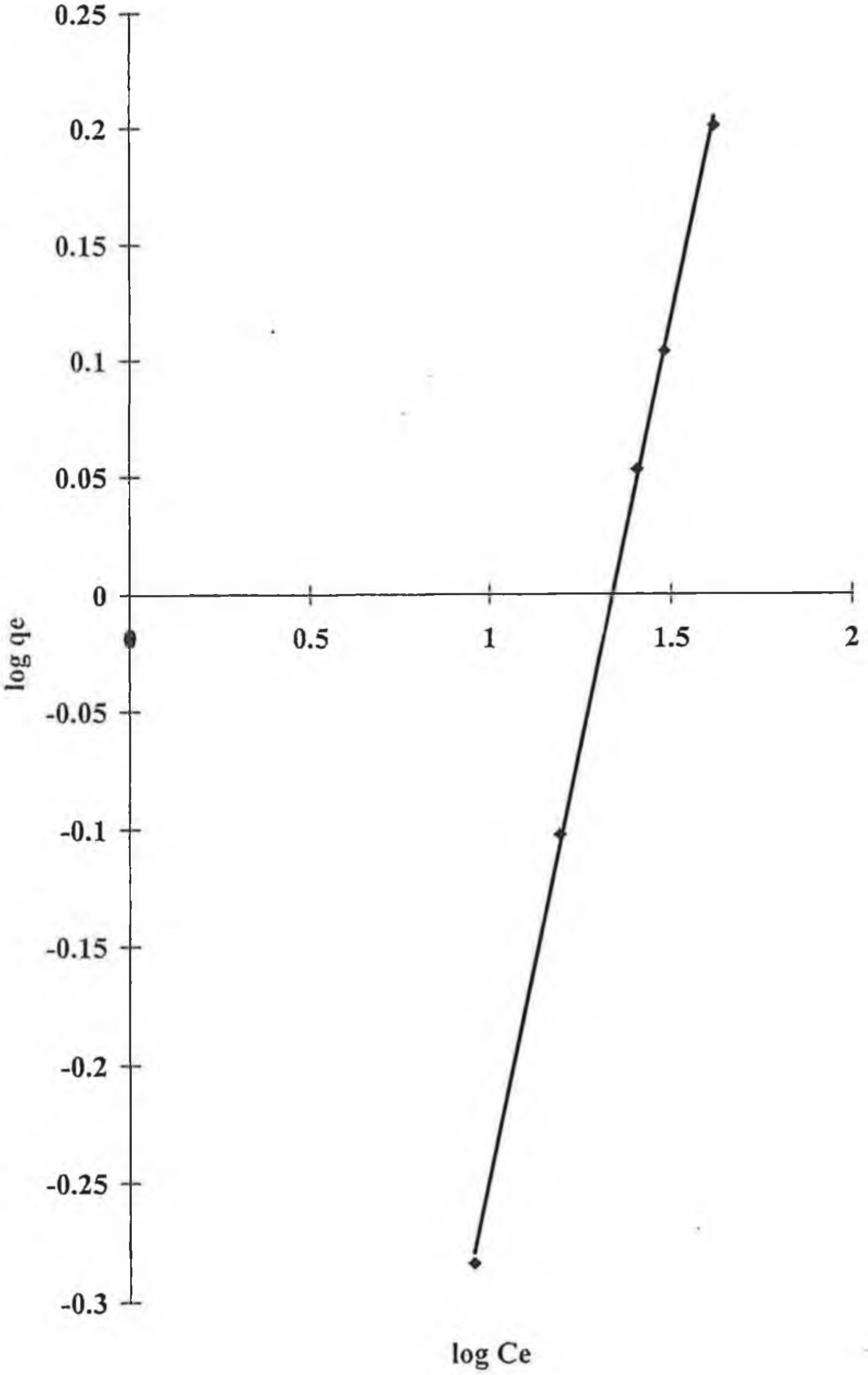
Graph 4.9 Langmuir Isotherm for the Adsorption of Gold onto Bare XAD 7 Resin



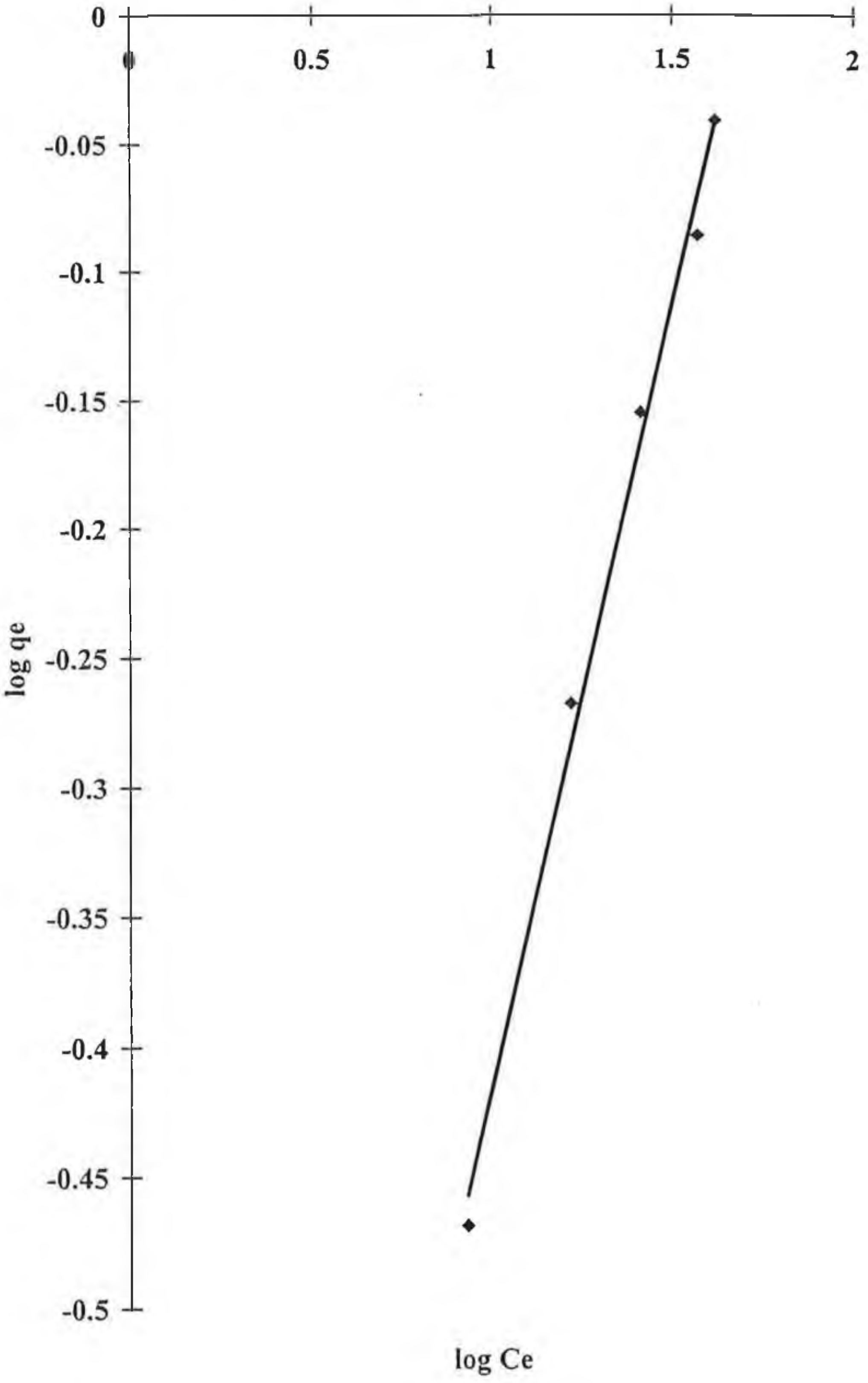
Graph 4.10 Freundlich Isotherm for the Adsorption of Gold onto Bare XAD 2 Resin



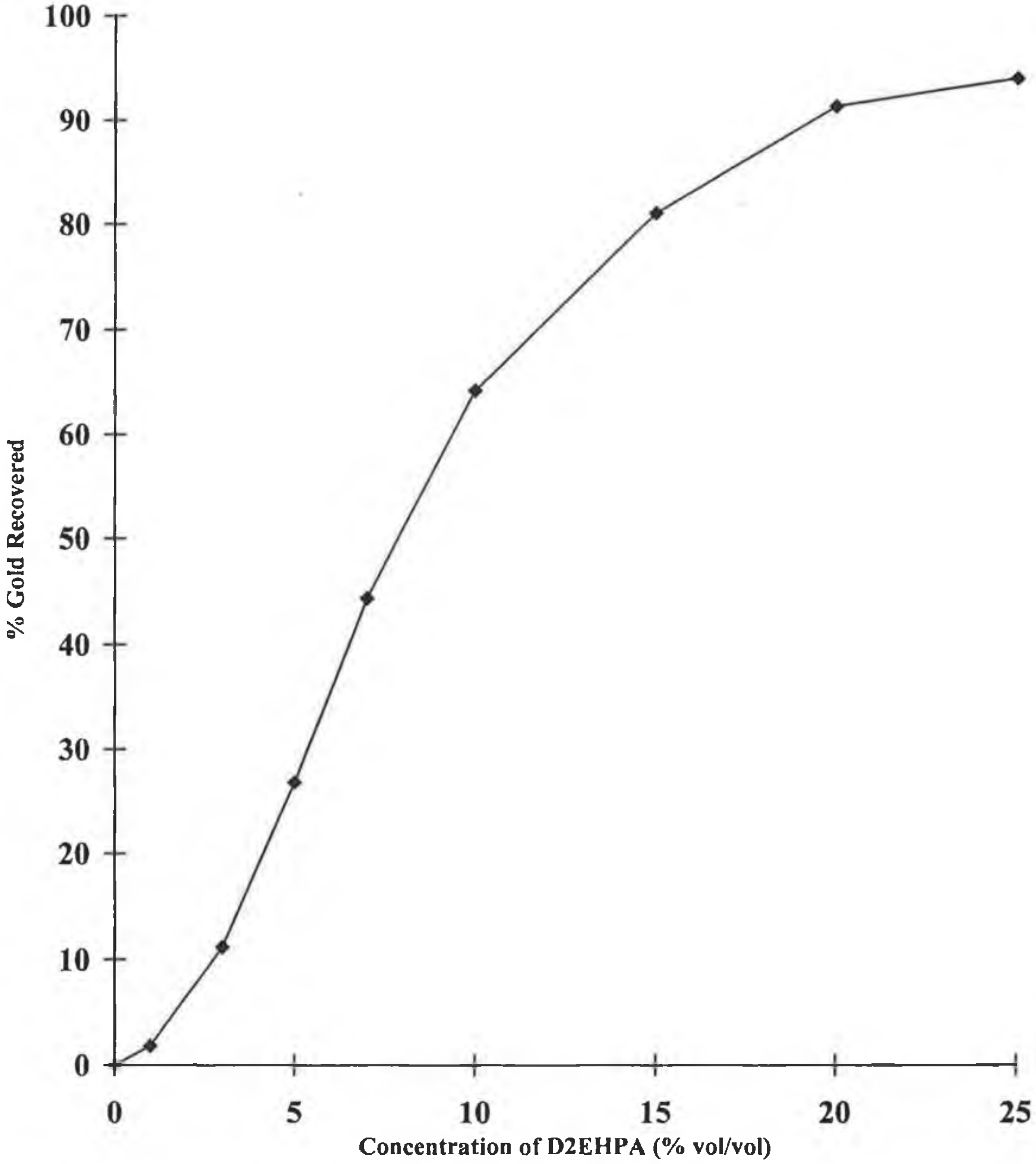
Graph 4.11 Freundlich Isotherm for the Adsorption of Gold onto Bare XAD 4 Resin



Graph 4.12 Freundlich Isotherm for the Adsorption of Gold onto Bare XAD 7 Resin



Graph 4.13 The Liquid/Liquid Extraction of Gold by D2EHPA in Kerosene



References

1 Redox Potential of the Gold(I)Thiourea Complex. V.P. Kazakov, A.I. Lapshin and B.I. Peshchevitskii. Russian Journal of Inorganic Chemistry. Vol. 9, No. 5, pp 708-709, (1964).

2 Caroline Bowden. MSc Thesis, N.U.I, (1994).

3 Infrared Absorption Spectra of Inorganic Co-ordination Complexes. XIV. Infrared studies of Some Metal Complexes. A. Yamaguchi, R.B. Penland, S. Mizushima, T.J. Lane, C. Curran and J. V. Quagliano. J. Am. Chem. Soc. Vol. 80, pp 527-529, (1958).

4 Vogel's Textbook of Quantitative Chemical Analysis, 5th Edition. Chapter 21. G.H. Jeffery, J. Bassett, J. Mendham, R.C. Denney. Longman Scientific & Technical.

5 Varian SpectraAA 200 Software (Help Section).

6 Leaching of Precious Metals from Complex Sulphide Ores: On the Chemistry of Gold Lixiviation by Thiourea. Z.H. Fhang and M. Muhammed. Mineral Processing and Extractive Metallurgy Review. Vol. 11, pp39-60, (1992).

7 J. McLoughlin. PhD thesis (in preparation).

8 Hydrometallurgical Extraction and Reclamation. E. Jackson. Ellis Horwood Series in Industrial Metals, (1986).

9 Stoichiometric Relation for the Extraction of the Gold-Thiourea Complex with D2EHPA. K. Sun-Gyu, L. Hwa-Young, O. Jong-Kee and L. Eung-Cho. Hydrometallurgy, Vol 38, pp 7-13, (1995).

10 Amberlite XAD Polymeric Adsorbents. Information Booklet. Rohm and Haas Company, (1995).

11 Elements of Physical Chemistry, 2nd Edition. S. Glasstone and D. Lewis. Macmillan Education (1960).

12 The Elements of Physical Chemistry, 2nd Edition. P.W. Atkins. Oxford University Press (1996).

13 Gold and Silver Recovery from Thiourea Leach Solutions. W.W. Simpson, L. Peterson, R.G. Sandberg (US Bureau of Mines). Pacific Northwest Metals and Minerals Conference, Portland, Oregon, (April 29-May 2, 1984).

Chapter 5

The Capacity of Solvent Impregnated Resins for Gold and the Recovery of Gold from the Resins

5.1 A Study of the Physical Capacity of Amberlite XAD 2, XAD 4 and XAD 7 Resins at Increasing Levels of Impregnation.

Since S.I.R.s appear to extract gold from solution by both solvent extraction and adsorption, it is difficult to apply their behaviour to any single theoretical model, such as an adsorption isotherm or solvent extraction distribution ratio, from which a theoretical capacity could be calculated. To overcome this problem, the capacity of the S.I.R.s for gold(I)thiourea was studied from an experimental approach and was determined as the mass of gold recovered by the resin after continuous additions of gold(I)thiourea to solution.

In order to study the effect of *the level of impregnation* on the final capacity of the resin, the three resins were impregnated to five different levels of D2EHPA impregnation.

Each of the resins was contacted with a gold solution (20ppm) (100ml) for one hour. After 1 hour, a sample (5ml) was taken from the solution for AAS gold analysis and at the same time a 5ml aliquot of gold(I)thiourea (400ppm) was added. The addition was equivalent to increasing the overall concentration of the solution by 20ppm. For each of the three sets of resins, this procedure was repeated until a total mass of up to 30mg of gold had been added to the solution.

Note:
When calculating the total mass of gold added to the solution, the mass of gold taken from solution for analysis was subtracted from the total mass of gold added to solution.

5.2 Study of the Experimental Capacity of XAD 2 Resins at Increasing Levels of Impregnation.

Five Resins were chosen. Their impregnation levels are given below.

Resin No.	Level of impregnation (g D2EHPA/g Resin)
1	0.003
2	0.029
3	0.074
4	0.124
5	0.285

Table 5.1 The levels of impregnation of the XAD 2 resins chosen for the capacity studies on the resins.

The recovery of gold by the resins is tabulated below. The change in the recovery of each of the resins illustrates the effect of impregnation on the resin's capacity for gold.

Results

XAD 2-RESIN NO. 1

Total Mass of Gold Added to Solution (mg)	Mass of Gold in Solution at Equilibrium (mg)	Mass of Gold Recovered by Resin (mg)	% Gold Recovered From Total Added
2.08	1.55	0.53	25.37
4.19	2.94	1.25	29.80
6.22	5.39	0.83	13.41
8.14	6.95	1.19	14.67
9.98	8.59	1.39	13.89
11.73	9.88	1.85	15.77
12.85	11.69	1.16	9.04
13.88	13.63	0.25	1.81
14.79	14.00	0.79	5.33
15.68	15.20	0.48	3.05
16.51	16.37	0.14	0.83

Table 5.2 The recovery of gold by XAD 2 impregnated resin no. 1.

XAD 2-RESIN NO. 2

Total Mass of Gold Added to Solution (mg)	Mass of Gold in Solution at Equilibrium (mg)	Mass of Gold Recovered by Resin (mg)	% Gold Recovered From Total Added.
2.08	1.27	0.81	39.12
4.20	3.33	0.88	20.86
6.22	4.91	1.31	21.05
8.16	6.31	1.85	22.71
10.03	8.07	1.97	19.59
11.81	9.37	2.44	20.67
12.96	10.76	2.20	16.95
14.03	12.14	1.89	13.49
15.01	12.89	2.12	14.13
15.96	15.31	0.65	4.07
16.78	15.11	1.67	9.97

Table 5.3 The recovery of gold by XAD 2 impregnated resin no. 2.

XAD 2-RESIN NO. 3

Total Mass of Gold Added to Solution (mg)	Mass of Gold in Solution at Equilibrium (mg)	Mass of Gold Recovered by Resin (mg)	% Gold Recovered From Total Added.
2.08	0.90	1.19	56.99
4.22	2.30	1.92	45.45
6.28	3.44	2.85	45.31
8.29	4.69	3.60	43.39
10.23	6.18	4.06	39.66
12.11	6.19	5.92	48.91
13.41	7.74	5.67	42.29
14.64	8.98	5.66	38.65
15.78	10.00	5.78	36.65
16.86	11.37	5.49	32.55
17.88	11.26	6.62	37.01

Table 5.4 The recovery of gold by XAD 2 impregnated resin no. 3.

XAD 2-RESIN NO. 4

Total Mass of Gold Added to Solution (mg)	Mass of Gold in Solution at Equilibrium (mg)	Mass of Gold Recovered by Resin (mg)	% Gold Recovered From Total Added.
2.08	0.36	1.72	82.80
4.22	0.63	3.59	80.43
6.31	1.56	4.74	75.23
8.36	2.54	5.82	69.57
10.63	4.64	5.99	56.39
12.56	6.12	6.44	50.97
14.14	7.77	6.38	45.12
15.37	8.98	6.39	41.55
16.51	9.84	6.67	40.39
17.61	10.71	6.90	39.17
18.66	11.95	6.71	35.96

Table 5.5 The recovery of gold by XAD 2 impregnated resin no. 4.

XAD 2-RESIN NO. 5

Total Mass of Gold Added to Solution (mg)	Mass of Gold in Solution at Equilibrium (mg)	Mass of Gold Recovered by Resin (mg)	% Gold Recovered From Total Added.
2.08	0.41	1.67	80.25
4.24	0.89	3.35	79.01
6.38	1.31	5.07	79.53
8.49	1.76	6.73	79.27
10.58	2.10	8.49	80.20
12.09	2.16	9.93	82.14
13.60	2.72	10.88	80.04
15.08	3.18	11.90	78.94
16.51	3.31	13.20	79.95
17.93	4.23	13.70	76.41
19.31	4.34	14.97	83.47

Table 5.6 The recovery of gold by XAD 2 impregnated resin no. 5.

5.2.1 Comparison of the Recovery Capacities of the Five Impregnated XAD 2 Resins

One of the major problems with XAD 2 resin was its tendency to become significantly more hydrophobic upon impregnation. Losses of resin due to hydrophobicity occurred through adhesion onto pipettes etc. when taking samples. This limited the study of XAD 2 impregnated resins, because resin losses become too high when repeated sampling was necessary. For this reason, the total mass of gold added to the solution for XAD 2 resins was less than 20mg. The mass of gold added to XAD 4 and XAD 7 resins was nearer 30mg.

Resin no.1 was impregnated to a very low level, 0.003g D2EHPA/g XAD 2. The recovery efficiency of the resin was low. Even for the first addition of gold (20.81ppm), recovery was only 25%. Recovery of gold by the impregnated resin was similar to recovery by a bare resin under similar conditions. The efficiency of the resin was at no time higher than 30%. In comparison with recovery rates achieved with other methods of recovery (1), (2), (3), this could not be considered satisfactory.

Resin no. 2 was impregnated at 0.029g D2EHPA/g XAD 2. The recovery of gold by this resin also remained quite low. The final mass of gold recovered was 1.67mg of gold per gram of resin. The percentage gold recovered decreased steadily from an initial maximum of 40% to a low of 4% with the gradual increase in the total mass of gold in solution. Again, the efficiency of the resin was at no stage high enough for a satisfactory level of gold recovery from the solution. After a total addition of 16.78 mg of gold, only 1.67mg had been recovered.

The final mass of gold recovered by XAD 2 resins 1 and 2 is very low in each case, however, looking at the mass of gold recovered by the resin after each addition reveals that the recovery over the total number of additions of gold fluctuates significantly and that at earlier stages in the experiment, higher levels of gold recovery had been achieved While the reason for this type of behaviour was not established, it appears to be characteristic of resins with low solvent loading. It is possible that the redissolution of gold into solution occurs when gold, recovered by an adsorption process, is desorbed from the resin, back into solution. In the case of low level impregnated resins, the extent to which gold adsorption (rather than solvent extraction) occurs, is much more significant than for higher level impregnated resins, therefore desorption becomes more of a problem.

Resin no. 3 was impregnated to 0.074g D2EHPA/g XAD 2. Recovery in this case was significantly higher than for the lower level resins, with an initial recovery rate of 56%. Over the next four additions, 10.23mg of gold was added and recovery decreased to 40%. The final mass of gold recovered was 6.62mg, from a total mass of 17.88mg added, corresponding to a 37% final recovery rate. Again, recovery by the impregnated resin became inefficient once the total mass of gold added to the solution had increased.

Resin no. 4 (0.124g D2EHPA/g XAD 2). The initial efficiency of the resin was 82.80%. The level of efficiency remained between 73% and 80% for up to 6.3mg of gold added to solution. The rate of recovery then decreased steadily. After a total addition of 18.66mg of gold the recovery rate had decreased to 36%, corresponding to 6.71mg of gold. The recovery rate of the resin was quite similar to resin no. 3 even though the level of impregnation was significantly higher. While the initial efficiency of the resin was better in this case, the final mass of gold recovered by the resin was still quite low.

Resin no. 5 had the highest level of impregnation. At 0.285g D2EHPA/g XAD 2, it had almost one hundred times more solvent than resin no. 1. Initial recovery by the resin was 80%. The percentage gold recovered did not decrease significantly even over the total addition of 19.31mg of gold to the solution. The final mass of gold recovered by the resin was 14.97mg corresponding to 83.47%. Since the efficiency of recovery of the resin did not decrease with the increase in the mass of gold added to solution, it is most likely that the resin will recover more gold before the resin recovery process becomes inefficient. However, because of problems with the losses of resin during sampling (due to the hydrophobic nature of impregnated XAD 2 resins) and the steadily increasing concentration of gold remaining in solution (43.40ppm), the study of the capacity of the resin was not extended.

On comparing the recovery efficiency of each of the five impregnated XAD 2 resins, it can be clearly seen that the level of impregnation of the resin greatly affects the efficiency of recovery and the final capacity of the resin for gold(I)thiourea. The total mass of gold added to the solution was below 20 mg in each case. At this point the recovery rate of four out of five of the resins had become inefficient. Of these resins, only resins 3 and 4 have a final recovery greater than 30%. The final mass of gold recovered by the resins 1 to 4 could not be considered efficient.

The highest level resin, i.e. XAD 2 resin no. 5, had a much more satisfactory recovery capacity. It did not show the same drop in efficiency as the lower level resins and gold recovery was almost constant at approximately 80%, even after the final addition of gold. It is anticipated that the total capacity of the resin could be significantly higher.

5.3 Study of the Experimental Capacity of XAD 4 Resins at Increasing Levels of Impregnation.

Resins studied

Resin No.	**Level of impregnation g D2EHPA/g Resin**
1	0.019
2	0.075
3	0.126
4	0.235
5	0.406

Table 5.7 The levels of impregnation of the XAD 4 resins used for capacity studies.

The recovery of gold by the resins is tabulated below. The change in the recovery of each of the resins illustrates the effect of impregnation on the resin's capacity for gold.

Results

XAD 4-RESIN NO. 1

Total Mass of Gold Added to Solution (mg)	Mass of Gold in Solution at Equilibrium (mg)	Mass of Gold Recovered by Resin (mg)	% Gold Recovered From Total Added.
2.10	0.65	1.45	68.96
4.50	1.65	2.85	63.42
6.92	3.08	3.85	55.56
9.33	4.24	5.09	54.56
11.74	4.76	6.98	59.42
14.14	7.01	7.14	50.47
16.32	8.67	7.66	46.88
18.48	9.38	9.10	49.23
20.65	10.85	9.80	47.48
22.80	12.41	10.39	45.57
24.39	12.89	11.50	47.15
25.66	14.32	11.34	44.20
26.87	15.41	11.46	42.66
28.01	16.42	11.60	41.40
29.11	17.38	11.74	40.31
30.16	18.06	12.10	40.12
31.17	17.32	13.85	44.44

Table 5.8 The recovery of gold by XAD 4 impregnated resin no. 1.

XAD 4-RESIN NO. 2

Total Mass of Gold Added to Solution (mg)	Mass of Gold in Solution at Equilibrium (mg)	Mass of Gold Recovered by Resin (mg)	% Gold Recovered From Total Added.
2.10	0.39	1.71	81.27
4.51	0.69	3.83	84.79
6.94	1.32	5.62	81.04
9.36	2.08	7.28	77.76
11.78	3.15	8.63	73.25
14.19	3.80	10.39	73.23
16.38	5.17	11.21	68.43
18.56	6.44	12.13	65.33
20.74	7.36	13.38	64.53
22.91	8.99	13.92	60.76
24.67	9.65	15.02	60.86
26.11	10.65	15.49	59.22
27.49	11.86	15.64	56.88
28.82	12.53	16.27	56.52
30.11	13.64	16.47	54.69
31.34	14.49	16.86	53.79
32.54	15.58	16.96	52.12

Table 5.9 The recovery of gold by XAD 4 impregnated resin no. 2.

XAD 4-RESIN NO. 3

Total Mass of Gold Added to Solution (mg)	Mass of Gold in Solution at Equilibrium (mg)	Mass of Gold Recovered by Resin (mg)	% Gold Recovered From Total Added.
2.10	0.26	1.84	87.50
4.53	0.45	4.08	90.06
6.96	0.84	6.12	87.97
9.38	1.57	7.82	83.31
11.80	2.10	9.71	82.25
14.22	2.73	11.49	80.79
16.41	3.58	12.83	78.18
18.61	4.57	14.04	75.46
20.79	5.54	15.25	73.35
22.97	6.54	16.44	71.55
24.85	7.45	17.40	70.01
36.40	7.78	18.62	70.55
27.93	9.53	18.40	65.88
29.37	10.57	18.80	64.01
30.76	11.71	19.05	61.93
32.09	12.43	19.66	61.27
33.39	13.63	19.77	59.19

Table 5.10 The recovery of gold by XAD 4 impregnated resin no. 3.

XAD 4-RESIN NO. 4

Total Mass of Gold Added to Solution (mg)	Mass of Gold in Solution at Equilibrium (mg)	Mass of Gold Recovered by Resin (mg)	% Gold Recovered From Total Added.
2.10	0.30	1.81	85.84
4.55	0.67	3.88	85.29
6.99	1.21	5.78	82.69
9.40	1.47	7.93	84.32
11.82	1.54	10.28	86.97
12.79	1.62	11.17	87.31
14.95	2.14	12.81	85.68
17.14	2.75	14.39	83.96
19.34	3.26	16.08	83.16
21.53	3.73	17.80	82.67
23.55	3.94	19.61	83.36
25.28	4.56	20.72	81.96
26.97	5.29	21.68	80.38
28.62	5.63	22.99	80.33
30.26	6.60	23.66	78.20
31.84	6.95	24.89	78.17
33.41	7.64	25.77	77.13

Table 5.11 The recovery of gold by XAD 4 impregnated resin no. 4.

XAD 4-RESIN NO. 5

Total Mass of Gold Added to Solution (mg)	Mass of Gold in Solution at Equilibrium (mg)	Mass of Gold Recovered by Resin (mg)	% Gold Recovered From Total Added.
2.10	0.38	1.73	82.19
4.51	0.60	3.92	86.75
6.93	1.27	5.66	81.68
9.35	1.52	7.83	83.77
11.77	2.12	9.65	82.03
12.72	1.43	11.30	88.74
14.93	2.04	12.89	86.35
17.12	2.46	14.67	85.64
19.32	3.06	16.26	84.14
21.51	3.60	17.92	83.27
23.54	3.25	20.29	86.19
25.30	3.87	21.43	84.70
27.02	4.80	22.23	82.25
28.70	5.20	23.51	81.91
30.36	5.74	24.62	81.08
31.99	6.06	25.92	81.03

Table 5.12 The recovery of gold by XAD 4 impregnated resin no. 5.

5.3.1 Comparison of the Recovery Capacities of Five Impregnated XAD 4 Resins

XAD 4 resins impregnate more readily than XAD 2 or XAD 7 resins, because they have a larger surface area. Therefore, the range of levels of impregnation achieved for XAD 4 resins are higher than the ranges for either XAD 2 or XAD 7.

XAD 4 resin no. 1 had an impregnation level of 0.019g D2EHPA /g XAD 4. Its initial recovery rate was 68.96%. The recovery rate decreased steadily with the addition of gold to the solution. Over the gradual addition of 31.17mg of gold, 13.85mg were recovered, corresponding to 44.44%.

Resin no. 2 (0.075g/g) had an initial recovery of 81%. The recovery rate decreased with the increase in the mass of gold added to solution, but its final recovery rate remained higher than XAD 4 resin no. 1. Over the gradual addition of 32.54mg of gold, 16.96mg were recovered corresponding to 52.12%.

Resin no.3 (0.126g D2EHPA/g) had an initial recovery of 87.50%. Again the rate of recovery decreased steadily with increased mass of gold added to solution. The final rate in this case was almost 60% corresponding to 19.77mg of gold, recovered from a total mass of 33.39mg of gold added.

Resin no. 4 (0.255g D2EHPA/g) again has an initial recovery of over 80%. In this case, the recovery of the resins did not decrease significantly with the increase in the mass of gold added to solution. The final mass of gold recovered by the resin was 23.66mg or 78.2% of the total mass of gold added to the solution. The fact that the recovery rate of the resin did not decrease significantly, suggests that the recovery efficiency of the resin had not reached saturation at this point. It is likely that the capacity of the resin for gold is higher than the level achieved in this study. The study was stopped at this point because the total mass of gold remaining in solution had reached over 76ppm of gold. This concentration is almost four times higher than the typical concentration of gold chosen for this study (20ppm) and the behaviour of the resin in such a high concentration solution could not be directly compared with a similar resin contacted with a lower concentration of gold.

The recovery of gold by resin no. 5 was very similar to resin no. 4, even though the level of impregnation of this resin is much higher (0.406g D2EHPA/g). The final mass of gold recovered by the resin was 25.85mg from a total mass of 33.60mg or 76.91%. This compares with 25.77mg of gold recovered from a total mass of 33.41mg added, for resin no. 4. Since the level of impregnation of resin no. 5 was much higher than resin no. 4, it might have been expected that the final mass of gold recovered by resin no. 5 would be higher. However, since the rate of recovery of the resin has not decreased from its initial value of over 80%, it is likely, that after further additions of gold to resins no. 4 and 5, the differentiation between the two resins would become more apparent and the capacity of resin no. 5 would eventually be seen to be higher than the capacity of resin no. 4. It may also be possible that the rate of recovery of the resins at this level of impregnation is governed by the rate of phase transfer of the gold complex from the aqueous to the organic layer; further studies on this aspect of gold recovery by D2EHPA would be useful. Again, because the concentration of gold remaining in solution had become significantly higher than the 20ppm typical concentration chosen for this study, the experiment was stopped at this point.

5.4 Study of the Experimental Capacity of XAD 7 Resins at Increasing Levels of Impregnation.

Resins studied:

Resin No.	Level of impregnation (g D2EHPA/g Resin)
1	0.002
2	0.021
3	0.055
4	0.199
5	0.214

Table 5.13 The levels of impregnation of the XAD 7 resins used for the capacity studies of the resins.

The recovery of gold by the resins is tabulated below. The change in the recovery of each of the resins illustrates the effect of impregnation on the resin's capacity for gold.

Results

XAD 7-RESIN NO. 1

Total Mass of Gold Added to Solution (mg)	Mass of Gold in Solution at Equilibrium (mg)	Mass of Gold Recovered by Resin (mg)	% Gold Recovered From Total Added.
2.11	1.06	1.05	49.72
4.34	2.39	1.95	44.92
6.51	3.97	2.54	39.04
8.59	5.55	3.04	36.22
10.60	7.15	3.46	32.61
12.53	8.70	3.83	30.59
13.75	9.54	4.21	30.63
14.93	10.42	4.51	30.18
16.06	11.83	4.23	26.36
17.12	13.12	4.00	23.39
18.12	13.79	4.33	23.91
19.39	14.09	5.27	27.32
20.64	15.49	5.16	24.98
21.83	16.68	5.15	23.58
22.95	17.06	5.90	25.69
24.06	18.58	5.48	22.77

Table 5.14 The recovery of gold by XAD 7 impregnated resin no. 1.

XAD 7-RESIN NO. 2

Total Mass of Gold Added to Solution (mg)	Mass of Gold in Solution at Equilibrium (mg)	Mass of Gold Recovered by Resin (mg)	% Gold Recovered From Total Added.
2.11	0.62	1.48	70.42
4.36	1.47	2.90	66.40
6.57	2.52	4.05	61.66
8.73	3.59	5.14	58.86
10.84	5.17	5.67	52.33
12.87	6.72	6.15	47.82
14.19	7.68	6.50	45.84
15.45	8.35	7.10	45.97
16.69	9.02	7.67	45.93
17.89	11.10	6.79	37.96
18.99	10.92	8.07	42.02
20.40	11.74	8.67	42.48
21.78	13.23	8.55	39.27
23.07	14.40	8.68	37.61
24.31	15.32	8.99	36.99
25.51	16.95	8.56	33.54

Table 5.15 The recovery of gold by XAD 7 impregnated resin no. 2.

XAD 7-RESIN NO. 3

Total Mass of Gold Added to Solution (mg)	Mass of Gold in Solution at Equilibrium (mg)	Mass of Gold Recovered by Resin (mg)	% Gold Recovered From Total Added.
2.11	0.33	1.78	84.57
4.38	0.74	3.64	83.11
6.63	1.73	4.89	73.86
8.82	2.05	6.78	76.83
11.01	2.87	8.14	73.93
13.15	3.66	9.50	72.20
14.62	4.31	10.32	70.55
16.06	5.28	10.78	67.12
17.45	6.29	11.16	63.97
18.79	7.25	11.54	61.40
20.08	7.13	12.95	64.49
21.68	8.26	13.42	61.88
23.23	9.30	13.93	59.96
24.72	9.63	15.09	61.04
26.20	10.99	15.21	58.07
27.61	12.39	15.22	55.14

Table 5.16 The recovery of gold by XAD 7 impregnated resin no. 3.

XAD 7-RESIN NO. 4

Total Mass of Gold Added to Solution (mg)	Mass of Gold in Solution at Equilibrium (mg)	Mass of Gold Recovered by Resin (mg)	% Gold Recovered From Total Added.
2.11	0.43	1.67	79.44
4.37	1.23	3.14	71.79
6.59	1.24	5.36	81.26
8.82	2.00	6.82	77.36
11.00	2.53	8.48	77.05
13.16	2.18	10.98	83.40
14.71	2.81	11.90	80.89
16.22	3.53	12.69	78.23
17.70	3.98	13.72	77.52
19.15	4.25	14.90	77.82
20.59	4.26	16.33	79.31
22.34	5.12	17.22	77.09
24.04	5.98	18.06	75.13
25.70	7.06	18.65	72.55
27.31	7.73	19.58	71.71
28.88	8.82	20.06	69.46
30.40	9.97	20.43	67.21

Table 5.17 The recovery of gold by XAD 7 impregnated resin no. 4.

XAD 7-RESIN NO. 5

Total Mass of Gold Added to Solution (mg)	Mass of Gold in Solution at Equilibrium (mg)	Mass of Gold Recovered by Resin (mg)	% Gold Recovered From Total Added.
2.11	0.24	1.87	88.84
4.38	1.12	3.26	74.47
6.61	1.21	5.40	81.65
8.84	1.54	7.30	82.61
11.04	1.60	9.45	85.56
12.29	1.18	11.11	90.37
13.88	1.71	12.18	87.71
15.45	1.82	13.63	88.23
17.01	2.20	14.82	87.10
18.56	2.38	16.18	87.20
20.09	2.36	17.74	88.28
21.93	2.83	19.10	87.10
23.80	3.27	20.53	86.28
25.59	3.99	21.61	84.42
27.05	4.55	22.50	83.17
28.79	5.14	23.64	82.13
30.49	5.75	24.73	81.13

Table 5.18 The recovery of gold by XAD 7 impregnated resin no. 5.

5.4.1 Comparison of the Recovery Capacities of the Five Impregnated XAD 7 Resins

Resin no. 1 initially recovered 49.72% of gold in solution. Its impregnation level was 0.002g D2EHPA/g XAD 7. The rate of recovery decreased steadily with the increase in the mass of gold added to solution and after a total addition of 24.06mg of gold, only 22.77% had been recovered. This corresponded to 5.48mg of gold recovered.

Resin no. 2 (0.021g D2EHPA/g) had an initial recovery rate of 70.42%. The decrease in the rate of recovery was immediate, indicating a gradual saturation in the resins ability to recover gold. The final recovery was 33.54%, after a total addition of 25.51mg of gold. The final mass of gold recovered was 8.56mg.

Resin no. 3 (0.055g D2EHPA/g) recovered 84.57% of gold in solution during the first hour. This remained steady up to a recovery of 3.64mg of gold from a total mass of 4.38mg added to solution. The recovery rate then began to decrease, although the rate of decrease was not as marked as for the first two resins. The final recovery rate was 55.14% or 15.22mg of gold from a total mass of 27.61mg.

Resin no. 4 (0.199g D2EHPA/g) had an initial recovery of 79.44%, which was slightly lower than the initial recovery of gold by resin no. 3. However, the effect of the increase in the level of impregnation of resin no. 4 was seen as an almost steady rate of recovery of gold by the resins over the total addition of 30.40mg of gold. The final rate of recovery of the resin was 67.21%, corresponding to 20.43mg of gold recovered by the resin.

Resin no. 5 (0.214g D2EHPA/g) had an initial recovery rate of 88.84%. The recovery of gold from the resin remained between 80% and 90% over the addition of gold to the solution. After a total addition of 30.49mg of gold to the solution, 24.73mg were recovered. Since the recovery rate of the resin did not decrease significantly, it is likely that the total mass of gold recovered by the resin, under laboratory conditions, would be higher. However since the concentration of gold remaining in the solution at the end of the experiment was 57.53ppm, the experiment was stopped at this point.

5.5 Determination of the Physical Capacity of the Resins

To establish a capacity for each of the impregnated resins, the mass of gold recovered *after the efficiency of recovery has decreased by 10%* of its maximum value was taken as a working capacity for that resin. It should be noted that this is a purely arbitrary method of determining the capacity, chosen so that a valid comparison of the resins can be made. It is not proposed that the calculated values should represent the *maximum* capacity of the resins for gold, or that they should be taken as absolute figures for capacity. However, the values indicate the levels of gold loading which can be achieved, using the resins under the given set of practical conditions, with the additional constraint of maintaining recovery efficiency to above 10% of its initial figure. It may be argued that in the case of some of the lower level impregnated resins the initial level of recovery is so low that the process is at no stage efficient, however this is mirrored in the calculated values for these resins.

XAD 2 Resins

Resin No.	Level of Impregnation (g D2EHPA /g XAD 2)	Initial Recovery Rate %	Final Recovery Rate %	Working Capacity (kg of gold /t Resin)
1	0.003	25.37	14.67	1.19
2	0.029	39.12	22.71	1.85
3	0.074	56.99	45.31	2.85
4	0.124	82.80	69.57	5.82
5	0.285	80.25	83.47	>14.97

Table 5.19 The calculated working capacity of the five XAD 2 impregnated resins.

XAD 4 Resins

Resin No.	Level of Impregnation (g D2EHPA /g XAD 2)	Initial Recovery Rate %	Final Recovery Rate %	Working Capacity (kg of gold /t Resin)
1	0.019	68.96	55.56	3.85
2	0.075	81.27	68.43	11.21
3	0.126	87.50	75.46	14.04
4	0.235	85.84	77.13	>25.77
5	0.406	82.19	81.03	>25.92

Table 5.20 The calculated working capacity of the five XAD 4 impregnated resins.

XAD 7 Resins

Resin No.	Level of Impregnation (g D2EHPA /g XAD 2)	Initial Recovery Rate %	Final Recovery Rate %	Working Capacity (kg of gold /t Resin)
1	0.002	49.72	39.04	2.54
2	0.021	70.42	58.86	5.14
3	0.055	84.57	73.93	8.14
4	0.199	79.44	69.46	20.06
5	0.214	88.84	81.13	>24.73

Table 5.21 The calculated working capacity of the five XAD 7 impregnated resins.

The mass of gold recovered by each of the resins before the process becomes inefficient is given in tables 5.19 to 5.21. The capacity of the resins increases with the increase in the initial level of impregnation of the resin. In the case of the higher level impregnated resins, a decrease in efficiency of greater than 10% did not always occur. In these cases, the capacity of the resin is indicated to be higher than the value given. It is likely that further additions of gold to these solutions would result in an increased capacity for gold for these resins, with an eventual decrease in the efficiency of the resin beyond 10% of the initial maximum. The experiment was discontinued at this point because the concentration of gold remaining in solution had become too high.

In order to more realistically mirror the recovery of gold from an actual process solution, the concentration of the gold solution should be kept to a constant concentration of approximately 20ppm by filtering the resins and contacting the resins with a fresh gold solution. It is anticipated that this method could cause problems due to the loss of resin during filtering and recontacting. The pumping of the gold solution continuously through a packed resin column would allow the resin to be contacted with a fresh gold solution each time. Edwards et al used a fixed bed, 3 column, counter current system using bare XAD 7 resins (4). This overcomes some of the problems due to the hydrophobicity of the resin and the loss of resin when taking samples.

5.5.1 A Comparison Between XAD 2, XAD 4 and XAD 7 Impregnated Resins for Capacity for Gold

XAD 2 resins are difficult to work with in solution once they are impregnated. Their increased hydrophobicity upon impregnation inhibits the resins ability to disperse homogeneously through the solution. The resins also adhere to pipettes etc. used for sampling, resulting in the loss of resin from solution.

The overall capacity of XAD 2 resins is low in comparison to XAD 4 and XAD 7. The maximum recovery of a XAD 2 resin was 14.97mg of gold, achieved for a resin impregnated to 0.285g D2EHPA/g XAD 2. Recovery capacities for resins at lower levels of impregnation were very low and at no stage could they be considered efficient.

XAD 4 impregnated resins had a much greater capacity for gold than XAD 2. This can be attributed to the higher surface area of XAD 4 (750g/m$^{2)}$ in comparison to XAD 2 (330g/m^2) (5). The higher surface area allows for a higher level of impregnation of the resin which in turn results in a higher recovery of gold. However, even when comparing the resins at similar levels of impregnation, it is clear that XAD 4 is a much more satisfactory recovery medium than XAD 2. XAD 2 resin no. 3 and XAD 4 resin no. 2 are impregnated to a similar level, as are XAD 2 resin no. 4 and XAD 4 resin no. 3. The final capacities of these resins are 2.85 mg and 11.21 mg of gold and 5.82 mg and 14.04 mg of gold respectively. This illustrates the effect of the resins behaviour in solution on their ability to recover gold. XAD 4 resins are more hydrophilic than XAD 2 and they disperse satisfactorily through the solution upon agitation.

They also settle on the surface of the containing vessel after agitation minimising resin losses during sampling. XAD 2 resins are hydrophobic, they float on the surface of the solution after agitation, they do not disperse well and they do not settle after agitation. It is likely that these problems diminish XAD 2's ability to recover gold from solution, in comparison with XAD 4 and XAD 7, even when comparing resins impregnated to similar levels.

XAD 7 higher level impregnated resins recovered gold to a satisfactory level. The final capacities of the impregnated resins mirrored XAD 4 resins at similar levels of impregnation. The resins did not have any of the hydrophobicity problems of XAD 2 though they do not impregnate as easily as XAD 4, due to XAD 7's lower surface area ($450m^2/g$).

The physical durability of XAD 7 is its main failing. The resin pulverised with prolonged stirring, when Pyrex containers were used or if the resin was stirred using a magnetic stirring bar. Stirring times of 24 hours or greater resulted in a powdery resin which did not recover gold and also caused problems for filtration. While this problem was largely overcome by shaking the resin in polypropylene containers, some breakage of the resin did occur over time.

The effect of agitation on the resin was established by magnifying the beads after agitation, using scanning electron microscopy (SEM). Preparation of the resins and details of instruments used for SEM analysis are given in Chapter 3, (Sec. 3.7).

Figure 5.1 is an SEM of XAD 7 resin beads at 25X magnification, after 48 hours agitation in a polypropylene container. Some of the beads have been fractured, even though agitation was not aggressive. This was not seen in SEMs of XAD 2 and XAD 4 resins, under similar conditions. It is anticipated that the break up of XAD 7 during recovery would become more pronounced in an industrial situation, where the resin would be under constant physical stress and would be used repeatedly. The ability of the resin to withstand repeated impregnation, agitation, stripping, reimpregnation and reagitation over a long period of time is necessary if the resins are to compete with established methods of recovery, from an economic point of view, since resins are more expensive and therefore need to be fully recyclable in order to be cost effective.

5.5.2 A Comparison of SIR Recovery with Alternative Recovery Methods

Simpson et al (1) tested ion exchange resins and solvent extraction for the recovery of gold and silver from thiourea leach solutions.

Of the resins studied, an AG-50W-X8 cationic exchange resin achieved the highest loading (0.873kg Au/t) for batch recovery. The resin was eluted with a 0.2M NaCN-0.2M NaOH solution and 95% of gold was recovered.

Best results for solvent extraction of gold were achieved with a batch shake out using a 12:1 D2EHPA:TBP (Tri-Butyl-Phosphate) mixture. 68% recovery was achieved, however no figures for the loading capacity of the solvent mixture are given.

Deschênes (2) tested the recovery of gold from thiourea leach solutions using activated carbon. The initial concentration of gold in the leach liquor was 31-43ppm, thiourea concentration was 10g/L and iron concentration was 8.2-9.4g/L. Maximum gold loading of 5.4 kg Au/t, corresponding to 79% recovery, was achieved using 5g/L of carbon. 99% gold recovery was achieved when carbon levels were increased to 50g/L, however in this case loading was only 0.72kg Au/t. Deschênes suggested that gold loading would increase if thiourea concentrations were lower. Dissolved oxygen was also found to inhibit gold recovery with activated carbon.

Tests with ion exchange resins on the same leach solution achieved maximum loading of 0.978 Au kg/t corresponding to 97.9% recovery, using a Bio-Rad AG50W-X8 resin (in accordance with Simpson). The resin was washed with 5% $Na_2S_2O_3$ at pH 9 and 90% of gold was eluted from the resin.

Deschênes also tested D2EHPA as part of a synergistic extractant with TBP. 77.4% of gold in solution was recovered with a mixture of D2EHPA (15%) in TBP (50%), however no values for the loading of the solvent mixture for gold are given.

The recovery of gold by SIRs compare very favourably with methods tested by Simpson and Deschênes. However, it is important to note that recovery by the SIRs in this study was from a *clean* gold solution and the effect of interfering ions such as iron and copper and also the effect of excess thiourea in solution have not been addressed. A study of the effect of interferents on the recovery of gold by the SIRs is presented in Chapter 6.

5.6 Stripping of Gold From Resins After Recovery

One of the most important factors in the development of a satisfactory S.I.R. system, is the easy elution of the recovered gold from the S.I.R. for reduction of the bis-thiourea gold complex to elemental gold. A significant problem with the use of ion exchange resins for the recovery of precious metals, is that the greater the attraction of the resin for the particular metal, the more difficult it becomes to strip the resin of its recovered metal, e.g. weak base resins can be stripped by a simple sodium hydroxide solution while strong base resins require more aggressive eluting conditions (6). This can greatly add to the cost of recovery of gold from the resins. A process where elution of gold from the resin is straightforward and does not involve aggressive eluants and elevated temperatures and pressures would be a great advantage. For S.I.R. recovery systems, a simple method of eluting the precious metal from the resin is to wash the resin with an organic solvent which will strip the impregnated solvent from the resin and at the same time strip any gold complexed by solvent on the resin, back into solution.

The recovery of gold from the resin was achieved by washing the loaded resins with methanol. Methanol was used as the diluent for the solvent for the impregnation of the resin and also to strip the resin of solvent for mass balance studies. It therefore followed that methanol would wash any gold complexed to the solvent back into solution i.e. it would strip the resin of gold.

5.6.1 Elution of Gold From Loaded Resins

To elute the recovered gold from the resins, a weighed amount of the resin was washed in methanol (25ml) overnight. The methanol solution was then analysed for gold by AAS.

The conditions for AAS analysis of an organic solution are similar to those for aqueous solutions (7), except that the flow rate of acetylene must be lowered to allow for the contribution of methanol to the flame. In this case the flow rate of acetylene was lowered from 1.8dm^3 min^{-1} to 1.2dm^3 min^{-1}. The sensitivity of the spectrophotometer increased twofold for methanol, limiting analysis of gold solutions to 10ppm or lower (aqueous solutions have a linear plot of gold concentration vs. absorption for absorbencies up to 0.5 absorbance units, this corresponds to 20ppm Au in aqueous solution but only corresponds to 10ppm in methanol). Therefore standard solutions of 2ppm to 10 ppm were made up in methanol and all samples requiring dilution for analysis were diluted in methanol. The blank used for analysis was also methanol. A calibration curve for gold standards in methanol is given in Fig. 5.2 below.

Results

5.6.2 Elution of Gold from XAD 2 Impregnated Resins

Resin No.	Mass of Gold Recovered by Resin (mg)	Mass of Gold Eluted from Resin (mg)	% Balance
1	0.69	0.68	99.27
2	1.67	1.70	101.79
3	6.71	6.92	103.13
4	6.62	7.13	107.70
5	14.97	14.13	94.38

Table 5.22 The mass balance of gold recovered by the resins and gold stripped from the resins for XAD 2 resins.

5.6.3 Elution of Gold from XAD 4 Impregnated Resins

Resin No.	Mass of Gold Recovered by Resin (mg)	Mass of Gold Eluted from Resin (mg)	% Balance
1	12.10	7.62	62.98
2	16.86	11.45	67.91
3	19.66	17.11	87.03
4	24.89	21.58	86.67
5	25.92	22.53	86.92

Table 5.23 The mass balance of gold recovered by the resins and gold stripped from the resins for XAD 4 resins.

5.6.4 Elution of Gold from XAD 7 Impregnated Resins

Resin No.	Mass of Gold Recovered by Resin (mg)	Mass of Gold Eluted from Resin (mg)	% Balance
1	5.477	4.12	75.32
2	8.555	7.35	85.86
3	15.222	13.30	87.39
4	20.430	21.63	103.87
5	24.734	23.22	93.88

Table 5.24 The mass balance of gold recovered by the resins and gold stripped from the resins for XAD 7 resins.

The percentage gold recovered *from* the resins is much higher for XAD 2 and XAD 7 than for XAD 4, although for the series of five XAD 4 and XAD 7 resins, the percentage gold recovered increases steadily with the level of impregnation. It is possible that the percentage of gold eluted from the resin is related to the percentage of gold which has been recovered by a solvent extraction process (as opposed to an adsorption system). Therefore, the more dominant the solvent extraction process is, the higher the percentage of gold eluted from the resin. In the case of lower impregnated resins, especially for resins which readily adsorb gold when bare and where a large mass of gold is being forced onto the resin, the adsorption process becomes more significant and more gold will be recovered onto the resin by adsorption. For resins where the level of impregnation is higher, adsorption is not as relevant and the percentage recovered by solvent extraction is higher, therefore the percentage of gold eluted by washing the resin in methanol should also increase.

It should be noted that only an initial study on the stripping of gold from the resins for final recovery was carried out. Results indicate that gold recovered by solvent extraction is easily recoverable by simply washing the solvent from the resin, however, gold adsorbed onto bare sites on the resin may need more rigorous conditions for stripping. Also, a system of stripping which achieved high levels of gold recovery without washing solvent from the resin would be more convenient and more economical since it would eliminate the need to reimpregnate after each gold loading.

5.7 Experimental Error

Experimental error was kept to a minimum in all tests by standard methods such as repeating experiments in duplicate or triplicate. In the case of the studies on the capacity of the resins at varying levels of impregnation, it was not possible to repeat experiments under exact conditions. For this reason, the error involved in this experiment cannot be quantified.

One of the main sources of error during the experiment was the addition of gold to the solution since it was taken that exactly 5ml is added and any difference to this cannot be accounted for. Also, losses of resin during sampling and errors due to dilution of high concentration gold solutions may have contributed to overall error. The final mass balance of gold washed off the resin was, in some cases over 100% and this is obviously due to experimental error. While this error has not been quantified, trends prevail through each of the three sets of resins which indicate the general overall behaviour of the resins. It would be expected that, for similar experimental studies, the resins would show similar trends. The results for the capacity of the resins and the mass balance of gold should be taken therefore as scoping tests, that is, tests showing the general expected behaviour of the resins under similar conditions rather than exact details on the capacity of the resins. It is clear from the tests which resins performed best for gold recovery and it is this information which is most valuable. Any further work on the recovery of gold by the impregnated resins could concentrate on one or two of the higher capacity resins and from there, more detailed tests on the exact capacity of these resins could be carried out.

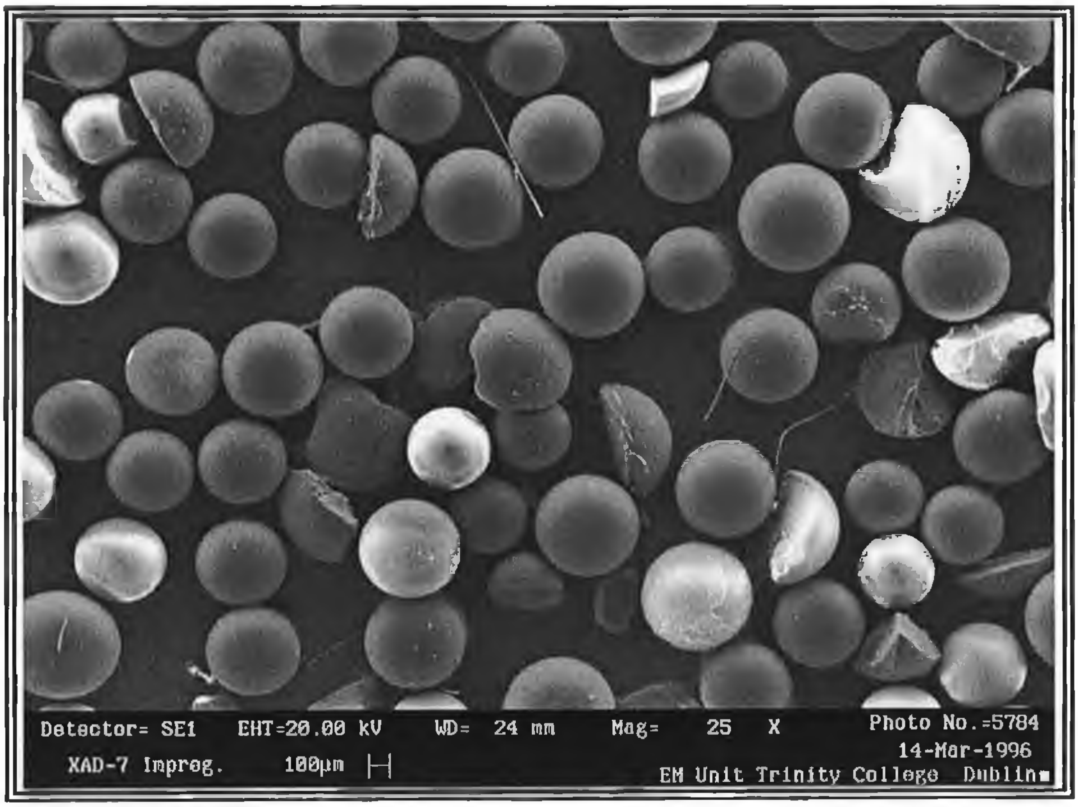


Fig. 5.1 SEM of XAD 7 bare resin after agitation. Magnification: 25X

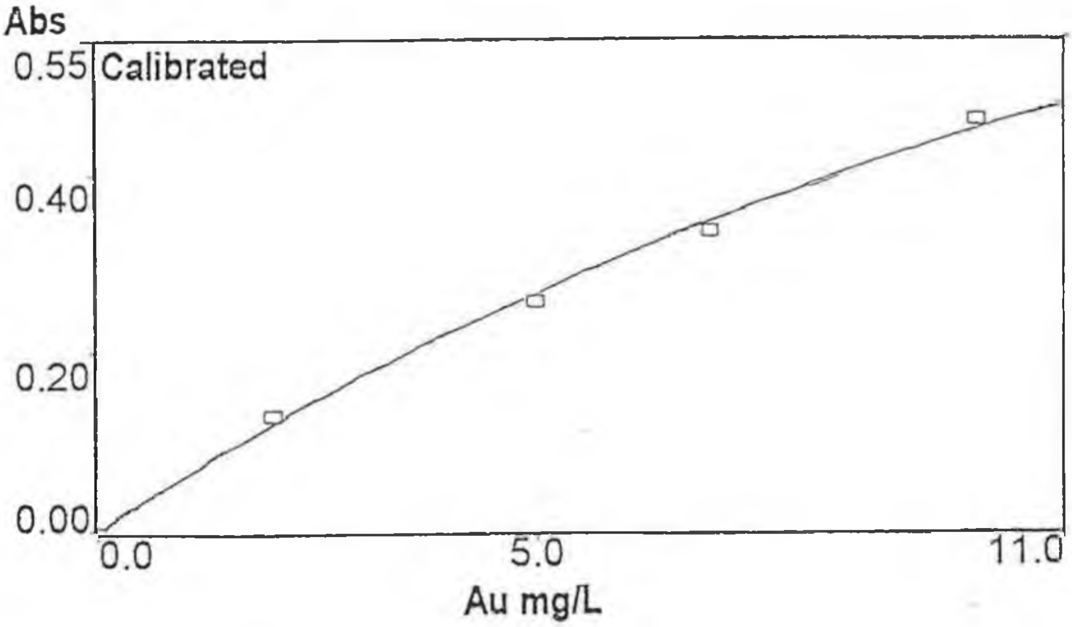


Fig. 5.2 AAS calibration curve for gold in methanol, taken from a Varian Spectra AA 200.

References

1 Gold and Silver Recovery from Thiourea Leach Solutions. W.W. Simpson, L. Peterson, R.G. Sandberg (US Bureau of Mines). Pacific Northwest Metals and Minerals Conference, Portland, Oregon, (April 29-May 2, 1984).

2 Literature Survey on the Recovery of Gold from Thiourea Solutions and the Comparison with Cyanidation. G. Deschênes. C.I.M. Bulletin, Vol. 79, pp 895, (November 1986).

3 The Loading Capacity of Selected Cation Exchange Resins and Activated Carbons for Gold-Thiourea Complex. R. Mensah-Biney, K.J. Reid and M.T. Hepworth. Minerals Engineering, Vol. 8, Nos1/2, pp 125-146, (1995).

4 The Separation of Gold from Acidic Leach Liquors with Amberlite XAD 7. R.I. Edwards, A.K. Haines and W.A.M. Te Riele. The Theory and Practice of Ion Exchange. M. Streat (Ed), SCI, London (1976).

5 Amberlite XAD Polymeric Adsorbents. Information Booklet. Rohm and Haas Company, (1995).

6 CIP and RIP - Where to next? C. A. Flemming. Hydrometallurgy: Fundamentals, Technology and Innovations. Chp 24. J.B. Hiskey and G.B. Warren, (Eds). SME. (1993).

7 An Introduction to Atomic Absorption Spectroscopy. L. Ebdon. Heydon and Son Ltd, (1982).

Chapter Six

The Effect of Interfering Species on the Efficiency of Gold Recovery by Solvent Impregnated Resins.

The effects of three separate interferents were studied:

1. Excess Thiourea.
2. Iron (as Fe $^{3+}$).
3. Copper (as Cu^{2+}).

The effect of the decomposition products of thiourea, in particular sulphur, on the surface of the resin was also studied using scanning electron microscopy and x-ray fluorimetry.

6.1 Analysis Techniques

Gold, copper and iron were analysed in solution using AAS. Thiourea and formamidine disulphide (RSSR) analysis was by High Performance Liquid Chromatography (HPLC).

6.2 Atomic Absorption Spectrophotometry

Conditions for AAS analysis of copper and iron were similar to gold analysis, except that the spectrophotometer was set up for analysis of the relevant element. Changes to the wavelength, slit width etc. were made automatically by the instrument.

6.3 High Performance Liquid Chromatography

HPLC is a chromatographic technique based on the retention of solute particles onto a stationary solid support. The sample is mixed with a mobile phase and is pumped through a chromatographic column containing a stationary phase. The components in the sample must be capable of interacting with the stationary phase, either by reacting chemically with it, being adsorbed onto it or dissolving in it. As a consequence of this interaction, the components become distributed between the two phases and their elution from the stationary phase can then be monitored using a suitable analysis technique e.g. uv spectrophotometry, fluorimetry etc.(1).

In this study, reverse phase ion pair chromatography was used for analysis. This is a partition type process, analogous to the ion association systems used in solvent extraction. For reverse phase chromatography, the sample component is partitioned between an *aqueous mobile phase* containing a low concentration of a counter ion and a *hydrophobic stationary phase*. This type of chromatography allows the separation of both ionised and non-ionised components under identical chromatographic conditions (2). This is important in the analysis of thiourea since it is necessary to simultaneously monitor both thiourea and its oxidation product RSSR in solution.

6.3.1 Choice of Stationary Phase

Any reverse phase column packing can be used as the stationary phase for ion pair applications. Greatest retention is achieved using the most alkyl-substituted bonded phase. Column stability is important using aqueous mobile phases as they have been found to be particularly aggressive towards column packing. Heavily substituted alkyl columns such as C_{18} are the most stable (3).

6.3.2 Choice of Mobile Phase

In reverse phase ion pair chromatography, the sample component is partitioned between an aqueous mobile phase and a non aqueous stationary phase. The most commonly used solvent combinations are water/methanol and water/acetonitrile. The choice is dictated by the solubility of the ion pair reagent; a water/methanol mixture is more useful because it readily dissolves more ion pair reagents, but an acetonitrile/water mixture gives better column efficiency, due to its lower viscosity.

6.3.3 HPLC Instrumentation

Chromatograph:	Shimadzu Liquid Chromatograph (LC-10AS).
Detector:	Shimadzu uv-vis Detector SPD-10A.
Column:	Phenomenex Ultracarb 5 ODS(30). Size: 150mm x 4.6mm.
Integrator:	Shimadzu CR5A Chromatopac.
Injection System:	Rheodyne fixed loop injector.

6.3.4 HPLC Conditions:

Detector Wavelength:	214nm.
Mobile Phase:	2.5mM TBAHS in 5% (vol) CH_3OH.
Flow Rate:	1ml/minute.
Injection Volume:	20µl.

6.3.5 Preparation of Mobile Phase

Tetrabutyl ammonium hydrogen sulphate (M_r = 339.54g), (1.698g) was dissolved in a 5% vol. CH_3OH/H_2O solution and made up to 2dm^3 in a volumetric flask. The solution was membrane filtered (0.5 µm filter), under vacuum, to remove any particles from solution and to de-gas the mobile phase. Dissolved gases in the mobile phase may affect the flow rate of the mobile phase through the column and can result in an unsteady baseline, when bubbles become trapped in the detector flow cell.

6.3.6 Retention Time

The retention time of a compound is the time it takes for its components to pass through the system from the point of injection to being detected. The chromatographic retention of the system can be altered by the introduction of long chained ionic alkyl compounds into the mobile phase. For the system used in this study, the retention time of thiourea was 1.9 minutes and the retention time of RSSR was 1.03 minutes.

6.4 Preparation Of Standards For AAS Analysis

6.4.1 Gold In Aqueous Solution

See Section 4.2.1

6.4.2 Ferric Iron

From a Spectrosol® standard solution of ferric nitrate-9-hydrate (1,000ppm), a stock solution of Fe^{3+} (10ppm) was prepared in H_2SO_4 (0.1M). From this solution, iron standards of 2, 5, 7 and 10 ppm were prepared in H_2SO_4 (0.1M). These concentrations are within the linear working range for the analysis of iron by AAS. The blank used was deionised water. Fig. 6.1 is the calibration curve for AAS analysis of iron, taken from a Varian Spectra AA 200 spectrophotometer.

6.4.3 Copper

From a Spectrosol® standard solution of copper (1,000ppm), a stock solution of Cu^{2+} (10ppm) was prepared in H_2SO_4 (0.1M). From this solution, copper standards of 1, 2, 5 and 7 ppm were prepared in H_2SO_4 (0.1M). These concentrations are within the linear working range for the analysis of copper by AAS. The blank used was deionised water. Fig. 6.2 is the calibration curve for AAS analysis of copper, from a Varian Spectra AA 200 spectrophotometer.

6.5 Preparation of Standards for HPLC Analysis

6.5.1 Thiourea

A stock solution of thiourea (1,000ppm) was prepared by dissolving thiourea (1.00g) in H_2SO_4 (0.1M) (1dm^3). From this solution, standards of 20 ,40 ,60, 80 and 100ppm were prepared in 0.1M H_2SO_4. A standard calibration curve for thiourea was constructed by plotting the peak area at the components retention time vs. the standard's concentration in ppm. See Graph 6.1.

6.6 Effect of Excess Thiourea on the Recovery of Gold by Solvent Impregnated Resins

The adsorption of thiourea onto the recovery medium, with its subsequent decomposition to RSSR, elemental sulphur and other oxidation products, is one of the biggest problems associated with the extraction and recovery of gold from thiourea leach slurries (4), (5), (6). These problems are detailed in Chapter 1.

Because of these problems, it was necessary to establish the extent of thiourea consumption caused by adsorption onto the resin and to determine whether the resins catalyse the oxidation of thiourea to RSSR and its further decomposition to elemental sulphur etc.. It was also necessary to establish whether the adsorption of thiourea affected the recovery of gold by the resins.

6.6.1 The Adsorption of Thiourea onto the Resins

For initial tests on the effect of thiourea on the resins, the resins were contacted with a clean thiourea solution, i.e. there was no gold present. The concentration of thiourea in solution was 492ppm (100ml) and the pH of the solution was adjusted to pH 3.5. 1g of resin was used in all cases and the resins were shaken in sealed polypropylene containers. Both the bare and the impregnated resins were studied.

Resins Studied

Resin No.	Resin type	Level of Impregnation (g D2EHPA/g)
1	XAD 2	BARE
2	XAD 4	BARE
3	XAD 7	BARE
4	XAD 2	0.066
5	XAD 4	0.179
6	XAD 7	0.121

Table 6.1 Resins studied for the adsorption of thiourea from solution. (No gold present).

Results

Resin No.	Concentration of Thiourea Remaining in solution (ppm)	Mass of Thiourea Adsorbed (mg)	% Thiourea Adsorbed
1	482.23	0.98	1.99
2	473.37	1.86	3.79
3	479.20	1.28	2.60
4	473.63	1.84	3.70
5	472.61	1.94	3.94
6	467.50	2.45	4.98

Table 6.2 The adsorption of thiourea onto the resins. $[\text{Thiourea}]_0 = 492\text{ppm}$.

For the adsorption of thiourea onto the resins from a solution containing only thiourea, adsorption rates were less than 5% in all cases. This compares favourably with adsorption rates reported for recovery of gold(I)thiourea using activated carbon, where adsorption of thiourea onto carbon resulted in the consumption of as much as 30% of thiourea by the recovery medium. No significant peak at the retention time for RSSR (1.03min) was seen on the chromatogram, indicating that decomposition of thiourea to RSSR had not occurred. This is significant since oxidation to RSSR is the first step in the irreversible decomposition of thiourea to elemental sulphur.

6.6.2 The Adsorption of Thiourea onto the Resins when Gold is Present in Solution.

The resins were contacted with a solution containing both thiourea and gold, in order to establish how thiourea affects the efficiency of gold recovery and to determine the competitive effect of thiourea on the recovery of gold by the resins.

A solution was prepared containing gold (22.46ppm) and excess thiourea (508ppm). The resins were contacted with the solution until equilibrium and the gold and thiourea remaining in solution was analysed by AAS and HPLC respectively. The mass of gold and thiourea retained by the resin was taken as the difference between the initial and final masses of gold and thiourea in solution.

Resins Studied

Resin No.	Resin type	Level of Impregnation (g D2EHPA/g)
1	XAD 2	BARE
2	XAD 4	BARE
3	XAD 7	BARE
4	XAD 2	0.183
5	XAD 4	0.107
6	XAD 7	0.121

Table 6.3 Resins studied for the recovery of gold from a solution containing excess thiourea.

Results

Resin No.	Concentration of Gold Remaining in Solution (ppm)	Mass of Gold Recovered (mg)	% Gold Recovered
1	18.98	0.30	13.17
2	16.15	6.31	28.11
3	18.36	0.42	18.89
4	5.91	1.74	77.54
5	1.93	2.16	96.20
6	5.51	1.70	75.46

Table 6.4 The recovery of gold from a solution containing excess thiourea. Initial gold concentration = 22.46ppm.

The recovery of gold from a solution containing excess thiourea is lower than recovery of gold from a 'clean' solution, i.e. when no excess thiourea is present in solution. Table 6.5 compares the recovery rate of each of the resins from (a) a clean solution and (b) a solution containing excess thiourea.

Resin	**% Gold Recovered From a 'Clean' Gold Solution**	**% Gold Recovered From a Gold Solution with Excess Thiourea**	**% Decrease**
XAD 2 Bare	26.94	13.17	49.15
XAD 4 Bare	31.97	28.11	12.07
XAD 7 Bare	27.93	18.89	32.37
XAD 2 Impregnated	96.51	77.54	19.66
XAD 4 Impregnated	97.73	96.20	1.57
XAD 7 Impregnated	93.21	75.46	17.75

Table 6.5 A comparison between gold recovered from a solution containing no excess thiourea and a solution containing 508 ppm of thiourea.

The decrease in gold recovery by the resins, ranges from almost 50% for bare XAD 2 resin to less than 2% for the impregnated XAD 4 resin. The effect of the surface area on the efficiency of the resins is again illustrated by the ability of the higher surface area resins to recover more gold from a solution containing excess thiourea. With the impregnated resins, the recovery of gold by XAD 4 ($750m^2/g$) is significantly higher than for XAD 2 ($330m^2/g$) or XAD 7 ($450m^2/g$), even though the impregnation levels of XAD 2 and XAD 7 are higher than that of XAD 4. The results indicate that the recovery of gold from a solution containing excess thiourea is highest for resins with the highest surface area (both in the case of the bare and the impregnated resins).

6.6.3 Adsorption of Thiourea by the Resins

Resin No.	Concentration of thiourea remaining in solution (ppm)	Mass of thiourea adsorbed (mg)	% Thiourea adsorbed
1	487.26	2.10	4.13
2	485.53	2.27	4.47
3	487.31	2.10	4.12
4	462.12	4.62	9.08
5	473.42	3.49	6.86
6	472.78	3.55	6.98

Table 6.6 The adsorption of thiourea onto the resins. $[\text{Thiourea}]_0$ = 508.3ppm.

The adsorption of thiourea does not follow the same pattern as gold recovery. In this case, recovery rates do not appear to be related to the surface area of the resins. Adsorption by the bare resins is between 4% and 4.5% for each of the three bare resins. For the impregnated resins, the level of thiourea adsorption is over twice the bare adsorption level for XAD 2 and approximately 1.5 times as high for XAD 4 and XAD 7. This indicates that there is some association between the impregnated solvent and thiourea. However, the selectivity of D2EHPA for thiourea is low and the level of thiourea adsorption for both the bare and impregnated resins remains much lower than the levels reported for activated carbon.

The recovery of thiourea onto the resins appears to occur mainly through simple adsorption, similar to the adsorption of gold onto the bare resins (although there appears to be *some* solubility of thiourea in the solvent). Adsorption, however, is not the dominant process for the recovery of *gold* onto solvent impregnated resins. In this case recovery is due mainly, though not exclusively, to solvent extraction by D2EHPA impregnated onto the resin. Assuming that D2EHPA does not show any significant selectivity to thiourea, it follows that, for the impregnated resins, the overall capacity of the resins will not be greatly affected since it is only that gold recovered by adsorption which may be affected by competition for adsorption sites with thiourea. In the case of higher level impregnated resins, the fraction of recovery which is due to adsorption is small, therefore thiourea interference should cause only a minimum loss of recovery capacity of the resins.

6.7 Effect of Thiourea on the Overall Loading Capacity of Gold

By the successive increase in the total mass of gold in solution, the effect of thiourea on the capacity of the resins for gold was studied. The concentration of thiourea in the gold solution was not increased during the study, since the decrease in thiourea concentration, by adsorption onto the resin and through sampling of the solution for analysis, is not significant because its initial concentration is much greater than that of the gold.

Resins studied:

Resin No.	Resin type	Level of Impregnation (g D2EHPA/g)
1	XAD 2	BARE
2	XAD 4	BARE
3	XAD 7	BARE
4	XAD 2	0.115
5	XAD 4	0.179
6	XAD 7	0.121

Table 6.7 Resins chosen.

Results

6.7.1 Analysis of Gold in Solution

Note:

Δ Au (mg) is the increase in the mass of gold recovered by the solvent impregnated resin after each successive addition of gold to the solution

Resin No 1

Total Mass of Gold Added to Solution (mg)	Total Mass of Gold Remaining in Solution (mg)	Mass of Gold Recovered (mg)	Δ Au (mg)	% Gold Recovered
2.21	1.93	0.28	-	12.60
4.36	3.86	0.50	0.22	11.53
6.50	4.77	1.73	1.23	26.60
10.75	8.83	1.92	0.19	17.84

Table 6.8 The recovery of gold by the bare XAD 2 resin, with increasing mass of gold in solution, when excess thiourea is present in solution.

Resin No.2

Total Mass of Gold Added to Solution (mg)	Total Mass of Gold Remaining in Solution (mg)	Mass of Gold Recovered (mg)	Δ Au (mg)	% Gold Recovered
2.21	1.61	0.60	-	27.10
6.50	5.35	1.15	0.56	17.75
8.63	6.31	2.32	1.17	26.87
10.76	7.93	2.83	0.51	26.20

Table 6.9 The recovery of gold by the bare XAD 4 resin, with increasing mass of gold in solution, when excess thiourea is present in solution.

Resin No 3.

Total Mass of Gold Added to Solution (mg)	Total Mass of Gold Remaining in Solution (mg)	Mass of Gold Recovered (mg)	Δ Au (mg)	% Gold Recovered
2.21	1.76	0.45	-	20.40
4.38	3.40	0.98	0.53	22.37
6.50	4.87	1.63	0.65	25.12
8.63	6.70	1.94	0.35	22.45
10.76	8.21	2.54	0.61	23.65

Table 6.10 The recovery of gold by the bare XAD 7 resin, with increasing mass of gold in solution, when excess thiourea is present in solution.

Resin No 4

Total Mass of Gold Added to Solution (mg)	Total Mass of Gold Remaining in Solution (mg)	Mass of Gold Recovered (mg)	Δ Au (mg)	% Gold Recovered
2.21	0.85	1.36	-	61.70
4.36	2.05	2.31	0.95	53.03
6.51	3.07	3.44	1.12	52.78
8.65	4.55	4.10	0.66	47.38
10.79	4.27	6.52	2.42	60.40

Table 6.11 The recovery of gold by the impregnated XAD 2 resin, with increasing mass of gold in solution, when excess thiourea is present in solution.

Resin No 5

Total Mass of Gold Added to Solution (mg)	Total Mass of Gold Remaining in Solution (mg)	Mass of Gold Recovered (mg)	Δ Au (mg)	% Gold Recovered
2.21	0.51	1.70	-	76.95
4.33	1.21	3.15	1.45	72.18
6.52	0.97	5.55	2.40	85.09
8.67	1.43	7.24	1.70	83.51
10.82	1.70	9.12	1.88	84.28

Table 6.12 The recovery of gold by the impregnated XAD 4 resin, with increasing mass of gold in solution, when excess thiourea is present in solution.

Resin No 6

Total Mass of Gold Added to Solution (mg)	Total Mass of Gold Remaining in Solution (mg)	Mass of Gold Recovered (mg)	Δ Au (mg)	% Gold Recovered
2.21	0.74	1.49	-	67.22
4.36	1.20	3.17	1.68	72.57
6.52	1.96	4.55	1.39	69.87
8.66	1.34	7.32	2.77	84.52
10.82	1.75	9.07	1.74	83.83

Table 6.13 The recovery of gold by the impregnated XAD 7 resin, with increasing mass of gold in solution, when excess thiourea is present in solution.

Resins 1, 2 and 3 are bare XAD 2, 4 and 7 respectively. Their recovery remains below 30% in all cases and a satisfactory level of recovery is not achieved at any stage. In the case of the impregnated resins, recovery of gold is just as good as for resins impregnated to a similar level recovering gold from a 'clean' solution. Table 6.14 is a comparison of the recovery of gold from a clean gold thiourea solution and from a solution containing excess thiourea. While no exact comparison can be made between the resins, since the mass of gold added to each solution is not exactly the same, it is still quite clear, that for resins of similar levels of impregnation and with a similar mass of gold added to solution in each case, the recovery of the impregnated resins is not any lower.

Clean Gold Solution			**Excess Thiourea in Solution**		
Resin	**Mass of Gold Added (mg)**	**% Gold Recovered**	**Resin**	**Mass of Gold Added (mg)**	**% Gold Recovered**
XAD 2 (0.124g/g)	10.63	52.39	XAD 2 (0.115g/g)	10.79	60.40
XAD 4 (0.126g/g)	11.80	82.25	XAD 4 (0.179g/g)	10.82	84.28
XAD 7 (0.199g/g)	11.00	77.05	XAD 7 (0.121g/g)	10.82	83.83

Table 6.14 A comparison of the recovery of gold from a clean gold solution and from a solution containing excess thiourea.

There was no distinct difference between the recovery of gold by the impregnated resins in a solution containing excess thiourea and recovery by the resins in a 'clean' solution. The indication is, that an excess of thiourea over gold of approximately 50 to 200 fold has no significant effect on gold recovery.

6.8 Effect of Interfering Metal Ions on the Recovery of Gold From Solution

The extraction of gold from ores such as chalcopyrite ($CuFeS_2$) is not cost effective using cyanide (7). The success of thiourea for the extraction of gold from this type of ore would result in the mining of gold deposits originally considered to be economically non-viable. Copper and iron are common constituents of many ores and concentrates and therefore it is important to determine the effect of these ions on the recovery of gold by solvent impregnated resins.

6.9 Ferric Iron

Iron bearing minerals are often associated with gold ores. Ferric iron is also a common oxidant used for the extraction of gold by thiourea. Therefore Fe^{3+} is a common interfering ion in extraction systems using thiourea. Its effect on the recovery of gold by solvent impregnated resins must be established in order to predict the effect of iron on the recovery capacity of the resins for gold.

Concentrations of iron in solution vary considerably but may be up to or greater than 1g of iron per litre of solution or 1,000ppm.

A solution containing gold (20ppm) and Iron (1,000ppm) was prepared using bis-thiourea gold(I) perchlorate and ferric nitrate-9-hydrate ($Fe(NO_3)_3.9H_2O$). The resins (1g) were contacted with the solution until equilibrium was established (3hr) and any gold and iron remaining in solution was analysed by AAS. The mass of gold and iron retained by the resin was taken as the difference between initial and final masses of gold and iron in solution.

Resins studied

Resin No.	**Resin type**	**Level of Impregnation (g D2EHPA/g)**
1	XAD 2	BARE
2	XAD 4	BARE
3	XAD 7	BARE
4	XAD 2	0.183
5	XAD 4	0.158
6	XAD 7	0.173

Table 6.15 Resins used for the study of the effect of iron on the recovery of gold by SIRs.

Results

6.9.1. Effect of Excess Iron on Gold Recovery

Resin	Mass of Gold Remaining in Solution (mg)	Mass of Gold Recovered (mg)	% Gold Recovered
1	1.30	0.46	26.19
2	0.66	1.11	62.87
3	0.83	0.94	53.12
4	1.61	0.16	8.79
5	1.24	0.53	29.93
6	1.20	0.56	31.75

Table 6.16 The recovery of gold by the resins in the presence of excess Fe^{3+}; $[Au]_0$ = 17.64ppm

The initial recovery rate for gold by the bare resins, in a solution containing excess iron, is higher than recovery from a clean gold(I)thiourea solution. While the exact mechanism of recovery by the resins is not understood, it is possible that the increase in the concentration of cations in solution augments the initial recovery rates of gold onto the resin. However, it is likely that the overall *capacity* of the bare resins for gold will be affected if high levels of iron are also adsorbed by the resins. Further work on cation adsorption by the resins needs to be undertaken in order to fully establish the mechanism of recovery.

In the case of the impregnated resins, the recovery of gold by the resins has been very significantly diminished by the presence of iron in solution. Gold recovery has decreased from over 90% to a maximum of approximately 30% for XAD 4 and XAD 7 impregnated resins. The decrease in gold recovery is due to the extraction of iron (III) by D2EHPA.

6.9.2 Analysis of Iron Recovered by the Resin

Resin	**Mass of Iron Remaining in Solution (mg)**	**Mass of Iron Adsorbed (mg)**	**% Iron Adsorbed**
1	93.51	1.21	1.3
2	92.50	2.22	2.3
3	93.24	1.48	1.6
4	89.13	5.59	5.90
5	83.32	11.40	12.04
6	80.52	14.20	15.00

Table 6.17 The recovery of iron by the resins. [Fe^{3+}] = 947.2ppm

The mass of iron recovered from solution is significantly higher for the impregnated resins than for the bare resins, indicating the selectivity of D2EHPA for iron(III). Although XAD 4 had the highest gold recovery in the presence of excess iron, it is clear that iron interference will significantly affect the capacity of the resin for gold.

6.9.3 Extraction of Iron by D2EHPA

$$Fe^{3+}_{(aq)} + 3(HX)_{2(org)} \longleftrightarrow FeX_6H_{3(org)} + 3H^{+}_{(aq)}$$

where X is the anion $(C_8H_{17}O)_2PO_2^-$ and $(HX)_2$ is the dimeric reagent.

The extraction of iron by D2EHPA has been studied by Sato et al (8), (9). They report that extraction is slower to attain equilibrium in a sulphuric acid solution in comparison with other mineral acids (HCl or HNO_3). Sato found that in the extraction of iron from sulphuric acid solutions, the distribution coefficient decreases monotonically with the increase in aqueous acidity while for extraction from HCL or HNO_3, the distribution coefficients decrease with increasing aqueous acidity up to 4-5M, then pass through a minimum and increase above this acidity. Sato suggests two separate extraction mechanisms, depending on the acidity of the aqueous solution; at low hydrogen ion concentrations, extraction proceeds through a cation exchange reaction in which hydrogen is liberated, while at higher concentrations, extraction is by a solvating reaction similar to that with non-ionic reagents. Extraction at higher concentrations for HCL and HNO_3 is given as:

$$Fe^{3+}_{(aq)} + 3NO_3^-{}_{(aq)} + 3/2(HX)_{2\,(org)} \longleftrightarrow Fe(NO_3)_3 \,.\, 3HX_{\,(org)}$$

Sato concludes that the extraction efficiency of iron(III) by D2EHPA is in the order:

nitric acid > hydrochloric acid > sulphuric acid

However, it is clear from data in this study that iron extraction by D2EHPA at low H_2SO_4 concentrations remains a significant problem. Since low acidity is required to maximise gold extraction by the SIRs, some method of iron passivation is required in order to ensure acceptable levels of gold recovery are maintained.

Some procedures exist for the precipitation of ferric iron from solution. These include selective precipitation as the hydroxide (10) during the extraction of nickel. Iron is oxidised and separated as $Fe(OH)_3$, using nickel hydroxide as the hydrolysing agent. Other techniques include the jarosite process, used for zinc. Jarosite is a naturally occurring mineral of iron. The process involves the precipitation of the mineral (or other jarosite type minerals) by the addition of calcine. The crystalline precipitate formed is then easily separated from the leach solution. This process has been modified for the recovery of silver and lead from similar types of leaches i.e. where excess iron causes interference problems for the recovery of the precious metal.

EDTA (ethylenediamine tetraacetic acid) can also complex ferric iron without affecting ions with a +1 charge. Since gold is present as the gold(I)thiourea ion, which has an overall charge of +1, it would be theoretically possible to pacify interfering iron in solution by complexing with EDTA before contact with the impregnated resins occurs. The complexation of EDTA with ferric iron has the added advantage of occurring in an acidic environment. Since the leach solution is at approximately pH 3.5 for gold recovery with S.I.R.s, no further adjustment of the solution's pH would be required for passivation of ferric iron using EDTA (11).

An alternative oxidising agent such as hydrogen peroxide could also help since it would not compete with gold for recovery by D2EHPA. This may have its own problems however, since hydrogen peroxide is known to rapidly degrade polystyrene based resins in the presence of catalysts such as trace levels of iron and copper . Degradation occurs as breaking of the crosslinked resin structure (12).

While this study identified the problems associated with ferric iron, it was not possible to undertake any detailed experimental work on the competitive nature of iron for the recovery of gold by D2EHPA. However, it is acknowledged that iron interference is a serious problem and it is likely that the S.I.R. system proposed in this study, would not achieve satisfactory levels of gold recovery in situations where iron concentrations in the leach solution remained high. Further work on excess iron in solution and methods of precipitation etc. are required before the resins can be applied to the recovery of gold from an ore containing iron, or in situations where ferric iron is added as an oxidant.

6.10 Copper

Copper is often found as an interferent in gold leachates. It is present in concentrates from chalcopyritic ores and other copper bearing minerals such as chalcocite (Cu_2S). For this study, a typical concentration of copper in solution was taken as 500ppm.

A solution containing gold (20ppm) and copper (500ppm) was prepared using bis-thiourea gold(I) perchlorate and cupric nitrate-3-hydrate ($Cu(NO_3)_2.3H_2O$. The solution was contacted with resin (1g) until equilibrium was attained (3hr) and any gold and copper remaining in solution was analysed by AAS. The mass of gold and copper retained by the resin was taken as the difference between initial and final masses of gold and copper in solution.

Resins Studied

Resin No.	Resin type	Level of Impregnation (g D2EHPA/g)
1	XAD 2	BARE
2	XAD 4	BARE
3	XAD 7	BARE
4	XAD 2	0.183
5	XAD 4	0.158
6	XAD 7	0.173

Table 6.18 Resins studied for the recovery of gold in an excess copper solution

Results

6.10.1 Effect of Excess Copper on Gold Recovery

Resin	Mass of Gold Remaining in Solution (mg)	Mass of Gold Recovered (mg)	% Gold Recovered
1	1.50	0.43	22.25
2	0.89	1.05	54.32
3	1.11	0.82	42.42
4	1.14	0.79	40.87
5	0.67	1.26	65.18
6	0.57	1.36	70.36

Table 6.19 The recovery of gold by the resins in the presence of excess Cu^{2+}; $[Au]_0 = 19.33$ppm

6.10.2 Analysis of Copper Recovered by the Resin

Resin	Mass of Copper Remaining in solution (mg)	Mass of Copper Adsorbed (mg)	% Copper Adsorbed
1	48.80	2.11	4.14
2	49.88	1.03	2.02
3	47.85	3.06	6.01
4	47.07	3.84	7.54
5	45.49	5.42	10.64
6	45.32	5.59	10.97

Table 6.20 The adsorption of copper onto the resins $[Cu]_0 = 551.93$ppm

The selectivity of D2EHPA towards copper is reported to be low. Akita et al reported a separation factor of 55.2 for the selective separation of Zn(II) from Cu(II)(13). Also, D2EHPA has been proposed for the selective removal of zinc from a copper amine solution, indicating low selectivity of the copper amine complex towards the solvent (14).

However, some selectivity of D2EHPA towards copper is evident from the results of this study. The presence of copper ions in solution significantly affects the recovery of gold by the resins. While gold recovery rates are not as low as for iron interference, the effect of copper is still very significant and methods of pacifying copper before the S.I.R.s are added to the solution need to be studied.

Deschênes et al (7) removed interfering copper from a gold bearing chalcopyritic concentrate by cementation. Iron cementation is the most extensively used process for copper precipitation. Other metals used for copper cementation include nickel and zinc.

Since the concentration of copper leached by thiourea is much lower than similar ores leached using cyanide (e.g. 160ppm Cu^{2+} for thiourea; 5g/l Cu^{2+} for cyanide, under similar conditions (7)), copper interference is not as significant a problem at the recovery stage and its removal from solution should not be as troublesome.

6.11 Study of the Effect of the Oxidation Products of Thiourea on SIRs

The effects of the irreversible oxidation products of thiourea, in particular sulphur, were investigated using scanning electron microscopy (SEM). Preparation of the resins and details of instruments used for SEM analysis are given in Chapter 3 (section 3.7).

The impregnated resins (1g) were contacted with a solution containing the gold(I)thiourea complex (20ppm), excess thiourea (500ppm) and ferric iron (500ppm) for three weeks. Ferric iron was added to promote the decomposition of thiourea. Sulphur formed in solution was seen as a fine yellow suspension which also deposited onto the polypropylene containers.

The resins were filtered and micrographs of each of the resins were obtained. Figs 6.3, 6.4 and 6.5 show the effect of sulphur formation on the resins. The deposition of sulphur onto the surface of the resins can be seen as a rough, non continuous coverage on the surface of the resin. Fig. 6.6 is a micrograph of a XAD 7 resin at 1K magnification. The thickness of the sulphur coating was measured at 2.57μm.

Sulphur passivation of recovery media has previously been reported to be one of the main stumbling blocks for the introduction of thiourea as a lixiviant in the gold mining industry. The fine suspension of sulphur formed by the irreversible decomposition of thiourea covers the surface area of the resin, inhibiting diffusion through the resin and preventing gold recovery (6). Sulphur passivation can be a serious problem and the SEMs illustrate the need to maintain resin contact with sulphur containing solutions to a minimum. Further work on its prevention may be needed in order to fully utilise the high capacity potentials of these resins.

However, it should be noted that these micrographs show the *long term effects* of sulphur on the resins, in a solution containing a high concentration of a sulphur bearing species. Under the conditions proposed in this work, contact with thiourea solutions should not be longer than 1 hour. The concentration of sulphur in a normal leach solution should also be kept to a minimum if the concentration of oxidising agent added to the thiourea solution is properly controlled (15).

Once these parameters are maintained, the problems posed by sulphur passivation and its effect on gold recovery should be kept to a minimum.

6.12 X-Ray Fluorescence Elemental Analysis of the Resins

The elemental constituents of the resins before and after impregnation were analysed by a point analysis of the resin surface using x-ray fluorescence analysis (XRF). XRF is a non-destructive physical method used for the elemental analysis of solids and liquids. The specimen is irradiated with photons of sufficient energy to cause the elements in the sample to emit their characteristic x-ray line spectra (fluoresce). Elements in the specimen can be identified by their spectral line energies or wavelengths for qualitative analysis. The intensity of the emitted energy is related to the concentration of that element for quantitative analysis (16).

Figures 6.7 to 6.12 show the spectral analysis of the resins before and after impregnation of the resins with D2EHPA. The impregnated resins were also contacted with a solution containing gold (20ppm), excess thiourea (500ppm) and ferric iron (500ppm) for three weeks in order to establish whether sulphur formed in solution by the decomposition of thiourea became coated on the resin surface.

XRFs of the bare resins show the carbon peak of the polystyrene (XAD 2 and XAD 4) and acrylic ester (XAD 7) resins. Other peaks in the spectrum (particularly for XAD 7) are due to noise rather than any other elemental constituents of the resin.

For the impregnated resins (Figs. 6.10 to 6.12), the carbon peak is again seen, however significant peaks have also appeared for phosphorus and for iron. The spectra indicate the significant change in the composition of the resin's surface after impregnation and also the adsorption of particles from solution onto the resins surface. The size of the phosphorus peaks on the XRF spectrum in relation to the carbon peaks, give an indication of the level of impregnation of the resins, however this is not entirely quantitative and also depends on the particular point of the resin chosen for analysis. Peaks around the large phosphorus peak assigned to Al, Si etc. are more likely to be shoulder peaks of the larger P peak rather than an indication of the presence of these elements. The iron peak is due to the solvent extraction of iron from solution by

D2EHPA. The size of the iron peak again indicates the level of extraction of iron from solution by the impregnated resin and reaffirms the need to maintain iron levels in the recovery system to a minimum. A small peak for gold is marked on the spectra for XAD 4 and XAD 7, however, since the concentration of gold on the surface of the resin is very low in comparison to carbon, phosphorus and iron and also because the energy of emitted radiation for gold is close to that of phosphorus on the emission spectrum, the peak is not distinct and is partially hidden by the shoulder peak of the much larger P peak. Small peaks indicating the presence of sulphur on the resin surface are also seen, confirming the need to keep contact of the resins with solutions containing sulphur to a minimum.

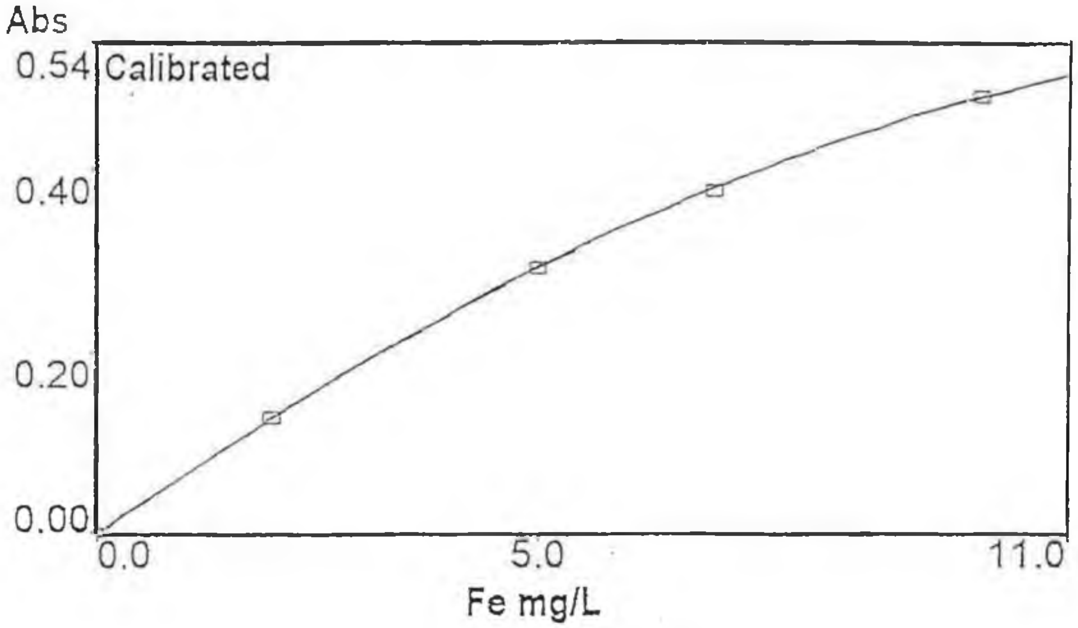


Fig. 6.1 AAS calibration curve for iron in aqueous solution, taken from a Varian Spectra AA 200

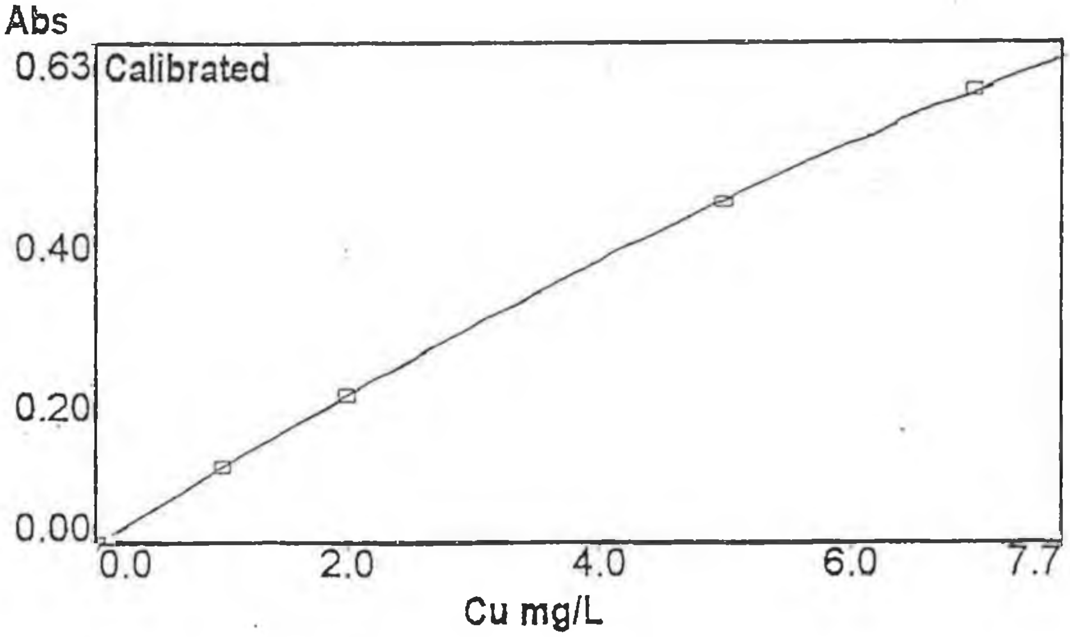


Fig. 6.2 AAS calibration curve for copper in aqueous solution, taken from a Varian Spectra AA 200

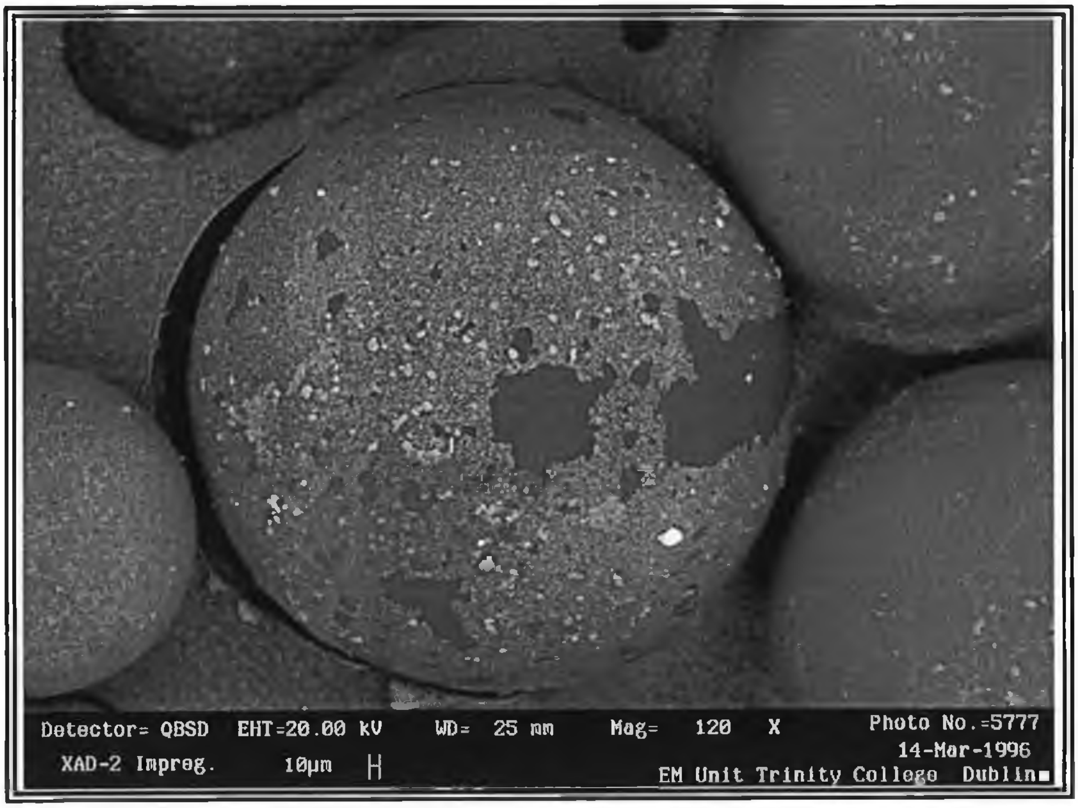


Fig. 6.3 Sulphur coating on a XAD 2 impregnated resin. Magnification: 120X

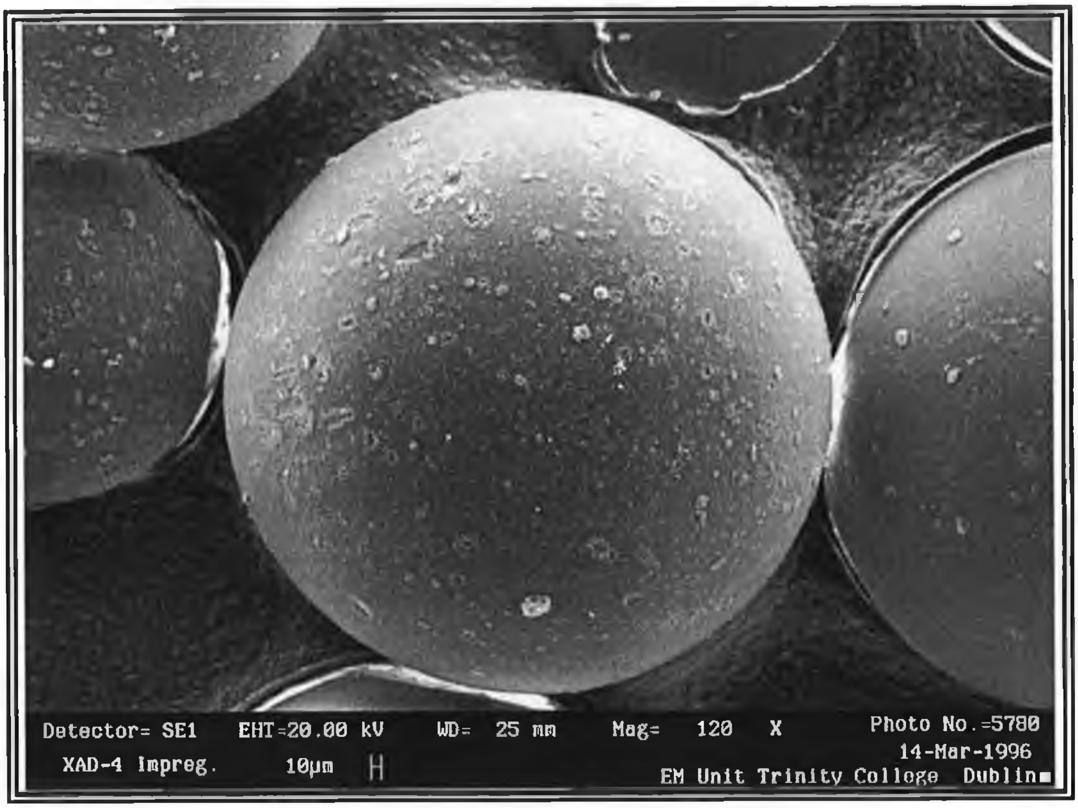


Fig. 6.4 Sulphur coating on a XAD 4 impregnated resin. Magnification: 120X

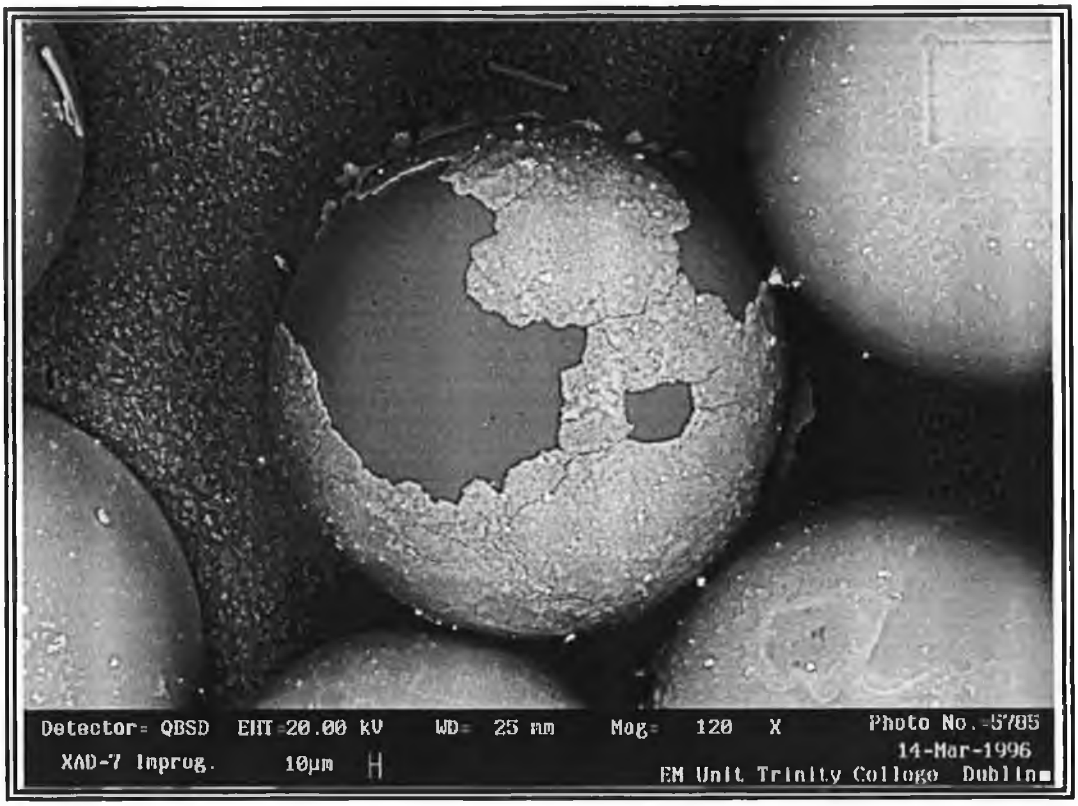


Fig. 6.5 Sulphur coating on a XAD 7 impregnated resin. Magnification: 120X.

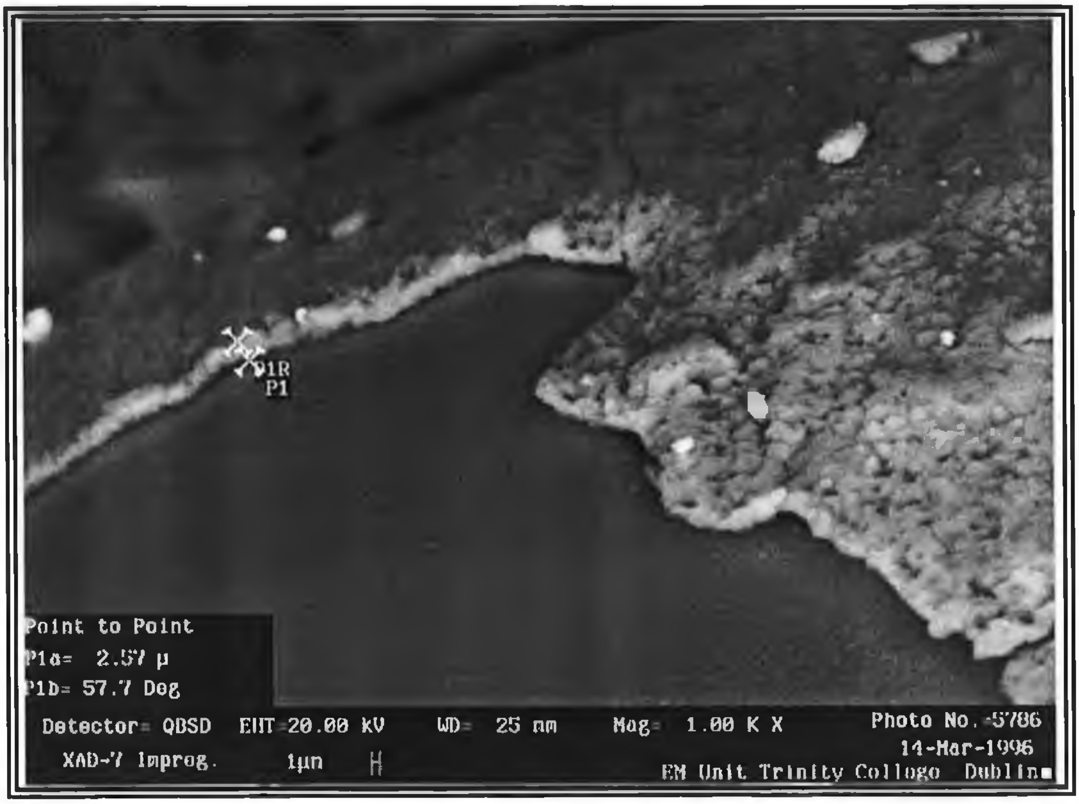
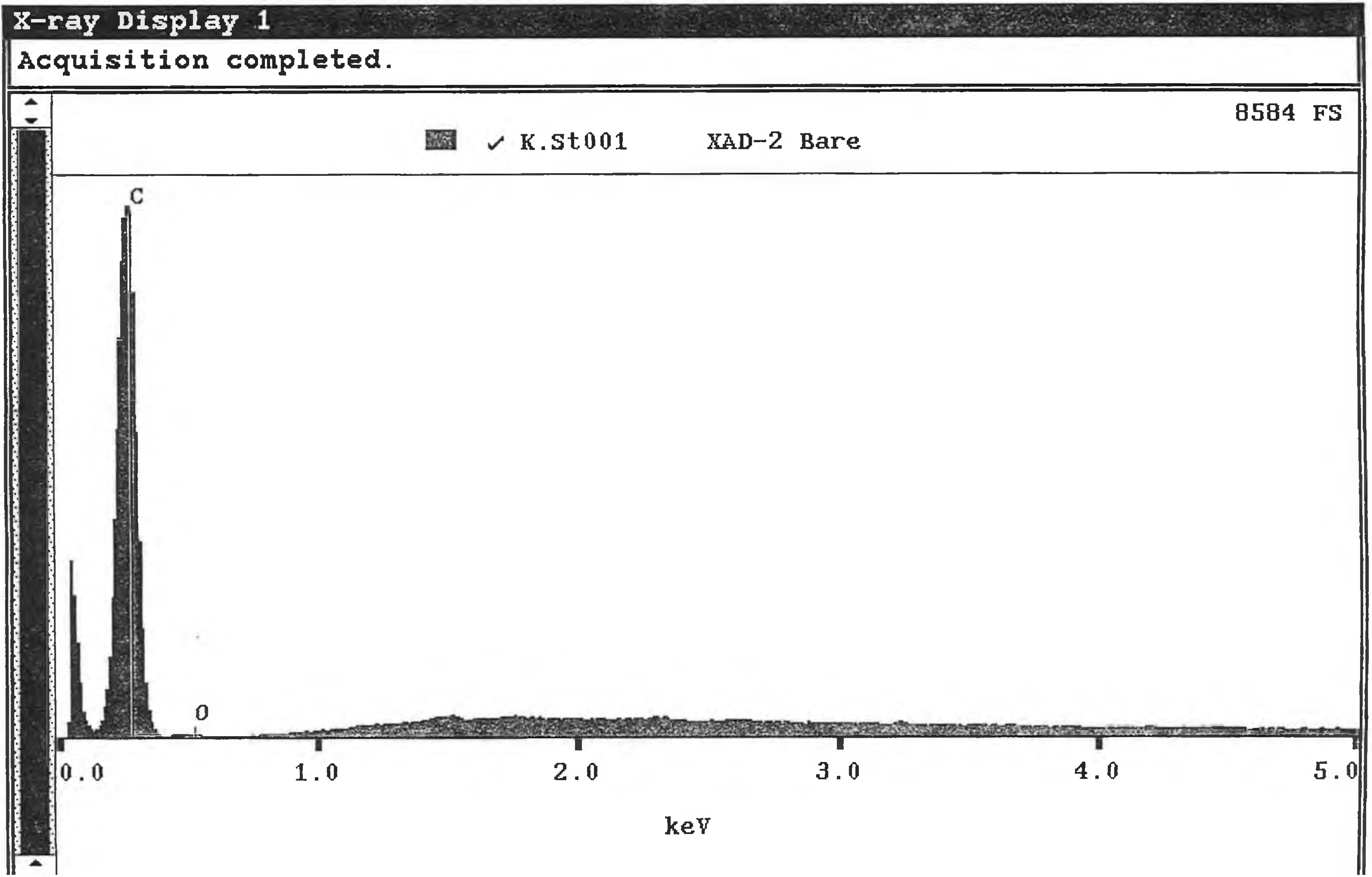


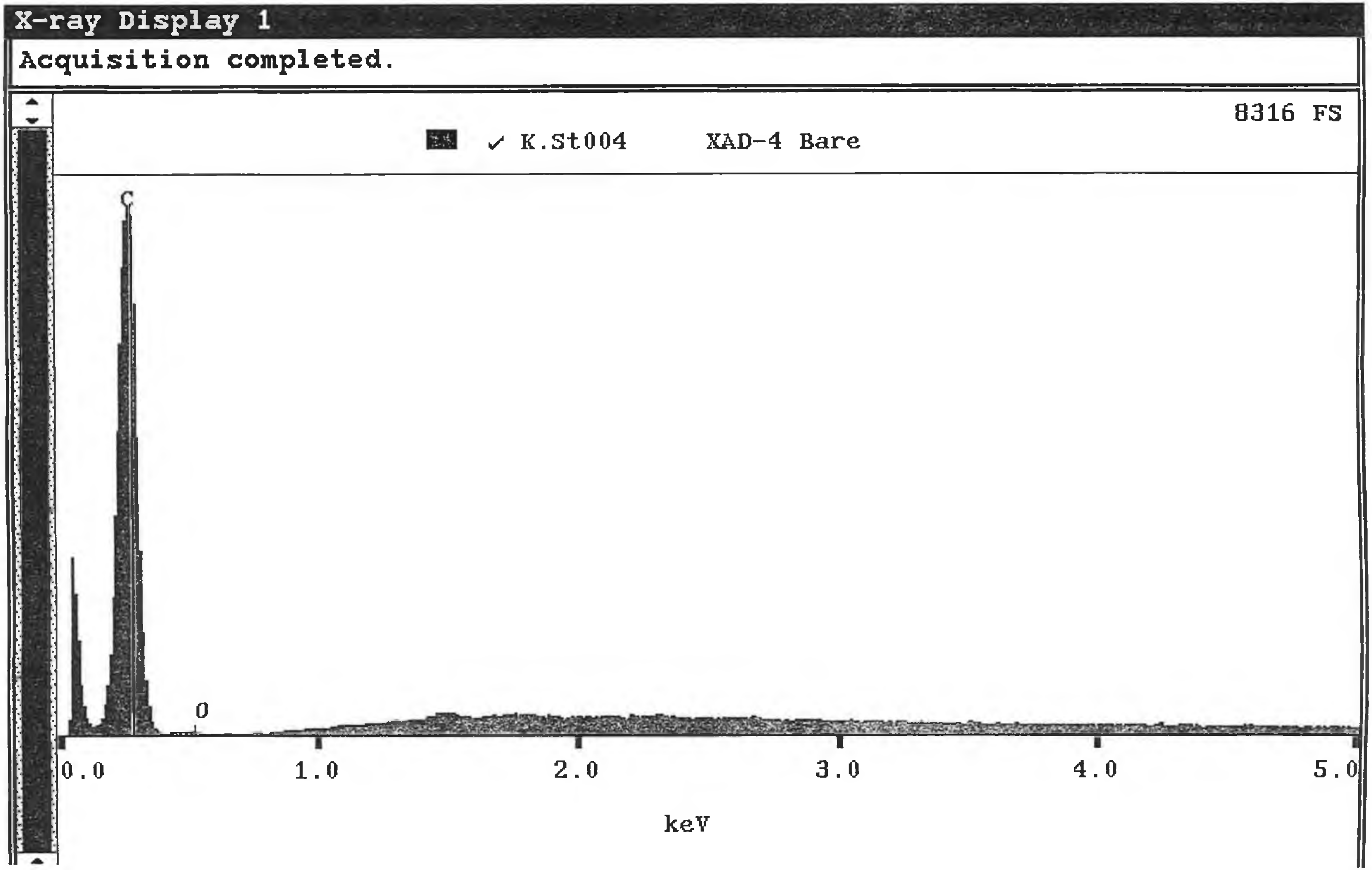
Fig. 6.6 Estimation of sulphur coating thickness on a XAD 7 impregnated resin. Magnification: 1,000X.



X-ray Display 1

Acquisition completed.

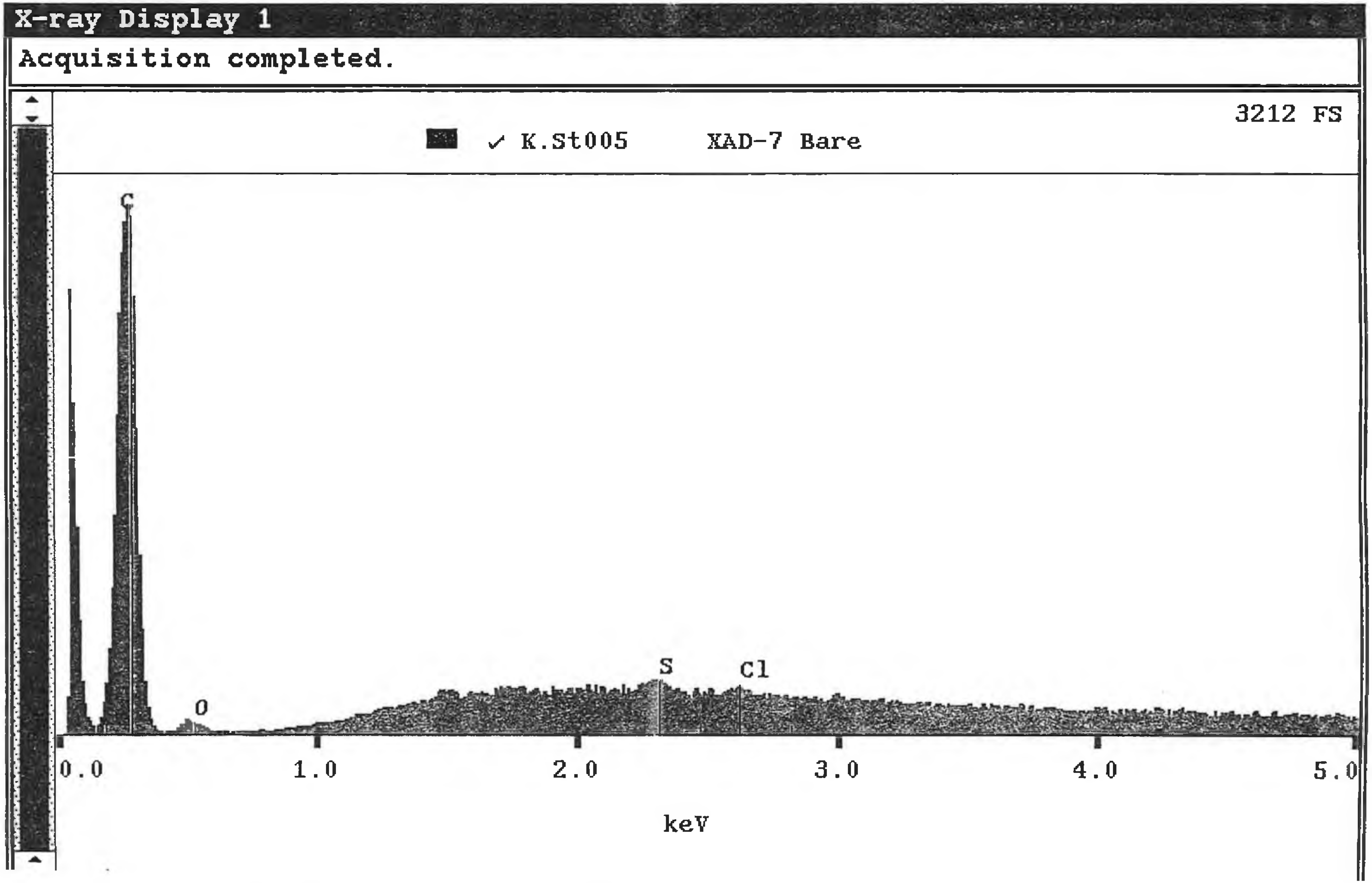
Fig. 6.7 X Ray Fluorescence spectrum of a bare XAD 2 resin.



X-ray Display 1

Acquisition completed.

Fig. 6.8 X Ray Fluorescence spectrum of a bare XAD 4 resin.



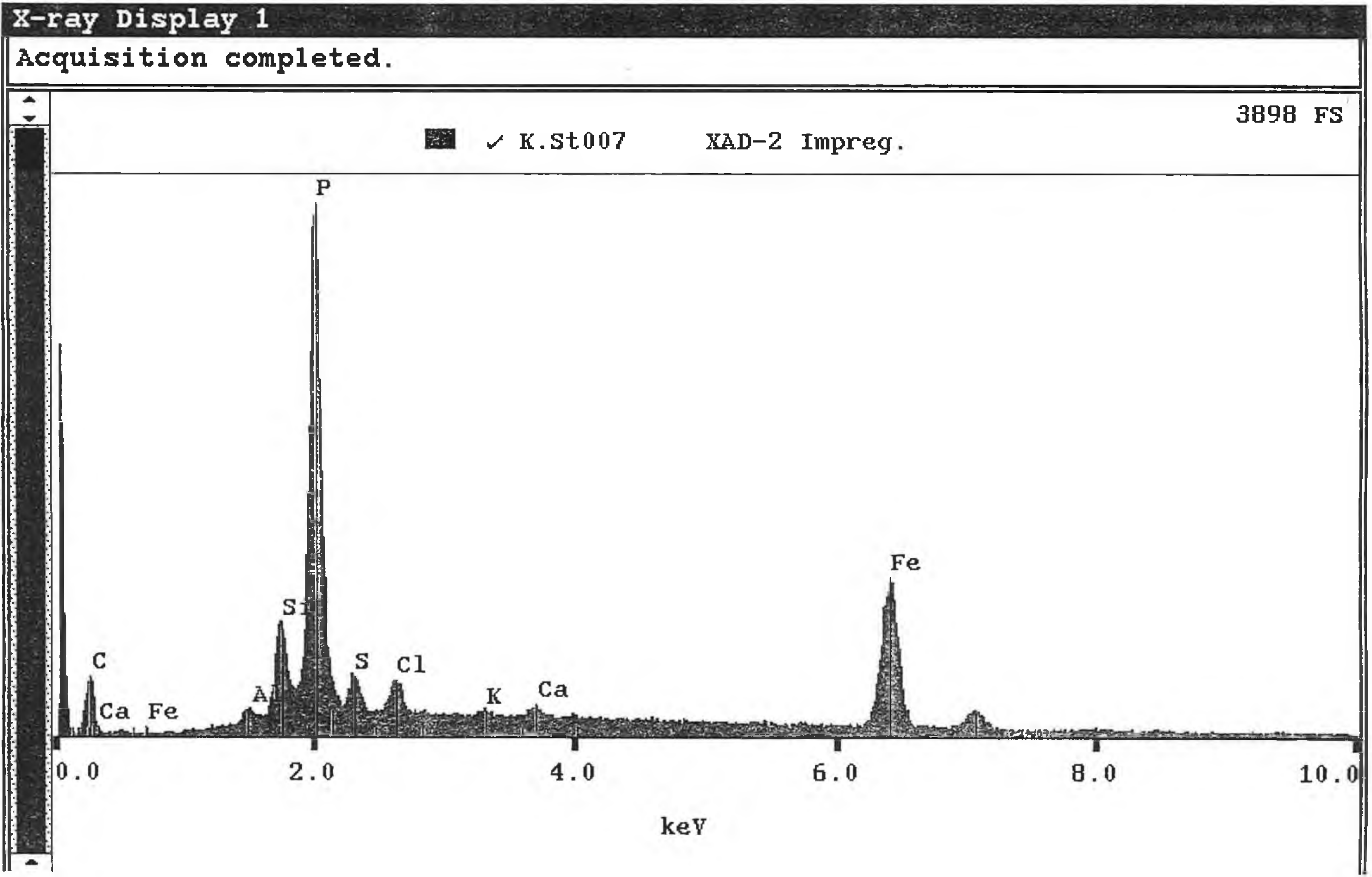
X-ray Display 1

Acquisition completed.

▆ ✓ K.St005 XAD-7 Bare

3212 FS

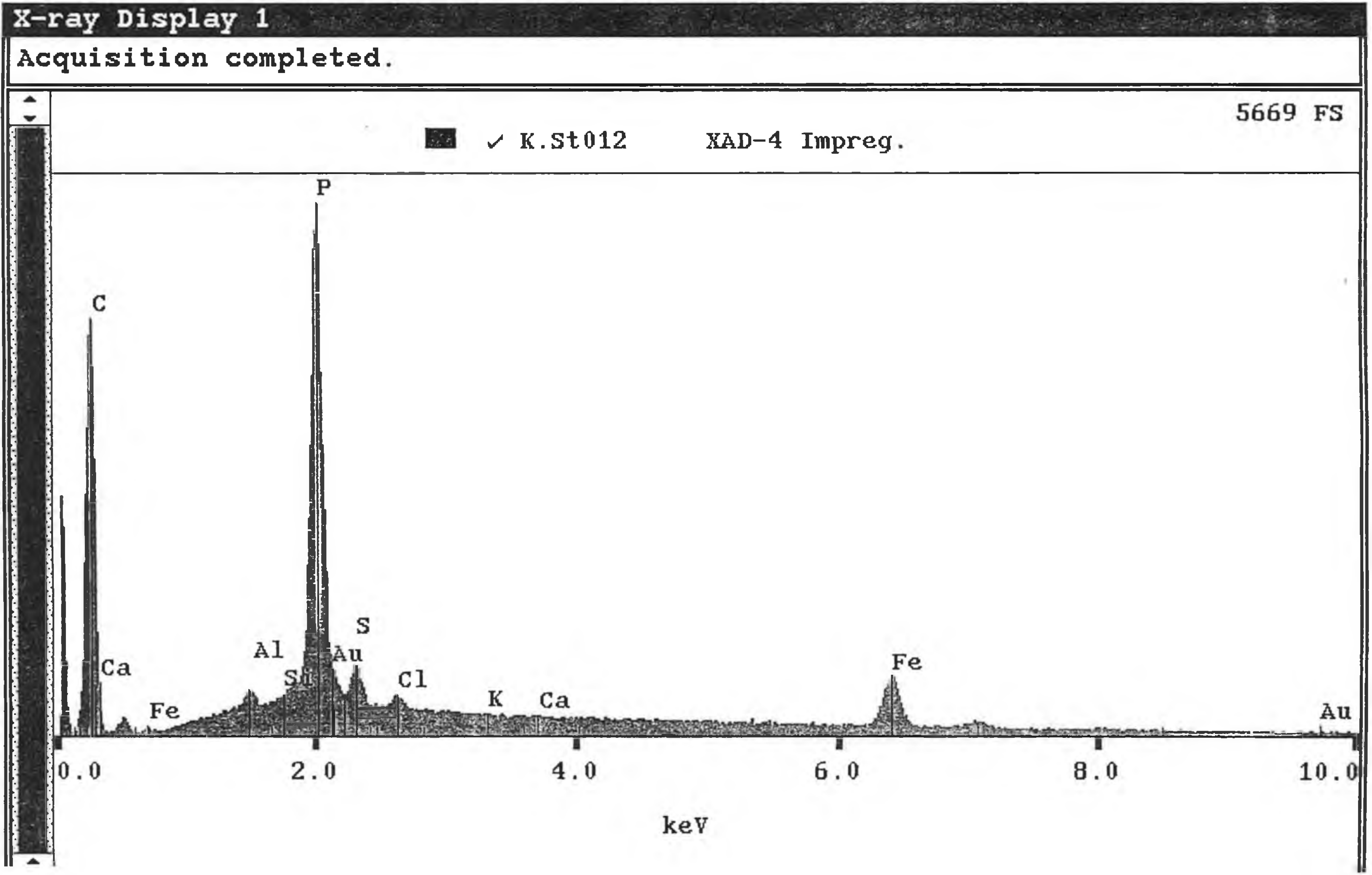
Fig. 6.9 X Ray Fluorescence spectrum of a bare XAD 7 resin.



X-ray Display 1

Acquisition completed.

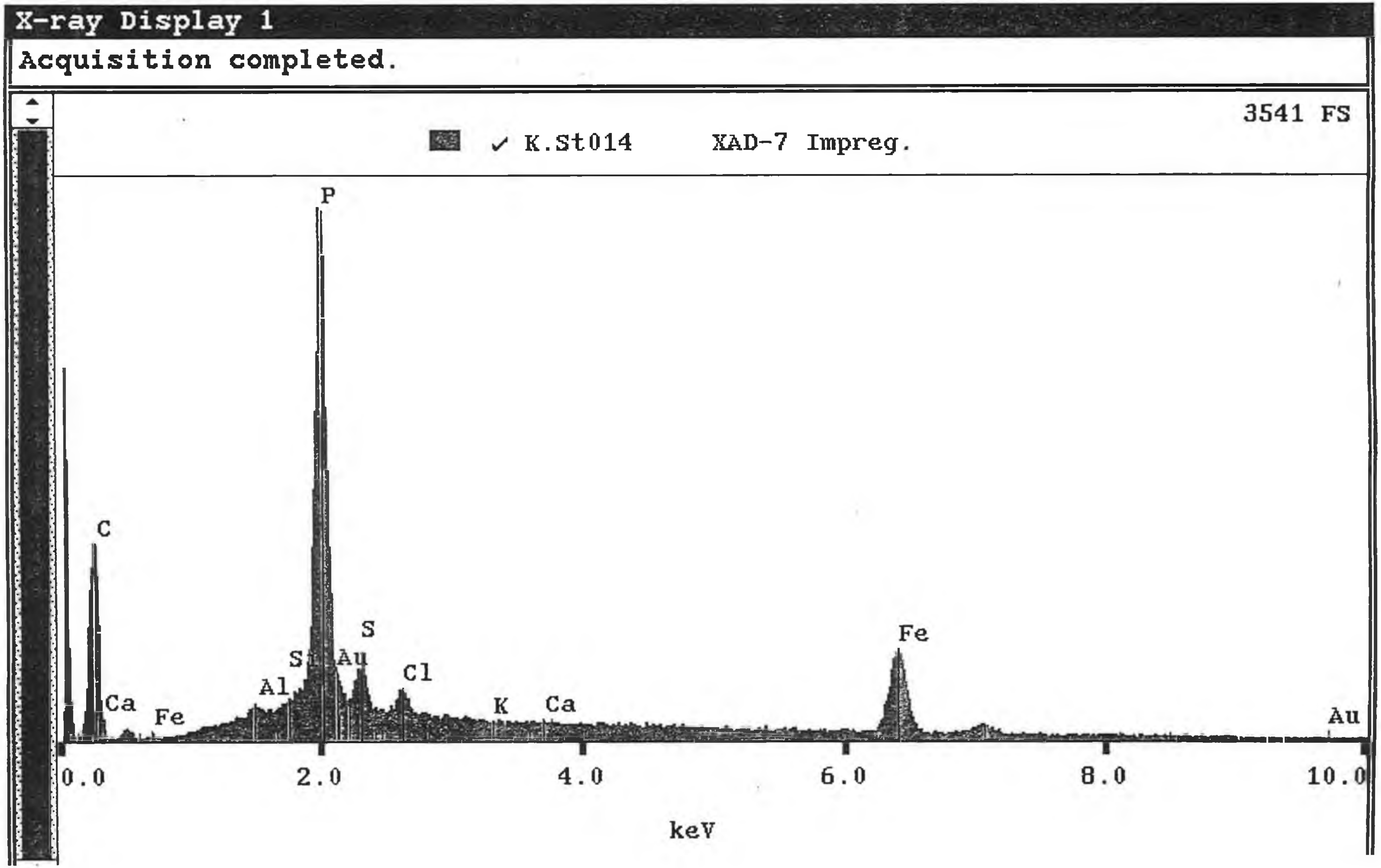
Fig. 6.10 X Ray Fluorescence spectrum of XAD 2 impregnated resin, after contact with gold / thiourea/ iron solution.



X-ray Display 1

Acquisition completed.

Fig. 6.11 X Ray Fluorescence spectrum of XAD 4 impregnated resin, after contact with gold / thiourea/ iron solution.



X-ray Display 1

Acquisition completed.

3541 FS

▨ ✓ K.St014 XAD-7 Impreg.

Fig. 6.12 X Ray Fluorescence spectrum of XAD 7 impregnated resin, after contact with gold / thiourea/ iron solution

References

1 Vogel's Textbook of Quantitative Chemical Analysis, 5th Edition. Chp. 8. G.H. Jeffery, J. Bassett, J. Mendham, R.C. Denney. Longman Scientific & Technical.

2 B. Grigorova and S.A. Wright. J. of Chromatography, Vol. 368, pp 444-449, (1986).

3 R. Gloor and E.L. Johnson. J. Chromatog. Sci., Vol. 15, pp 413-423 (1977).

4 Literature Survey on the Recovery of Gold from Thiourea Solutions and the Comparison with Cyanidation. G. Deschênes. C.I.M. Bulletin, Vol. 79, pp 895, (November 1986).

5 Gold and Silver Recovery from Thiourea Leach Solutions. W.W. Simpson, L. Peterson and R.G. Sandberg. Pacific Northwest Metals and Minerals Conference. Portland, Oregon, (April 29-May 2 1984).

6 Research and Development Activities for the Recovery of Gold from Non-Cyanide Solutions. R.Y. Wan and M. LeVier. Hydrometallurgy: Fundamentals, Technology and Innovations. Editors: Hiskey J.B. and Warren, G.B.. Chapter 27, SME (1993).

4 A Comparison of Cyanide, Thiourea and Chlorine as Lixiviants for Gold. A.O. Filmer, P.R. Lawrence and W. Hoffman. Gold Mining, Metallurgy and Geology (The Aus. I.M.M. Perth and Kalgoorlie Branches, Regional Conference on...), pp 279-287, (1984).

7 A Preliminary Techno-Economic Evaluation of the Extraction of Gold from a Chalcopyrite Concentrate using Thiourea. G. Deschenês, D. Bernard, P.J.H. Prud'Homme and D. Laforest. Minerals Engineering, Vol. 7, No. 4, pp 435-448, (1994).

8 The Extraction of Iron(III) from Aqueous Acid Solutions by Di(2-Ethylhexyl) Phosphoric Acid. T. Sato, T. Nakamura and M. Ikeno. Hydrometallurgy, Vol. 15, pp 209-217, (1985).

9 Extraction of Iron(III) from Sulphuric and Hydrochloric Acid Solutions by Di-(2-ethylhexyl)phosphoric Acid. T. Sato and T. Nakamura. Proc. Int. Solvent Extraction Conference, pp 238-248, ISEC '71. The Hague, Netherlands.

10 Hydrometallurgical Extraction and Reclamation. E. Jackson. Ellis Horwood Series in Industrial Metals, (1986).

11 Vogel's Textbook of Quantitative Chemical Analysis, 5th Edition. Chapter 12. G.H. Jeffery, J. Bassett, J. Mendham, R.C. Denney. Longman Scientific & Technical.

12 The Oxidative Degradation of Ion Exchange Resins and its Prevention. L.S. Goldring. The Theory and Practice of Ion Exchange. M. Streat (Ed), SCI, London, (1976).

13 Sorption and Separation of Divalent Metals by a Macromolecular Resin Containing Organophosphorus Acids. S. Akita and H. Takeuchi. Journal Of Chemical And Engineering Data, Vol. 37, No. 3, pp 303-306, (1992).

14 Purification of Copper Amine Solution During the Production of Copper Oxide. L.D. Jayaweera, D. Etheridge and A.O. Filmer. Fourteenth Austrailasian Chemical Engineering Conference: Chemeca 86, Adelaide, (1986).

15 New Aspects in Thiourea Leaching of Precious Metals. R.G. Schulze. Journal of Metals, Vol. 6, pp 62-65, (June 1984).

16 Analytical Chemistry Handbook, J.A. Dean. McGraw and Hill, Inc (1993).