PRECONCENTRATION OF SOME PRECIOUS METALS USING DEBT IMPREGNATED RESIN

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

HÜRMÜS REFİKER

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR

THE DEGREE OF MASTER OF SCIENCE

IN

CHEMISTRY

AUGUST 2005

Approval of the Graduate School of Natural and Applied Sciences.

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ABSTRACT

PRECONCENTRATION OF SOME PRECIOUS METALS USING DEBT IMPREGNATED RESIN

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August 2005, 107 pages

In this thesis, trace amounts of gold and silver have been determined by flame absorption spectrometry (FAAS) after preconcentration by N,N-diethyl-N'-benzoylthiourea (DEBT) impregnated resin (Amberlite XAD-16).

In the first part of the thesis, sorption behaviours of gold and silver with DEBT impregnated resin under optimized conditions; stirring time, pH, desorption of metals and metal ion capacities of the resin have been studied in batch process. Metal ion capacity of resin is calculated as 0.17 mmol/g resin and 0.104 mmol/g resin for silver and for gold, respectively.

In the second part of the thesis, preconcentration of gold and silver was tried by DEBT impregnated resin using column process under optimized conditions; pH, flow rate and volume of sample solution, nature of eluent, flow rate and volume of eluent However, due to partial leaching of DEBT by time, no satisfactory and reproducible results could be obtained.

In the final part of the study, metal chelates prepared in aqueous solutions were passed through the column under optimized conditions and satisfactory sorption-desorption and selective preconcentration could be achieved. Under optimized conditions, silver and gold ions at the concentrations of 0.05 µg/mL and 0.015 µg/mL with preconcentration factors of 7.7 and 6.7, respectively could be determined by FAAS. The proposed method is highly selective without the need for any interference elimination process.

Keywords: Precious metals, Solid-phase extraction, DEBT, Amberlite XAD-16

ÖZ

BAZI KIYMETLİ METALLERİN DEBT-TUTTURULMUŞ REÇİNE İLE ÖNDERİŞTİRİLMESİ

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Ağustos 2005, 107 sayfa

Bu çalışmada, eser miktarlardaki altın ve gümüş N,N-dietil-N'-benzoiltiyoüre (DEBT) tutturulmuş reçineyle (Amberlite XAD-16) önderiştirildikten sonra alevli atomik absorpsiyon spektrometri (alevli AAS) kullanarak ile tayin edilmiştir.

Tezin ilk bölümünde, DEBT impregne olmuş reçine üzerine altın ve gümüş sorpsiyon davranışları optimize edilen deney şartlarında ki bunlar ; karıştırma zamanı, pH, metallerin desorpsiyonu ve reçinenin metal iyonu kapasiteleri yığın (batch) prosesi ile çalışılmıştır. Reçinenin, metal iyon kapasitesi sırası ile, gümüş için 0.17 mmol/g reçine ve altın için 0.104 mmol/g reçine olarak bulunmuştur.

Tezin ikinci bölümünde, DEBT impregne edilmiş reçine ile kolon prosesi uygulanarak optimize edilen şartlarda ki bunlar ; pH, örnek hacmi ve akış hızı, eluent yapısı, eluentin hacmi ve akış hızı altın ve gümüşün önderiştirilmesine çalışılmıştır.

Ancak, DEBT’in zamana bağlı olarak yüzeyden kısım kısım uzaklaşması nedeni ile başarılı ve tekrarlanabilir sonuçlar elde edilememiştir.

Çalışmanın son bölümünde, sulu çözeltide oluşturulan metal şelatları optimize edilmiş deney şartlarında kolondan geçirilmiş, başarılı sorpsiyon – desorpsiyon ve seçici önderiştirme işlemi elde edilmiştir. Optimize edilen şartlarda, gümüş ve altının, sırası ile 0.05 µg/mL ve 0.015 µg/mL derişimlerde, önderiştirme faktörleri ; 7.7 ve 6.7 olmak üzere alevli AAS ile tayin edilebileceği gösterilmiştir. Önerilen yöntem çok seçici olması nedeniyle girişimi elimine etmek için herhangi proses gerektirmeyen bir önderiştirme metodu olarak sunulmaktadır.

Anahtar Kelimeler : Kıymetli metaller, Katı-Faz Ekstraksiyonu, DEBT, Amberlite XAD-16.

To My Family…

ACKNOWLEDGEMENTS

I would like to express my appreciation my supervisor Prof. Dr. R. Sezer Aygün for her guidance, support and great care in writing of this thesis.

I would like to thank sincerely my co-supervisor Assoc. Prof. Dr. Melek Merdivan for her suggestions and help.

I would like to thank much Prof. Dr. O. Yavuz Ataman for his kind suggestions, great interest and time he spent for me.

I would like to thank Prof. Dr. Gülhan Özbayoğlu for directing me to Mr. Halil Evdim and also thank Mr. Erdoğan Fide and Mr. Metin Yalçın (Doba Investments) for supplying me real Cu-ore samples from Cyprus Mines Corporation.

I would like to thank Assoc. Prof. Dr. Orhan Acar for supplying SRMs.

I would like to thank the committee members in advance for their contributions to my thesis.

Endless love and thanks to my parents for always loving and supporting me. Also, thanks for believing and encouraging me during these stressful times.

Many thanks to my cousins, Meltem and Bahadır Ege for their close interest in my health.

Lots of thanks to Murat Kaya for his patience and endless help for everything. Also, thanks Serap Tekin, Mukadder Kısa and Serhan Demirci for all of their moral supports and friendships.

Thanks to all the members of Analytical Chemistry Group for their understanding and support.

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CHAPTER 1

INTRODUCTION

1.1 Precious Metals

Platinum group elements (PGEs); Ruthenium (Ru), Rhodium (Rh), Palladium (Pd), Osmium (Os), Iridium (Ir), Platinum (Pt) together with Gold (Au) and Silver (Ag) are called precious metals (PMs). This term, ‘precious’ reflects their economic value as well as their rare occurrences. Gold occurs as metal; silver, gold and the platinum metals are also recovered in the electrolytic refining of copper. The precious metals do not have tendency to form oxides under standard condition with the exception of Osmium which smells even at room temperature due to formation of OsO_4. Silver and gold are not susceptible to oxidation by hydrogen ions under standard conditions, and this noble character accounts for their use, together with platinum, in jewelry and ornaments [1].

Because of their resistance to corrosion and oxidation, high melting points, electrical conductivity, catalytic activity and biological inertness, these elements have wide applications in chemical, electrical, electronic, glass, medicine and automotive industries [1].

This study is mainly concerned with two of the precious metals; gold and silver.

1.1.1 Gold

Gold is probably the first metal discovered by man. Gold and the search for it have been among the major factors in exploration, conquest, and growth of civilization. Archaeological studies have shown that the goldsmith's art dates from at least 4000 BC in Mesopotamia and that it then spread throughout the whole group of ancient civilizations around the eastern Mediterranean, including Egypt. It also arose in the New World in the Pre-Columbian cultures of Peru and Mexico, as well as in the Asian civilizations.

Gold is widely distributed throughout the world, normally in very low concentration and generally in native form as metal. It is usually alloyed with silver and often contains small amounts of copper. The only compounds of gold found in nature are the tellurides, typically calaverite ($AuTe_2$), petzite ($(AuAg)_2Te$), sylvanite ($(AuAg)Te_2$), among others. Gold is found in native form in both lode and alluvial deposits. In the largest gold reefs of the world, in South Africa, gold is present as veins and stringers in a quartz matrix accompanied with pyrite and quartz sand. Many pyrite and pyrrhotite minerals contain gold from which the metal is recovered during the extraction of copper, silver, lead, zinc and nickel. Although in low concentrations, gold is also present in the sea water, being conservatively estimated that the oceans contain 70 million tons of gold in solution. The major world producers of gold are South Africa, the countries of the old USSR, Canada, the United States and Australia [2].

1.1.2 Uses of Gold

Some uses of gold are as follows;

- as coinage metal, standard for monetary systems in many countries,
- in jewellery, decoration,
- in dentistry,
- in plating for coating space satellites, as it is a good IR reflector and is inert,
- in photography; as chlorauric acid ($HAuCl_4$) for toning the silver image,
- in medicine; as disodium aurothiomalate which is administered (intramuscular) as a treatment for arthritis and ^{198}Au is used for treating cancer and other conditions and
- in electronics [3].

1.1.3 Abundances of Gold

It is known that the constituent of gold mineral is complicated. In mineral, the gold content is very low and the distribution of gold is heterogeneous [4]. In Table 1.1 a summary of gold abundances and its trace amounts are given.

Table 1.1 Abundances of gold [3].

Abundance	(μg/kg)
Universe	0.6
Sun	1
Meteorite (Carbonaceous)	170
Crustal rocks	3.1
Sea water	0.05
Stream	0.002
Human	100

1.1.4 Some Gold Compounds

Some of the important gold compounds and its oxidation state are given in the Table 1.2.

Table 1.2 Some of gold compounds [2]

Oxidation State	Substances
Au^-	$[Au\ (NH_3)_n]^-$ in liquid NH_3
Au^0	gold clusters (exp ($[Au_8\ (PPh_3)_8]^{2+}$)
Au^+	Au_2S, $[Au\ (CN)_2]^-$ and other complexes.
Au^{2+}	rare but some complexes are known
Au^{3+}	Au_2O_3 , $Au\ (OH)^{4-}$ (aq), $AuCl_4^-$ (aq), $AuCl_3\ (OH)^-$ (aq), Au_2S_3 , AuF_3 , Au_2Cl_6 , $AuBr_3$, complexes
Au^{5+}	AuF_5
Au^{7+}	AuF_7

1.1.5 Silver

Silver is known by the mankind since Pre-Historical times, and its discovery is estimated to be shortly after that of copper and gold. The Egyptians considered gold to be a perfect metal, and gave it the symbol of a circle. Since silver was the closest to gold in perfection, it was given the symbol of a semi-circle. Later this semi-circle led to a growing moon symbol, probably due to the likeness between the shining metal and the moon glow. The Romans called silver argentum, keeping this as the international name of the element, from where its chemical symbol derives.

The main silver mineral is the argentite (Ag_2S), which usually occurs associated to other sulfides as copper or lead sulfide. Other silver minerals are cerargirite ($AgCl$), proustite ($3Ag_2S.Ag_2S_3$), pirargirite ($3Ag_2S.Sb_2S_3$), stefanite ($5Ag_2S.Sb_2S_3$) and native silver. The silver occurs in most of the lead and copper ores, and associated to cobalt and gold arsenide. Most of the produced silver is a by-product of the extraction process of these metals. However there are some mines especially devoted to the extraction of this element.

The largest world producers of silver are the USA, Canada, Mexico, Bolivia, former-USSR, Australia and Germany [2].

1.1.6 Uses of Silver

Some uses of silver are as follows:

- as sterling silver for jewelry and silverware,
- in photography ($AgBr$, $AgNO_3$),
- in dental alloys,
- in solder and brazing alloys,
- for electrical contacts,
- in high capacity silver-zinc and silver-cadmium batteries,
- in some paints which are used for making printed circuits,
- in mirror production,
- as AgI for seeding clouds to produce rain and
- as coinage metal [3].

1.1.7 Abundances of Silver

The increasing use of silver compounds and silver containing preparations in industry and medicine has resulted in an increased silver content of environmental samples. Silver also enters the environment in industrial waters because it often occurs as an impurity in copper, zinc, arsenic and antimony ores. In addition, low level exposure to silver compounds is widespread owing to soluble silver compounds where they were used to disinfect drinking water. Silver with a concentration of up to 20-200 μg/mL is permitted to control antimicrobial activity with no risk to human health [5]. In Table 1.3, a summary of silver other abundances and its trace amounts are given.

Table 1.3 Abundances of silver [3].

Abundance	**(μg/kg)**
Universe	0.6
Sun	1
Meteorite (Carbonaceous)	140
Crustal rocks	80
Sea water	0.1
Stream	0.3
Human	No data

1.1.8 Some Silver Compounds

Some of the important silver compounds and its oxidation state are given in the Table 1.4.

Table 1.4 Some of Silver Compounds [2].

Oxidation State	Substances
Ag^0	Rare Ag $(CO)_3$ at 10 K
Ag^+	Ag_2O, Ag $(OH)_2^-$ (aq), Ag $(H_2O)_4^+$ (aq), AgF, AgCl, etc., Ag^+ salts (exp: $AgNO_3$) , Ag_2S, Ag $(CN)_2^-$, and other complexes
Ag^{2+}	AgF_2 , [Ag $(C_5H_5N)_2$ $]^+$, AgO is not Ag^{2+} but $Ag^+Ag^{3+}O_2$
Ag^{3+}	rare AgF_4^-, AgF_6^{3-}

1.2 Preconcentration and Separation of Precious Metals

The precious metals occur in geological and technological samples at trace and ultra-trace levels and at the complex compositions of the materials. A sensitive and selective separation together with preconcentration is necessary. Separation is a process in which the components constituting the starting mixture are separated from each other. Preconcentration is a technique by which the ratio of concentration (or the amount) of trace components to the concentration (or the amount) of macro component is increased. In separation, the components constituting the mixture may or may not differ in concentration from each other. Separation and preconcentration of metals are usually affected by the same methods such as extraction, precipitation, co-precipitation, sorption, crystallization, sublimation etc [6]. By this way their trace or ultra-trace amounts can be detected by modern instrumental methods such as; atomic absorption spectrometry (AAS**),** inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) and neutron activation analysis (NAA) [7].

The use of sorbents (solid phases) for preconcentration and separation has received great attention from analytical chemists in the last two decades. Among wide range of solid phases such as; active carbon, cellulose, polyurethane foam surfactant coated alumina, poly (acrylonitrile), styrene-divinylbenzene matrix, clay and silica gel with chelating ligands have gained much importance for the metal ion enrichment [8].

Gomez and co workers described an on-line preconcentration method for the determination of silver by flow injection FAAS using sulfhydryl cotton [9]. Pei and Fang determined silver in geological materials using FAAS coupled with on-line flow injection preconcentration by coprecipitation with diethyl dithiocarbamate [10]**.**

The sorption of silver, gold and palladium by thiourea immobilized on the silica gel was studied [11]. In 2004, Afsaneh and coworkers described a new and satisfactory method related with the easy synthesis of directly bonded 2-mercaptobenzothiazole silica gel. This reagent was used for the solid phase extraction of silver from aqueous solutions [8]. Kikuo Terada et al. used *p*-dimethylaminobenzylidenerhodanine supported on silica gel for preconcentration of silver (I), gold (III) and palladium (II) in sea water [12].

Many chelating resin have been reported in literature for selectively adsorbing noble metals. The chelating groups widely used for the purpose are poly (aniline), morpoline-4-carbodithioates, thiosemicarbazide, 8-hydroxyquinoline, thiazole and dithiocarbamate. Dithizone is another popular ligand which coordinates with transition metals as well as noble metals. Grote and Kettrup have reported ion exchange resins containing S-bonded dithizone and dehydrodithizone for sorption and desorption of noble and transition metals [13]. Rupal et al. reported the preconcentration and separation of palladium (II) and platinum (IV) on a dithiozone anchored poly (vinylpyridine)-based chelating resin [14].

The chelating adsorbents containing amidine groups exhibit very high selectivity to noble metal ions. The commercial product Srafion NMRR is an example of an adsorbent containing this group. Koster and Schmuekler first reported the application of this kind of adsorbent for the preconcentration and separation of noble metals [15]. Wang and coworkers incorporated amidine groups onto the polystyrene beads and used it for the adsorption of Pt (IV) and Pd (II) [16]. Su and coworkers prepared a polyacrylamidine thiocyanate fiber and found that it had very high selectivity to Au (III) and Pd (II) [17]. Recently, the application of Srafion NMRR to the on-line preconcentration and separation of Au (III) from iron rich matrices for its ICP-AES determination was also reported [4]. Shaoming Zhang and co workers used amidinothioureido-silica gel for on-line preconcentration of silver, gold and palladium in determination with flame atomic absorption spectrometer [18].

1.3 Solid-Phase Extraction (SPE)

The history of solid-phase extraction dates back at least to the early 1970s, when columns packed with Rohm and Haas XAD resin particles were used to concentrate low concentrations of organic pollutants from water samples. However, activated carbons have been used several years prior to 1970 to accumulate organic solutes prior to analysis.

During the late 1980s and the 1990s, the development and analytical use of solid-phase extraction have expanded tremendously.

In solid-phase extraction solutes are extracted from a liquid into solid phase. The solid phase typically consists of small, porous particles of silica with bonded organic phase or of an organic polymer, such as cross linked polystyrene. The extraction can take place in a batch method in which the solid extract is intimately mixed with the liquid sample solution. In chemical analysis it is more common to take the packed solid extract into a small tube and pass the liquid sample through the tube [19]. Typical apparatuses for SPE are shown in Figure 1.1.

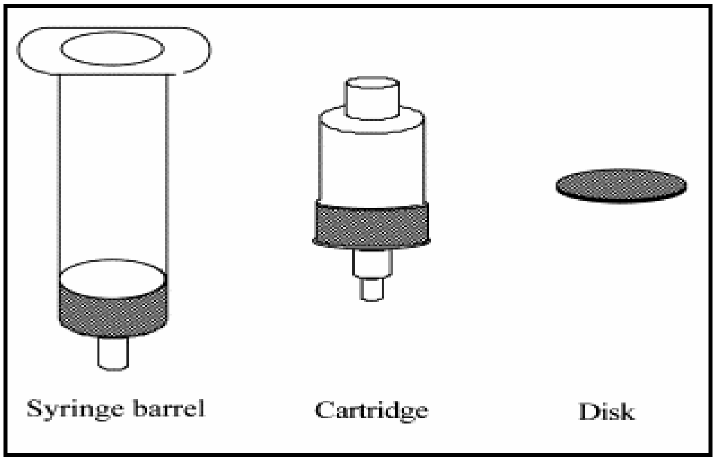


Figure 1.1 Disposable sorbent containers [19].

Substances that have been extracted by the solid phase can be removed by washing up with an appropriate solvent. For example, most organic analytes can be eluted from an SPE tube with an organic solvent such as acetone, acetonitrile, or methanol. Usually, the volume of solvent needed for complete elution of the analytes is much smaller than the original sample volume. A concentration of the analytes is thus achieved.

A summary of the comparison between liquid-liquid extraction, SPE and liquid chromatography (LC) is given in Table 1.5.

Table 1.5 Comparisons of LLE, SPE and LC [19].

	Liquid-Liquid Extraction	Solid-phase extraction	Liquid chromatography
Extractive phase	liquid emulsion	porous solid	porous solid
Typical Sample	Aqueous, 10-100 mL	Aqueous, 10-100 mL	Aq.-organic liquid or organic 5-50 μL
Partition equilibrium	single	multiple	multiple
Separation of individual analytes	no	no	yes
Easily automated	no	yes	no
Elution from extractive phase	seldom needed; pH control	Aq.-organic liquid	Aq.-organic liquid
Mixture concentration achieved	moderate	high	slight

1.3.1 Advantages of Solid-phase Extraction

Solid-phase extraction has several important advantages over liquid-liquid extraction.

1. Faster and easier manipulation. A sample can be quickly passed through a SPE column or cartridge by means of a pump or with gentle pressure of suction. After a quick rinse, the extracted substances can be washed from the column by a small amount of appropriate eluent. However, simple solvent extraction requires a considerable amount of manipulation in adding the extractive liquid, shaking, waiting for the emulsion to break, and carefully separating the two liquid phases. Often a washing step and a back extraction are required.

2. Much smaller amounts of organic solvents are used. The large volumes of organic solvents used in analytical separations have become an important environmental

concern. Aqueous samples have become contaminated with organic solvents and an evaporative concentration of the extracts pollute the air with organic vapors. Proper disposal of used organic solvents has become troublesome and expensive. Today, analytical chemists are working to replace liquid-liquid extraction with solid-phase extraction in analytical procedure in control laboratories.

3. Less stringent requirements for separation. SPE is a multistage separation method and as such requires only a reasonable difference at least 80 % in extractability to separate two solutes.

4. Higher concentration factor. The concentration factor is how many times more concentrated a substance is in the extract than it is in the original sample. In SPE, concentration factors of 100 or more are possible. The concentration factor in liquid-liquid extraction depends in part on the volume ratio of the liquids [19].

1.3.2 Process of Solid-phase Extraction

An SPE method always consists of three to four successive steps, as illustrated in Figure 1.2. First, the solid sorbent should be conditioned using an appropriate solvent, followed by the same solvent as the sample solvent. This step is crucial, as it enables the wetting of the packing material and the solvation of the functional groups. In addition, it removes possible impurities initially contained in the sorbent or the packaging. Also, this step removes the air present in the column and fills the void volume with solvent.

The nature of the conditioning solvent depends on the nature of the solid sorbent. Typically, for reversed phase sorbent (such as octadecyl-bonded silica), methanol is frequently used, followed with water or aqueous buffer whose pH and ionic strength are similar to that of the sample. Care must be taken not to allow the solid sorbent to dry between the conditioning and the sample treatment steps, otherwise the analytes will not be efficiently retained and poor recoveries will be obtained. If the sorbent dries for more than several minutes, it must be reconditioned.

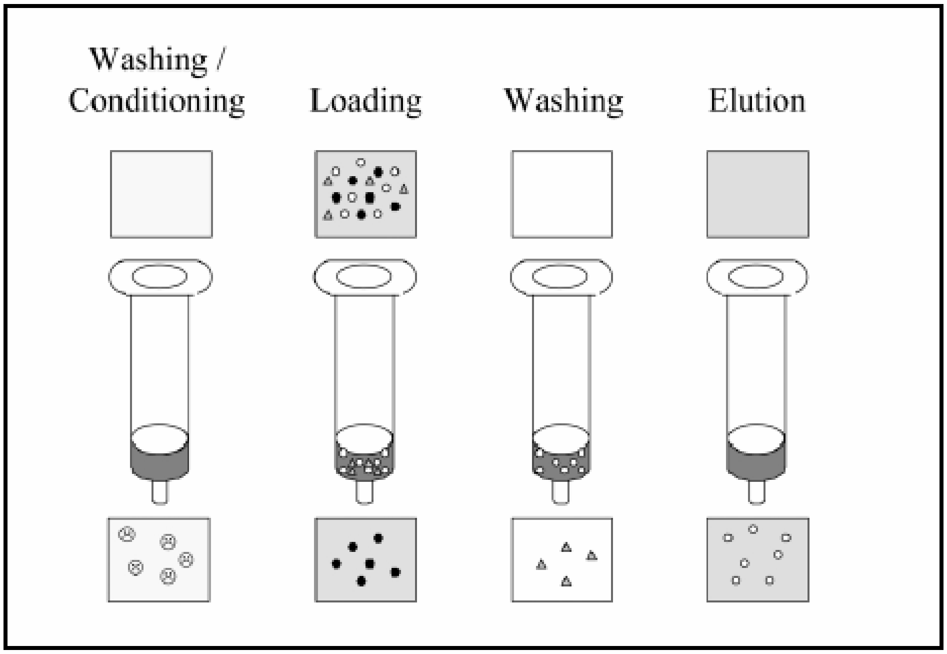


Figure 1.2 SPE Operation step.

The second step is the percolation of the sample through the solid sorbent. Depending on the system used, volumes can range from 1 mL to 1 L. The sample may be applied to the column by gravity, pumping, aspirated by vacuum or by an automated system. The sample flow-rate through the sorbent should be low enough to enable efficient retention of the analytes, and high enough to avoid excessive duration. During this step, the analytes are concentrated on the sorbent. Even though matrix components may also be retained by the solid sorbent, some of them pass through, thus enabling some purification (matrix separation) of the sample.

The third step (which is optional) may be the washing of the solid sorbent with an appropriate solvent, having low elution strength, to eliminate matrix components that have been retained by the solid sorbent, without displacing the analytes. A drying step may also be advisable, especially for aqueous matrices, to remove traces of water from the solid sorbent. This will eliminate the presence of water in the final extract, which, in some cases, may hinder the subsequent concentration of the extract and/or the analysis.

The final step consists in the elution of the analytes of interest by an appropriate solvent, without removing retained matrix components. The solvent volume should be adjusted so that quantitative recovery of the analytes is achieved with subsequent low dilution. In addition, the flow-rate should be correctly adjusted to ensure efficient elution. It is often recommended that the solvent volume be fractionated into two aliquots, and before the elution to let the solvent soak the solid sorbent [20].

1.4 Resins as Solid Sorbents

Solid sorbents may be hydrophobic or polar. It is common to call reversed-phase sorbents the packing materials that are more hydrophobic than the sample, which are frequently used with aqueous samples. On the other hand, normal-phase sorbents refer to materials more polar than the sample and they are used when the sample is an organic solvent containing the target compounds. When hydrophobic supports are used, retention of ionic metal species will require the formation of hydrophobic complexes. This can be achieved through addition of the proper reagent to the sample or thorough immobilization of the reagent on the hydrophobic solid sorbent. Immobilization may also provide a significant development in speciation analysis. The nature and properties of the sorbent are of prime importance for effective retention of metallic species. Careful choice of the sorbent is thus crucial to the development of SPE methodology. In practice, the main requirements for a solid sorbent are:

(1) The possibility to extract a large number of trace elements over a wide pH range (along with selectivity towards major ions);
(2) the fast and quantitative sorption and elution;

(3) a high capacity;
(4) regenerability;
(5) accessibility.

Ion exchange resins have been extensively used for the separation of noble metals. Unfortunately, the low selectivity of most commercially available ion exchange resins does not allow for effective separation without use of proper elution solutions and thus base metals being eluted along with precious metals.

The use of coordinating resins solves the problem when the most suitable functional group is selected, as their selectivity is higher than that of conventional resins. Resins with covalently bonded functional groups containing donor atoms such as sulfur or nitrogen can be highly efficient in the selective sorption of metals, and of these, those compounds with sulfur atoms are usually more selective. Some attempts have been made to synthesize polymers containing functional groups which have donor sulfur atoms such as thiol, thioureas, dithizone, thioglicolate, thiooxime, thiosemicarbazide and 2-mercaptobenzotiazol. On the other hand, the selective separation of precious metals with these sorbents is carried out by the application of different discriminating elution solutions, not solely by the polymers.

Sorbents that allow fast reaction rates are preferred to achieve faster extraction as well as higher loading capacities. The broad variety of sorbents available explains one of the most powerful aspects of SPE, which is selectivity.

Sorbents can be mainly categorized as organic based ones (natural polymers, as well as synthetic polymers) and inorganic based ones (silica gel SiO_2, alumina $A1_2O_3$, magnesia MgO and other oxide species) [20]. Summary of two types of sorbents is given in Figure 1.3.

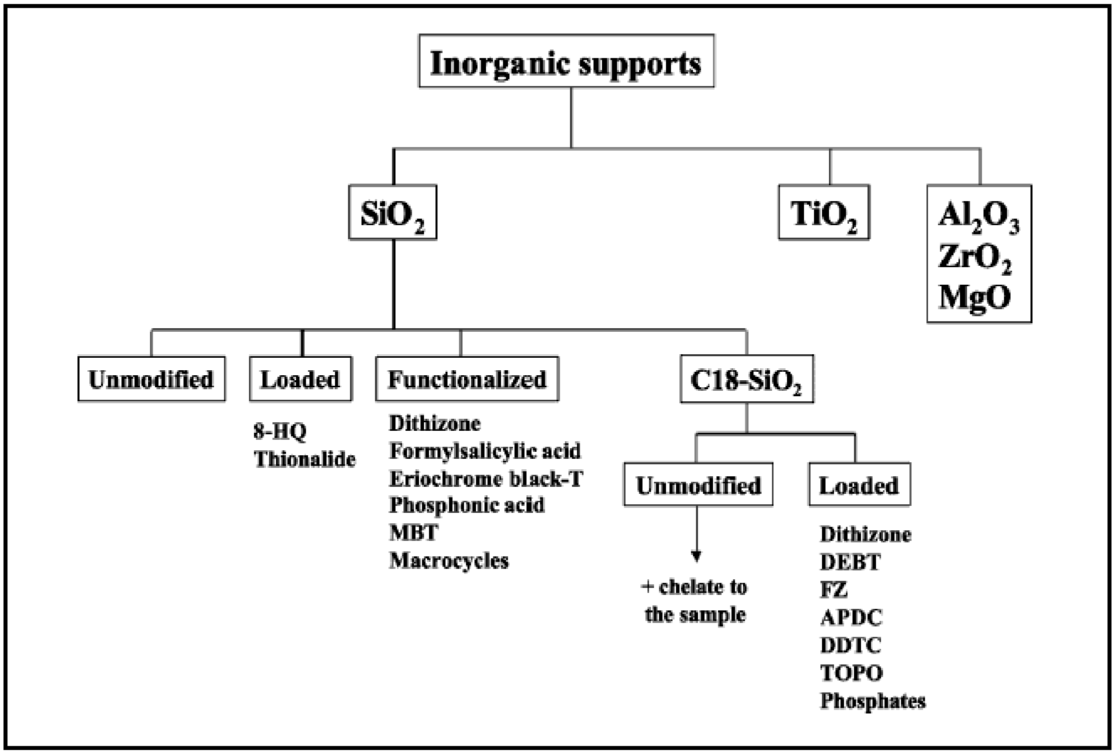


Figure 1.3.a Sorbents based on inorganic supports.

ABREVIATIONS:

8-HQ: *8-Hydroxyquinoline*, ***MBT:*** *2-Mercaptobenzothiazole****,*** ***DEBT:*** *N,N'-Diethyl-N'-benzoylthiourea****,*** ***FZ:*** *Ferrozine****,*** ***APDC:*** *Ammonium pyrrolidine dithiocarbamate****,*** ***DDTC:*** *Diethyldithiocarbamate****,*** ***TOPO:*** *Trinoctylphosphine oxide*

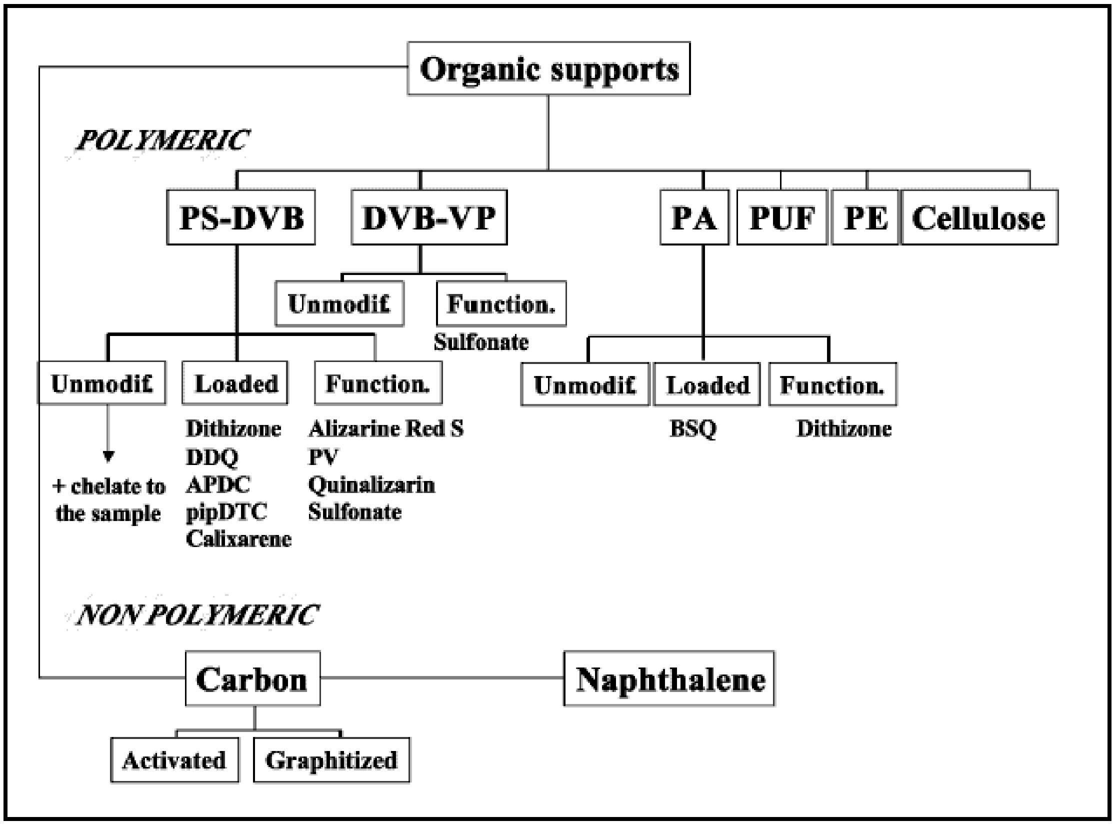


Figure 1.3.b Sorbents based on organic supports.

ABBREVIATIONS:

***PS-DVB**: Polystyrene-divinylbenzene **DVB-VP:** Divinylbenzene-vinylpyrrolidone, **DDQ:** 7-Dodecenyl- 8-quinolinol,* PipDTC*: Piperidine dithiocarbamate, **PV:** Pyrocatechol violet, **PA:** Polyacrylate, **PUF:** Polyurethane foam, **PE:** Polyethylene, **BSQ:** 8-(Benzenesulfonamido)quinoline*

1.4.1 Macroporous Resins

The nonionic resins may be classified into three categories: gel-type, macroporous and hypercrosslinked.

The gel-type resins have a homogeneous, nonporous structure. The polymeric network of the resin may swell in good solvents which are solvents capable of dissolving the monomers doubling its volume in some cases [21].

Macroporous resins were first developed in the 1960s. In this group, Amberlite series XAD-2, XAD-4, XAD-7 and XAD-16 are widely used in trace metal preconcentration. In this study, Amberlite XAD-16, one of the types of polymeric resins is used as solid support. Amberlite XAD-16 has a permanent porosity, which is the characteristic of macroporous styrene copolymer. They are capable of effectively sorbing organic pollutants, due to their porous polymeric matrix. Permanent porosity results from micro-phase separation of the initially homogeneous mixture consisting of styrene, enhanced the quantity of divinylbenzene (DVB) (above 8-15%) and also a porogen that is miscible with monomers, but precipitates by growing chains of the styrene copolymers. Micro volumes occupied by the separated porogen after evaporation, leave voids in the copolymer structure that represent interconnected macropores [21].

Macroporous materials are opaque and display a total pore volume of about 1 mL/g and an inner surface area of about 20-300 m^2/g. (Larger values of surface area imply the presence of small pores, in addition to macroporous) [21].

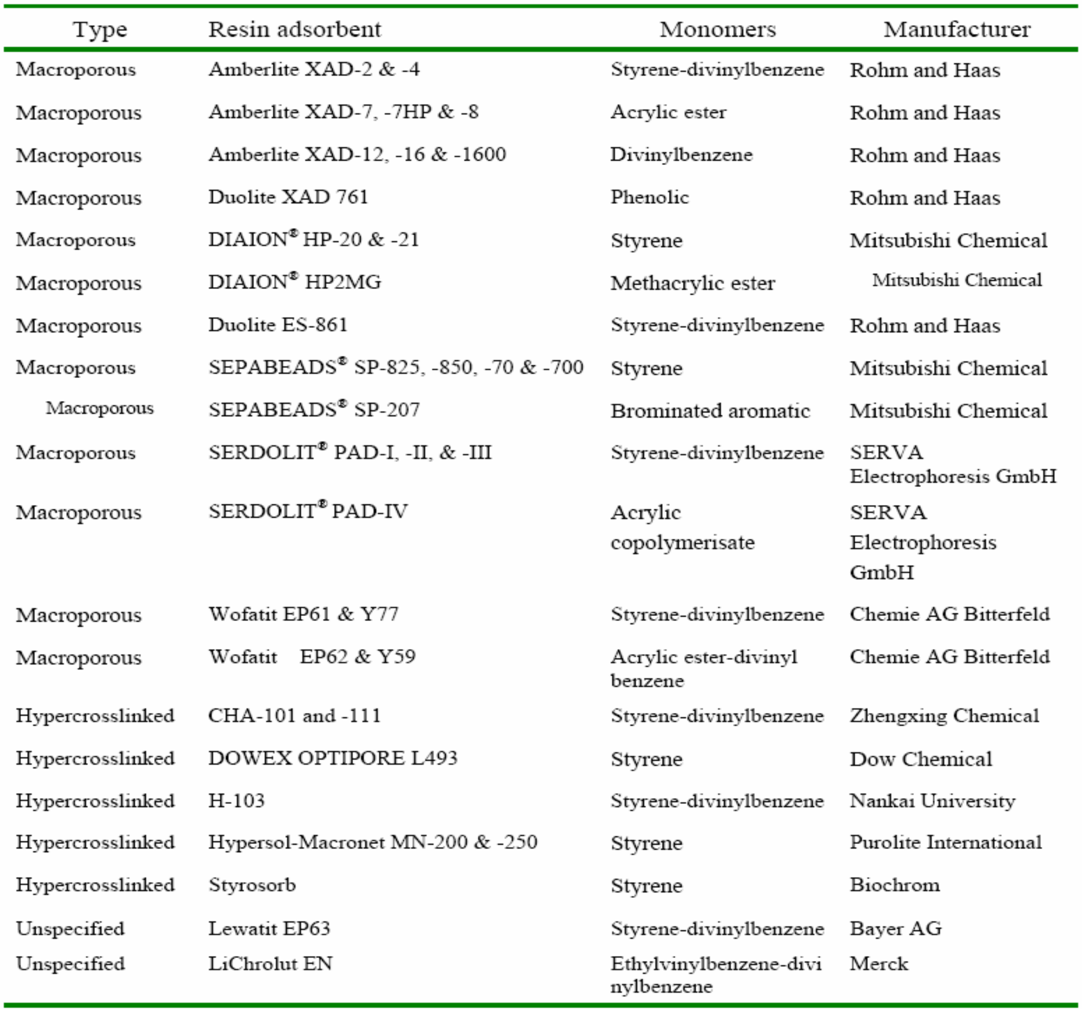
All those properties mentioned above make the macroporous polymers have higher capacities and be more highly selective than microporous resins. In addition, use of microporous matrix during preparation of polymers exhibit some problems, as the swelling of this kind of matrix is highly dependent on the consumption of the sample solution, thus making it difficult for data to be reproduced. However, macroporous resins are not affected by the concentration of the external solution or by the solvent [22].

Hypercrosslinked resin sorbents have also gained increasing interest. These sorbents are produced by crosslinking polymers of macroporous resin in a good solvent. The crosslinking tightens the structures and modifies the surface properties of the porous polymeric network.

One of the advantages of macroporous and hypercrosslinked resin sorbents is the possibility of controlling their resin structure, internal surface area, and pore size distribution. This can be achieved by varying the polymerization conditions, the most crucial of which are the amounts of monomers and pore-forming agent used in the polymerization reaction. Consequently, sorbents may be tailor made for specific applications. In addition to water and wastewater treatment, porous resin sorbents have also found applications in solid-phase extraction, bioseparation and blood purification.

The term “macroporous resin sorbents” in the literature can be found as ‘polymeric resin’, ‘nonionic polymeric resin’, ‘macroporous resin’, ‘macroporous polymeric adsorbent’, ‘macroporous copolymer’, ‘organic adsorption polymer’, ‘synthetic adsorber polymer’, ‘polymeric sorbent’, ‘nonionic macroreticular polymeric resin’, ‘macroporous synthetic adsorbent’, etc. The most common type of macroporous sorbent is styrene and divinylbenzene copolymer, which may be found as ‘polystyrene’, ‘styrene-divinylbenzene copolymer’ or simply ‘St-DVB copolymer’ [23]. Some of the commercially available resins are given in Table 1.6.

Table 1.6 Some of the commercially available resin adsorbents [23].



Type	Resin adsorbent	Monomers	Manufacturer
Macroporous	Amberlite XAD-2 & -4	Styrene-divinylbenzene	Rohm and Haas
Macroporous	Amberlite XAD-7, -7HP & -8	Acrylic ester	Rohm and Haas
Macroporous	Amberlite XAD-12, -16 & -1600	Divinylbenzene	Rohm and Haas
Macroporous	Duolite XAD 761	Phenolic	Rohm and Haas
Macroporous	DIAION® HP-20 & -21	Styrene	Mitsubishi Chemical
Macroporous	DIAION® HP2MG	Methacrylic ester	Mitsubishi Chemical
Macroporous	Duolite ES-861	Styrene-divinylbenzene	Rohm and Haas
Macroporous	SEPABEADS® SP-825, -850, -70 & -700	Styrene	Mitsubishi Chemical
Macroporous	SEPABEADS® SP-207	Brominated aromatic	Mitsubishi Chemical
Macroporous	SERDOLIT® PAD-I, -II, & -III	Styrene-divinylbenzene	SERVA Electrophoresis GmbH
Macroporous	SERDOLIT® PAD-IV	Acrylic copolymerisate	SERVA Electrophoresis GmbH
Macroporous	Wofatit EP61 & Y77	Styrene-divinylbenzene	Chemie AG Bitterfeld
Macroporous	Wofatit EP62 & Y59	Acrylic ester-divinyl benzene	Chemie AG Bitterfeld
Hypercrosslinked	CHA-101 and -111	Styrene-divinylbenzene	Zhengxing Chemical
Hypercrosslinked	DOWEX OPTIPORE L493	Styrene	Dow Chemical
Hypercrosslinked	H-103	Styrene-divinylbenzene	Nankai University
Hypercrosslinked	Hypersol-Macronet MN-200 & -250	Styrene	Purolite International
Hypercrosslinked	Styrosorb	Styrene	Biochrom
Unspecified	Lewatit EP63	Styrene-divinylbenzene	Bayer AG
Unspecified	LiChrolut EN	Ethylvinylbenzene-divinylbenzene	Merck

1.4.2 Retention of Trace Elements on Sorbents

Adsorption of trace elements on the solid sorbent is required for preconcentration. The mechanism of retention depends on the nature of the sorbent, and may include simple adsorption, chelation or ion-exchange. Also, for trace elements, ion-pair solid phase extraction may be used [20].

– ***Adsorption***: Trace elements are usually adsorbed on solid phases through van der Waals forces or hydrophobic interaction. Hydrophobic interaction occurs when the solid sorbent is highly non-polar (reversed phase). The most common sorbent of this type is octadecyl-bonded silica (C18-silica). More recently, reversed polymeric phases have appeared, especially the styrene-divinylbenzene copolymer that provides additional π-π interaction when π-electrons are present in the analyte. Elution is usually performed with organic solvents, such as methanol or acetonitrile. Such interactions are usually preferred with online systems, as they are not too strong and thus they can be rapidly disrupted. However, because most trace element species are ionic, they will not be retained by such sorbents.[18]

– *Chelation*: Chelation mechanism is explained in detail in Section 1.5.

– *Ion-pairing*: When a non-polar sorbent is to be used, an ion-pair reagent (IP) can be added to the sorbent. Such reagents contain a nonpolar portion (such as a long aliphatic hydrocarbonated chain) and a polar portion (such as an acid or a base). Typical ion-pair reagents are quaternary ammonium salts and sodium dodecylsulfate. The non-polar portion interacts with the reversed-phase non-polar sorbent, while the polar portion forms an ion-pair with the ionic species present in the matrix that could be either free metallic species in solution or complexes.

– *Ion exchange*: Ion-exchange sorbents usually contain cationic or anionic functional groups that can exchange the associated counter-ion. Strong and weak sites refer to the fact that strong sites are always present as ion-exchange sites at any pH, while weak sites are only ion-exchange sites at pH values greater or less than the pK. Strong sites are sulfonic acid groups (cation-exchange) and quaternary amines (anion-exchange), while weak sites consist of carboxylic acid groups (cation-exchange) or primary, secondary and tertiary amines (anion-exchange).

These groups can be chemically bound to silica gel or polymers (usually a styrene-divinylbenzene copolymer), the latter allowing a wider pH range. An ion-exchanger may be characterized by its capacity, resulting from the effective number of functional active groups per unit mass of the material. The theoretical value depends upon the nature of the material and the form of the resin. However, in the column operation mode, the operational capacity is usually lower than the theoretical one, as it depends on several experimental factors, such as flow-rate, temperature, particle size and concentration of the feed solution. As a matter of fact, retention on ion-exchangers depends on the distribution ratio of the ion on the resin, the stability constants of the complexes in solution, the exchange kinetics and the presence of other competing ions. Even though ion-exchangers recover hydrated ions, charged complexes and ions complexed by labile ligands, they are of limited use in practice for preconcentration of trace elements due to their lack of selectivity and their retention of major ions [20].

1.5 Chelating Agents and Metal Ions

Several functional group atoms are capable of chelating trace elements. The atoms most frequently used are nitrogen (e.g. N present in amines, azo groups, amides, nitriles), oxygen (e.g. O present in carboxylic, hydroxyl, phenolic, ether, carbonyl, phosphoryl groups) and sulfur (e.g. S present in thiols, thiocarbamates, thioethers). The nature of the functional group will give an idea of the selectivity of the ligand towards trace inorganic cations [20].

In practice, inorganic cations may be divided into 3 groups:

– group I- ‘hard’ cations (*Hard acids*; this classification was suggested by R.G. Pearson, or *Class a* suggested by Arland) [1]: These preferentially react via electrostatic interactions due to a gain in entropy caused by changes in orientation of hydration water molecules;this group includes alkaline and alkaline-earth metals (Na^{2+}, Li^{+} , Ca^{2+}, Mg^{2+}, etc.) that form rather weak outer-sphere complexes with only hard oxygen ligands.

– **group II- ‘borderline’ cations**: these have an intermediate character; this group contains Fe^{2+} , Co^{2+}, Ni^{2+} ,Cu^{2+} ,Zn^{2+} ,Pb^{2+} ,Mn^{2+} . They possess affinity for both hard and soft ligands.

– **group III- ‘soft’ cations** (*Soft acids or class b*): these tend to form covalent bonds. Hence, Cd^{2+} and Hg^{2+} possess strong affinity for intermediate (N) and soft (S) ligands.

For soft metals, the following order of donor atom increasing affinity is observed: O-N-S. A reversed order is observed for hard cations. For a bidentate ligand, affinity for a soft metal increases with the overall softness of the donor toms: (O, O)-(O, N)-(N, N)-(N, S).

The order is reversed for hard metals. In general, the competition for a given ligand essentially involves Group I and Group II metals for O sites, and metals of Group II and Group III for N and S sites. The competition between metals of Group I and Group III is weak**.**

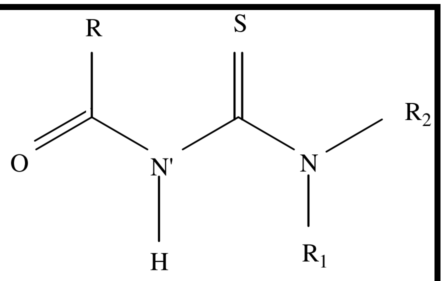
Chelating agents may be directly added to the sample for chelating trace elements, the chelates being further retained on an appropriate sorbent. An alternative is to introduce the functional chelating group into the sorbent. For that purpose, three different means are available:

(1) the synthesis of new sorbents containing such groups (new sorbents)
(2) the chemical bonding of such groups on existing sorbents (functionalized sorbents)
(3) the physical binding of the groups on the sorbent by impregnating the solid matrix with a solution containing the chelating ligand **impregnated** (coated or loaded sorbents).

The last one, which is used in this study, remains the most simple to be used in practice. Its main drawback is the possible flush of the chelating agent out of the solid sorbent during sample percolation or elution that reduces the lifetime of the impregnated sorbent [20].

1.5.1 N,N-diethyl-N’-benzoylthiourea (DEBT)

N,N-diethyl-N'-benzoylthiourea (DEBT) is one of a class of deceptively simple ligands based on the N,N-alkyl-N'-aroylthiourea motif below (Figure 1.4):



R = aryl or alkyl
R_1R_2 = alkyl; N,N-dialkyl-N'-aroylthiourea **HL**
R_1 = alkyl, R_2 = H; N-alkyl-N'-aroylthiourea **H_2L**

Figure 1.4 N, N-alkyl-N'-aroylthiourea motif.

One of the attractive features of these ligands is their facile synthesis from readily available and inexpensive starting materials, giving in the case of the N'-benzoylthiourea derivatives, usually high yields of pure product in a two-step synthesis. In general, ligands of type HL, derived from benzoyl chloride are stable, relatively hydrophobic substances, with one dissociable proton on the weakly acidic amido–C(O)NHC(S)- moiety. N, N-dialkyl substituted HL ligand assumes a twisted conformation in the solid state, with the sulphur and oxygen atoms pointing approximately in opposite directions as shown schematically below (Figure 1.5) [24].

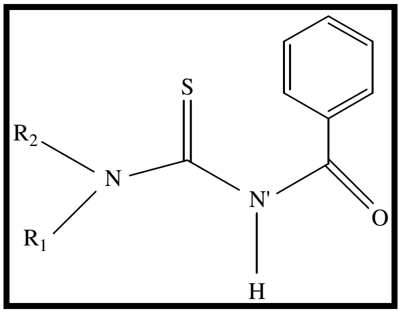


Figure 1.5 (DEBT).

One of the other vital properties of DEBT is being a selective complexing agent. This selectivity control is carried out by pH. It has very high resistance to hydrolysis and oxidation. Besides high pKs values, DEBT has the ability to increase the electron density at the sulphur donor atom in the presence of appropriate acceptors (by resonance effects). N,N-diethyl-N'-benzoylthiourea forms stable complexes only with class b and border line acceptors such as Co(II), Ni(II), Cu(II) etc. [25]. Noble metal ions, due to their specific class b properties form chelates with DEBT in low oxidation states in strongly acidic solutions. The formation of metal chelates in general and their open formula are given in Equation 1.1 and Figure 1.6, respectively.

$$M^{n+} + nHL \rightarrow ML_n + nH^+ \qquad \text{(Equation1.1)}$$

Where; M: Metal ion, L: Ligand

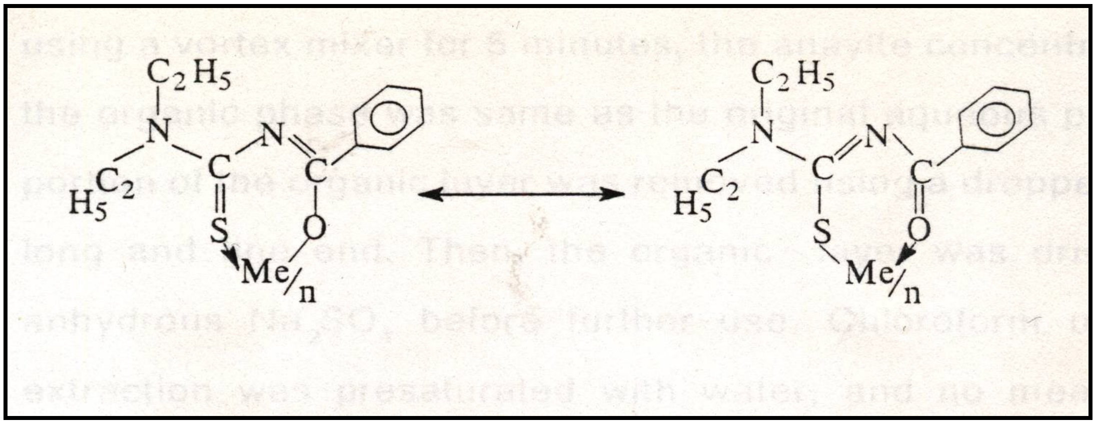


Figure 1.6 Open formula of metal chelates.

1.6 Applications of Solid-phase Extraction of Precious Metals

Summary of some studies related with applications of SPE of precious metals and their determination are given in Table 1.7.

Table1.7 Literature summary related with SPE of precious metals and their determinations.

Trace elements	Matrix	Sorbent	Eluent	Determination method	LOD (ng/L)	Ref.
Ag	Geological sample, Cu metal, Pb nitrate	MBT-Functionalized-SiO2	Thiourea	FAAS	660	26
Ag	Tap, spring waters	HT18C6	0.1 M $Na_2S_2O_3$	AAS	0.050	28
Au	Industrial waste waters	Silica gel-thiomacrocycle	-	ICP-MS	-	29
Au	Natural waters	Sulfhydryl cotton fibre column; FI	-	AAS	0.2	30

Table1.7 (continued).

Trace elements	Matrix	Medium for sorption	Sorbent	Eluent	Determination method	LOD and RSD%	Ref.
Pd, Ag, Au	Ag&Au in ore samples Pd in nickel alloy anode	0.1-6 M HNO_3 or HCl	Amidinothioureido-silica gel (ATUSG) (flow-injection & on-line)	Thiourea solution	FAAS	1.1ng/mL, Ag 13 ng/mL, Au 17 ng/mL, Pd 1.2 % Ag 1.2% Au 1.7 % Pd	27
Ag	Coar River Water	pH 1.0-9.0	Immobilized dithiozone on surfactant-coated alumina	Thiourea solution	FAAS	3.21 %	31
Au, Pt, Pd, Ir, Rh	Pt-ore	0.5-2 mol/L HCl	Tetraethylenepentamine (metalfix-chelamine) resin (flow-injection)	µwave resin-destruction protocol	ICP-MS	Au :1.2 ng/g, 4.5% Pd : 0.6 ng/g, 5.2% Pt: 0.45 ng/g, 1.5% Ir: 0.24 ng/g, 5.4% Rh:0.15ng/g, 3.3%	32

Table 1.7 (continued)

Trace element	**Matrix**	**Medium for sorption**	**Sorbent**	**Eluent**	**Determination method**	**LOD and RSD%**	**Ref.**
Au	environmental samples (rock, soil etc.)	5% (v/v) HCl	Spheron Thiol 1000 (Chelating sorbent)	NH_4SCN	ETAAS	0.5 ng/g 2.9%-5.1%	33
Au, Pd, Pt	-	0.1 M HCl	Amberlite IRA-35 (weakly basic anion exchange resin)	Thiourea-ethyl alcohol solution	GFAAS	-	34
Au, Pd, Pt	Geological sample	0.5 M HNO_3	Aminoisopropyylmer captan with polythioether backbone (chelating resin) used as adsorbent and chemical modifier	0.1 % (m/V) agar	ETV-ICP-AES	Au 75 pg, 4.4 % Pd 60 pg, 5.6 % Pt 217pg, 3.7%	35
Au	Gold ore sample & anode slime	pH 2 (HCl)	Amberlite XAD-16	KI in methanol	FAAS	0.046 mg/L	36
Au, Ag, Pt, Pd	Platinum ore	0.1 M HCl	Activated carbon	-	CPI-MIP-AES	Au; 43ng/g AC Ag; 24ng/g AC Pt; 550ng/g AC Pd; 57ng/g AC 1-4 %	37
Ag	Tin base alloy	pH 2 HNO_3	Amberlite XAD-16	KCN solution	FAAS	0.047 mg/L	38
Au, Pd, Pt	Pure copper and anodic slime	1 M HCl	Amberlite XAD-7	Acetone	FAAS	Au ; 32.0μg/L Pd ; 24.9 μg/L Pt ;102.5μg/L	39
Au, Ag, Pd	Geological samples	pH 1 (HCl & HNO_3)	Powdered activated carbon	Boiling with HNO_3-$HClO_4$	FAAS	10%	40

1.6.1 Some Solid-phase Extraction Studies with Amberlite Resin Series

In 1997, R. Türker and co workers developed a method for determination of trace levels of gold in geological materials and anode slimes by FAAS. The study involved the adsorption of the chloro complex of gold from hydrochloric acid solution on Amberlite XAD-16 in a column process. Elution was achieved by potassium iodide solution in methanol [36].

In 2000, A. Tunçeli determined silver in tin base alloys by FAAS using the previously developed preconcentration method. Metal complexes in solutions were prepared by adding potassium thiocyanate solution to standard silver solution adjusting the pH to 2 with HNO_3 solution and then the solutions were passed through the column. The elution of silver was achieved by potassium cyanide solution [38].

In 2003, L. Elçi and co workers proposed a method for preconcentration of Au, Pd, and Pt prior to their atomic absorption determinations. For this reason, metal complexes were prepared by adding KI to metal solutions in 2 M HCl. This solvent-extraction process was adapted to solid phase extraction using Amberlite XAD-7 resin prepared as column. The elution was achieved by acetone. Then the effluent was collected and carefully evaporated to dryness. The residue was diluted with 1 M HCl and gold ions in the final solution was determined by FAAS [39].

In 2003, M. Soylak and coworkers investigated the optimal analytical conditions for preconcentration of Cr, Co, Mn and Ni on Amberlite XAD-1180 without any chelating agent using different buffer solutions. The metal solutions at pH 9 were passed through the column. The retained metals were eluted with 1 M HNO_3 in acetone. The effluent was evaporated to dryness and the residue was diluted with 1 M HNO_3. The analyte in the solution was determined by FAAS [41].

In 2004, M. Soylak proposed Amberlite XAD-7 on column for solid phase extraction of Cu, Fe and Zn at trace level in environmental samples for their determination by FAAS. Metal solutions were prepared in 0.5 M KSCN in a 1 M HCl solution and passed through the column. Elution was achieved by 1M HNO_3 in acetone [42].

1.7 Atomic Absorption Spectrometry

Atomic absorption spectrometry (AAS) is the most widely used technique to measure the concentrations of the metals. The occurrence of atomic absorption was noted by Wollaston and Fraunhofer and explained by Kirchoff and Bunsen in the nineteenth century. In 1955, Walsh established the foundation of modern analytical atomic absorption spectroscopy by introducing a system that consists of hollow cathode light sources, flame atomizers, photomultipliers and a modulated system. When radiation of proper wavelength passes through a vapour containing ground state atoms, some of the radiation can be absorbed by excitation of the atoms and change in the intensity of the radiation at a wavelength corresponding to the energy of the photon is detected [43].

1.7.1 Flame Atomic Absorption Spectrometry

Walsh and Milatz proposed and demonstrated analytical flame atomic absorption spectroscopy (FAAS), in which radiation from a line source, such as a hollow cathode lamp, is absorbed by atomic vapour in the flame. The technique of FAAS became accepted in the 1960s after the introduction of the first commercial FAAS in 1959. Until recently, FAAS was the most widely used of all atomic spectral methods because of its simplicity, effectiveness, and relatively low cost. In flame atomization, a solution of the sample is aspirated into a flame by means of a nebulizer, which converts the sample solution into a mist made up of tiny liquid droplets. A complex set of interconnected processes then occurs; these processes eventually lead to a mixture of analyte atoms, analyte ions, sample molecules of the analyte, and certainly a variety of atomic and molecular species formed by reactions among the fuel, the oxidant, and the sample. With so many complex processes occurring, it is not surprising that atomization is the most critical step in flame spectroscopy and the one that limits the precision of such methods. Because of the critical nature of the atomization step, it is important to understand the characteristics of flame and the variables that affect these characteristics.

Generally air-acetylene flame and nitrous oxide-acetylene flame are used in AAS. The nitrous oxide-acetylene flame is the hotter flame (3150 K), in comparison to the air-acetylene flame (2500 K). The sensitivity of conventional FAAS is limited by several factors. Free analyte atoms generated in the flame where they absorb radiation from the external source pass rapidly; their residence time is around 0.1 ms. A further limitation is the poor nebulization efficiency; that is a maximum of 10% of the aspirated solution reaches the burner [44]. FAAS normally allows the qualification of the elements only at a mg/L level. Thus, a preconcentration step, which may include solid-phase extraction, solvent extraction and co-precipitation, is often required before FAAS analysis [6].

1.8 Sample Selection for the Determination of Precious Metals

1.8.1 Sampling

A sample by definition needs to be representative of the original material. Information such as nature/type of the sample, approximate analyte contents and purpose of the analysis is often necessary for successful sampling. Except when direct analysis may be carried out on a sample of suitable physical state (e.g. neutron activation analysis (NAA) of metal powders), non-homogeneity plays a major role in the number of steps in reducing grain size and selecting an optimum sample weight to be taken, etc.[45].

Because of the large variations in nature and the complexity of the samples, the techniques of sampling vary considerably.

Samples can be broadly divided into four groups, viz. geological, industrial, biological and miscellaneous (including environmental) [45].

1.8.2 Geological Samples

During this study, we were mainly concerned with geological samples. In the geological category there is a wide range of materials. These include ores, concentrates, rocks, minerals and soil. Preparation of a representative sample should address the significantly small amounts of PM distributed non-homogenously.

In general weighed portions of fine ground material are used for analysis after appropriate reduction of the original sample by cone and quartering. Concentrates, ores and alloys are treated in much the same way as geological materials [45].

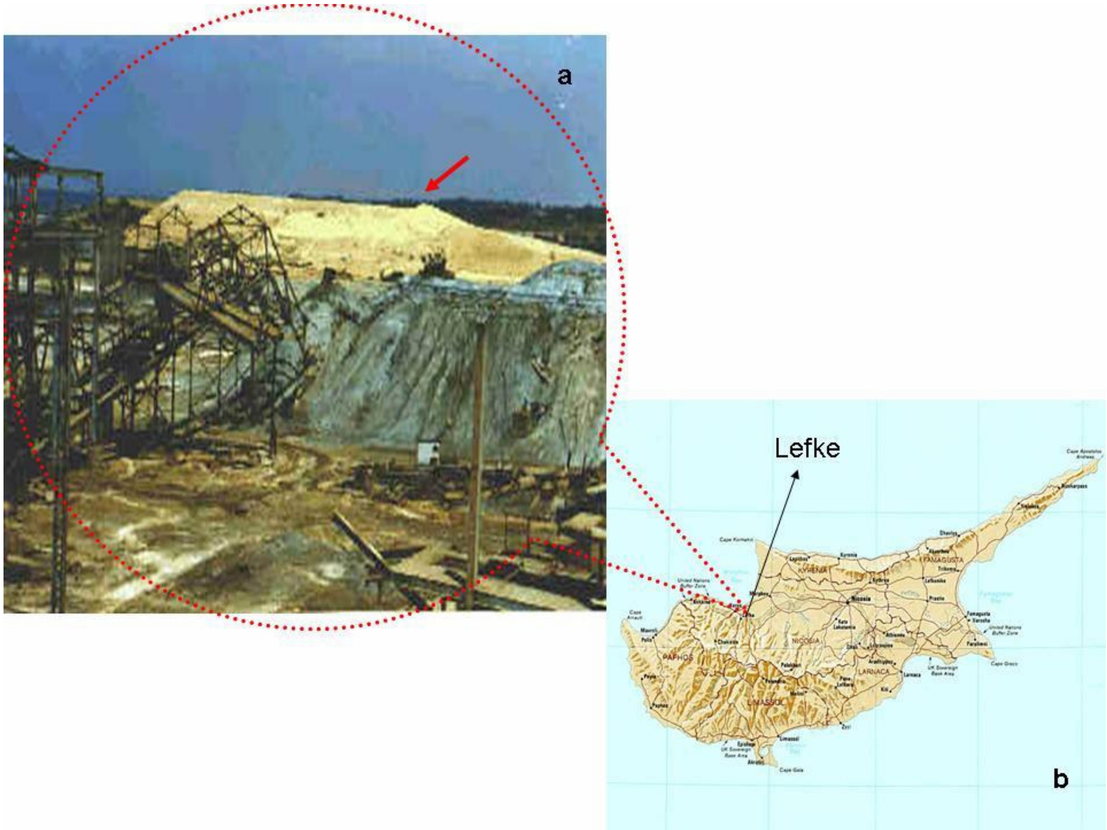
1.8.3 Cyprus Mines Corporation (CMC)

The story of the Cyprus Mines Corporation began with an American mining engineer, Charles Godfrey Gunther, who came to the Middle East and Cyprus for mining research. His exploration in Cyprus showed that there was a good opportunity in the Skouriotissa area for mining copper and gold ore. The owners of one of the mine companies in USA, Philip Wiseman and Seely Wintersmith Mudd, were interested in those ore deposits in Cyprus by the encouragement of Gunther, and they came to this area in 1913. Gunther adapted mining methods to the requirements of the site, trained farmers and shepherds to become miners, mechanics, and machine operators, and solved the difficulties of building a railroad and shipping facilities. Wiseman and Mudd got their permission from the British Government, which was ruling Cyprus at that time, and in March 1916, CMC, Cyprus Mines Corporation was formally launched and shares of stock authorized.

CMC, Cyprus Mines Corporation, established according to the codes of the New York State in 1916. After this year, the development process in Lefke region has started parallel with the growth of the CMC facilities. The Company brought experts and all drilling and other machineries from USA, and employed 350 people locally at the first instant. During those days Lefke had become an important central town for economic and social activities in the Northeastern part of the island. Increasing economic activity in the region, attracted population from various parts of the island, increased social activity and hence resulted in a high growth rate of regional income.

In 1919, CMC built a small jetty at Yeşilyurt and used the jetty at Gemikonağı, which was originally built for exporting citrus of the Lefke area, to export its mine ore to European Countries. In 1926, CMC built its main jetty at Gemikonağı, which is in ruins now, and built up a power plant, work shops, mill plant, leaching and flotation plants and sulphuric acid plant near the coast. The company expanded its operations year by year, and in the 1930's about 6000 people were employed. So many people came from all over Cyprus to work, and CMC constructed villages for workers at Lefke, Gemikonağı and Skouriotissa. Furthermore, CMC have built elementary schools and a hospital in order to serve for educational and health problems of the local population [46]. However, the ore has not being run for 31 years.

In this study, real samples are supplied from residue pile of copper ore from CMC. Samples were prepared according to the appropriate reduction of the original sample (see Picture 1.1) by cone and quartering.



Picture 1.1 **a:** Piles (300.000 tones) from CMC Copper Ore
b: Cyprus.

1.9 Objectives of the Study

M. Merdivan (in her PhD thesis, 1994) carried out complexation of platinum group metals (PGMs) with DEBT in aqueous solution and separation of metal chelates from the interfering inorganic matrix by extraction into nonpolar organic solvents. She applied the proposed method for determination of PGMs by thin layer chromatography densitometry [47].

In 2001 M. Merdivan and her co workers studied on sorption behavior of Uranium (VI) in synthetic mixtures with N, N-dibutyl-N'-benzoylthiourea (DBBT) impregnated on Amberlite XAD-16 resin [48].

In 1997 and 2000, R. Türker et al. studied on determination of gold and silver by FAAS after preconcentration on Amberlite XAD-16 resin [36, 38].

In literature, there are several studies indicating the use of DEBT and Amberlite XAD-16 for preconcentration of metals. However, preconcentration of precious metals using DEBT impregnated Amberlite XAD-16 has not been studied yet. Therefore in this study, our aim was to investigate;

- Sorption behaviours of gold and silver with DEBT-impregnated Amberlite XAD-16 by batch process.

- Applicability of DEBT impregnated Amberlite XAD-16 for preconcentration of gold and silver by column process.

- Application of the optimized method to the real samples.

CHAPTER 2

EXPERIMENTAL

2.1 Chemicals and Reagents

All the reagents used were of analytical reagent grade. Deionized water from a Milli-Q water system was used throughout the study unless otherwise stated. Au standard solutions were prepared by dilution of 1000 µg/mL stock solution (Spectrosol) with 1 M HCl (J.T. Baker, 36-38 % w/w). Ag standard solutions were prepared by fresh daily dilution of 1000 µg/mL stock solution (High-Purity Standards) with 0.05 M HNO_3 (J.T. Baker, 70 % w/w). For interference study, 1000 µg/mL standard solution of copper ions (Merck) was used. During batch process, NaOH (Acros, 50 % w/w) was used for pH adjustment. For desorption studies, thioureas was supplied from Allied Chemical (purity, 99.0%). Sodium thiosulfate was supplied from Bileşik Kimya Mekanik (extra pure).

2.2 Apparatus and Instrumentation

During gold studies, equipments made of PTFE were intentionally used to prevent sorption of gold on silica surfaces.

100 mL DuPont polyethylene containers were used for the storage and preparation of the solutions. 5-50 µL, 25-250 µL and 100-1000 µL adjustable micropipettes

(Transferpette, Treff Lab) with disposable polyethylene tips were used in preparation of solutions.

50 mL of Falcon tubes were used for metal sorption/desorption optimizations by batch process.

Magnetic stirrer was used for impregnation of DEBT and a NÜVE SL 350 horizontal shaker was used during sorption optimizations by batch process.

Column preparation: As columns, 12 mL syringe barrels (1.5 cm inner diameter, 7.8 cm height, made of PTFE) supplied from Supelco were used. Disposable porous frits were placed at the bottom of the barrel 1.0 g resin (unless otherwise stated) slurred in 50 mL water was poured and uniformly placed in column. At the top of the resin cotton wool was placed to prevent dispersion of resin beads with sample solutions. A tygon tubing R-3603 (Cole Palmer) was connected the outlet tip of the syringe barrel to a Gilson Miniplus peristaltic pump. In order to adjust desired flow rate, a calibration; flow rate mL/min versus rpm was carried out. This calibration was repeated for each column before the application. Each time, 15 mL blank solutions were passed before sorption and desorption studies at a flow rate of 1 mL/min.

Philips PU 9200 Atomic Absorption Spectrometer was used for determination of silver and gold ions. Operating conditions are given in Table 2.1. The results were printed by an Epson FX-850 printer connected to the spectrometer.

Table 2.1 Instrumental parameters used for the determination of Silver and Gold.

Element	Silver	Gold
Light Source	Silver Hollow Cathode Lamp	Gold Hollow Cathode Lamp
Wavelength (nm)	328.1	242.8
Band Pass (nm)	0.5	0.5
Lamp Current (mA)	4	10
Flame for Atomization	Air-acetylene	Air-acetylene
Deuterium background	On	On

2.3 Amberlite XAD-16

It is a macroporous resin (Styrene-divinyl-benzene copolymer). Its surface area is 800 m^2/g pore. It has a pore diameter of 10 nm and bead size 20-60 mesh. It can work properly in the pH range of 0 to 14 [49]. Schematic presentation is given in Figure 2.1.

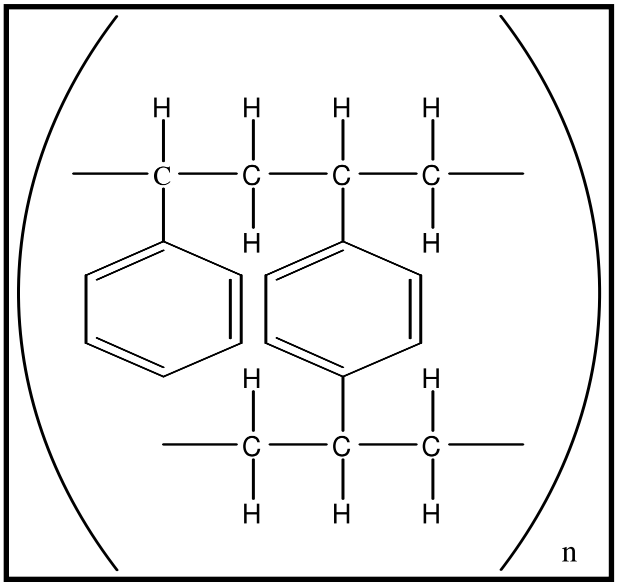


Figure 2.1 Amberlite XAD-16.

2.3.1 Pretreatment of Resin

Amberlite XAD-16 was initially purified with 4 M HCl solution by shaking for 3 hours on the horizontal shaker and filtered under vacuum. Then the resin was washed with deionized water for elimination of chlorides. After chloride test; in the absence of chloride it was taken into a beaker and stirred with ethanol-water (1:1) v/v solution for 5 minutes, filtered under vacuum and finally washed with water again. The resin was dried in oven at 60 ^{0}C [48].

2.4 Synthesis of DEBT

DEBT was synthesized according to the modified procedure in our laboratory [47].

0.1 mol of potassium thiocyanate (Fischer) was dissolved in 100 mL of anhydrous acetone (Riedel-deHaën) by stirring and heating in a reflux condenser. After cooling to room temperature, 0.1 mol of benzoyl chloride (Merck) was added dropwise. The reaction mixture was stirred about 30 minutes at room temperature. Then the precipitate of potassium chloride is removed by filtration. The orange-colour filtrate was reacted with 0.1 mol of diethylamine (Merck) dropwise. The reaction mixture was crystallized in 250 mL of 1 M HCl solution, which was already cooled with ice. Then the mixture was filtered and the residue was recrystallized with ethanol.

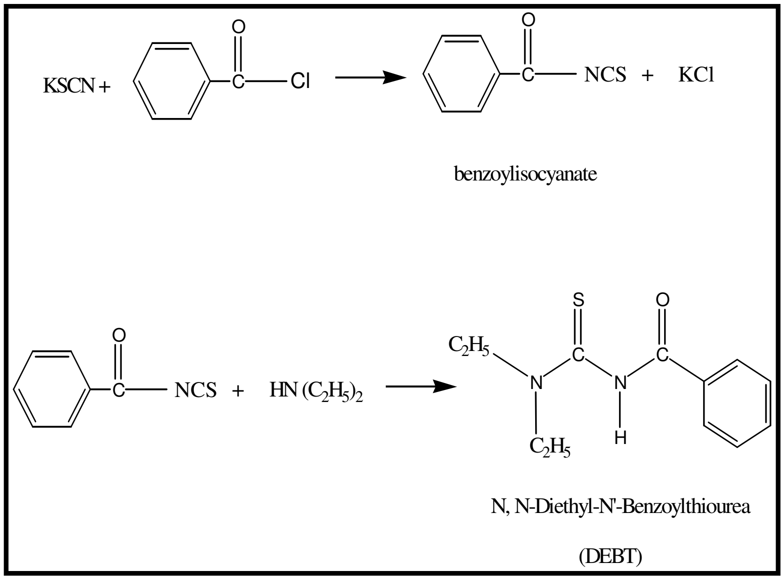


Figure 2.2 Schematic diagram of DEBT synthesis.

2.5 Characterization of DEBT

2.5.1 UV –Absorption studies

For the investigation of characteristic absorption bands of chelating agent (DEBT), DEBT dissolved in ethanol was examined using SHIMADZU UV-160, double beam UV-visible absorption spectrophotometer in the range of 200-400 nm with 10 mm capped quartz cells. Ethanol was used as blank.

2.5.2 IR Studies of DEBT and Impregnated Resin

A FTIR instrument (Unicam, Mattson 1000) in the 4000-400 cm^{-1} range frequencies was used for structural characterization of ligand and DEBT impregnated resin. 2 mg of finally ground sample was intimately mixed with 200 mg of dried potassium bromide powder by using an agate mortar. The mixture was then pressed into pellets under pressure. The pellet was investigated by FTIR.

2.5.3 IR Studies of Metal Chelates Retained on Resin

In order to confirm the retention of silver and gold on resin as metal-DEBT chelates, 3 mL 2x10^{-3} of DEBT solution was added to 7 mL of 10 mg/mL Ag^+ solution in 0.05 M HNO_3. Then the solution was percolated through the column (1.0 g resin) at a flow rate of 0.5 mL/min.

Similarly, 3 mL 2x10^{-3} of DEBT solution was added to 7 mL of 10 mg/mL Au^{3+} solution in 1 M HNO_3. Then the solution was percolated through another column (1.0 g resin) at a flow rate of 0.5 mL/min. After drying columns in air, resin samples from the top of columns were taken and pellets were prepared as mentioned in Section 2.5.2.

2.6 Impregnation of DEBT on Amberlite XAD-16

The impregnation process deals with physical interactions between the chelating agent and solid support by either inclusion in the pores of the support material or adhesion process or electrostatic interaction. Therefore, some parameters that control the impregnation should be optimized.

2.6.1 Determination of Optimum Stirring Time

According to procedure described elsewhere [48], impregnation of DEBT was carried out by stirring samples of resin with DEBT in ethanol. Then the impregnated resins was filtered under vacuum and finally dried in air and vacuum.

In order to find out optimum stirring time for impregnation of DEBT, samples of 0.1 g of pretreated resin were stirred with 10 mL of 0.025 M DEBT in ethanol on a magnetic stirrer. At different time intervals, resins were filtered under vacuum. DEBT contents of the organic phase were determined by UV spectrophotometry. Similarly, 0.1 g resin was stirred with 10 mL of ethanol and the filtrate was used as blank.

2.6.2 Determination of Chelating Agent Capacity of Resin

10 mL DEBT solutions in ethanol taken in the concentration range of 0.0001–0.027 M were stirred with samples of 0.1 g resin for 35 minutes. Then impregnated resins were filtered under vacuum and dried in air and vacuum. DEBT contents of the organic phase were determined by UV spectrophotometry.

<u>Batch Process</u>:

2.7 Sorption Behavior of Gold and Silver on DEBT Impregnated Amberlite XAD-16

In this part of the thesis, we aimed to investigate sorption behavior of high concentrations gold and silver on DEBT impregnated Amberlite XAD-16. Some critical parameters such as pH, stirring time, metal capacity of resin capacity and finally suitable desorbing agents have been studied to find out the optimum conditions and recovery of silver and gold.

2.7.1 Optimization of Parameters for Silver Ions

2.7.1.1 pH Effect

In order to investigate the pH effect on sorption of silver ions onto impregnated resin (2.5 mmol DEBT/g resin), different sets of 10 mL of 20 mg/L of Ag^+ solutions in the pH range of 1-4 were stirred with samples of 0.1 g impregnated resin for 30 minutes. The pH adjustments were carried out by HNO_3 and NaOH. Then the solutions were filtered under vacuum. Metal ion concentrations were determined by FAAS.

2.7.1.2 Effect of Stirring Time

Three different sets of 10 mL of 5 mg/L, 50mg/L and 150 mg/L of Ag^+ solutions in 0.05 M HNO_3 were stirred with samples of 0.1 g impregnated resin within time period from 5 minutes to 1 hour. Then the solutions taken at certain time intervals were filtered under vacuum and metal ion concentrations in the filtrate were determined by FAAS.

2.7.1.3 Silver Ion Capacity of Resin

In order to determine the resin capacity, samples of 0.1 g impregnated resin were stirred with 10 mL of silver ions in the concentration range of 5 mg/L to 500 mg/L in 0.05 M HNO_3 for 20 minutes. Then the solutions were filtered and metal ion concentrations were determined by FAAS.

2.7.1.4 Desorption of Silver Ions from Impregnated Resin

10 mL of 10 mg/L of Ag ions adsorbed resin samples were stirred with two different thiourea concentrations; 0.1% TU (m/v) and 0.5% TU (m/v), in two different acid concentrations; 0.05 M and 0.1 M HNO_3, at two different stirring times; 10 min. and 20 min. Thiourea solution is selected referring to literature [27].

2.7.2 Optimization Parameters for Gold Ions

2.7.2.1 pH Effect

In order to investigate the pH effect on sorption of gold ions onto impregnated resin, different sets of 10 mL of 10 mg/L of Au^{3+} solutions in the pH range 1-5 were stirred with samples of 0.1 g impregnated resin for 50 minutes. The pH adjustments were carried out by dilute HCl and dilute NaOH. The solutions were filtered by vacuum. Metal ion concentrations in the filtrate were determined by FAAS.

2.7.2.2 Effect of Stirring Time

Three different sets of 2 mg/L, 10mg/L and 100 mg/ L of 10 mL of Au $^{3+}$ solutions in 1 M HCl were stirred with samples of 0.1 g impregnated resin from the periods of 5 minutes to 1 hour. Then the solutions were filtered under vacuum. The metal ion concentrations in the filtrate were determined by FAAS.

2.7.2.3 Gold Ion Capacity of Resin

In order to determine the resin capacity, samples of 0.1 g of impregnated resin (1 mmol DEBT/g resin) were stirred with 10 mL of gold ions solutions in the concentration range of 2 mg/L to 600 mg/L in 1 M HCl for 15 minutes. Then the solutions were filtered and metal ion concentrations were determined by FAAS.

2.7.2.4 Desorption of Gold Ions from Impregnated Resin

10 mL of 10 mg/L of Au (III) ions adsorbed onto resin were stirred with different thiourea concentrations; 0.1 % TU (m/v), 0.5 % TU (m/v), in different concentrations; 0.1 M, 1 M, and 4 M HCl, at two different stirring times; 10 min and 30 min. Then the solutions were filtered by vacuum and metal ion concentrations were determined by FAAS.

The summary of impregnation of DEBT and sorption of metal ions by batch process is given with a flow chart in Figure 2.3.

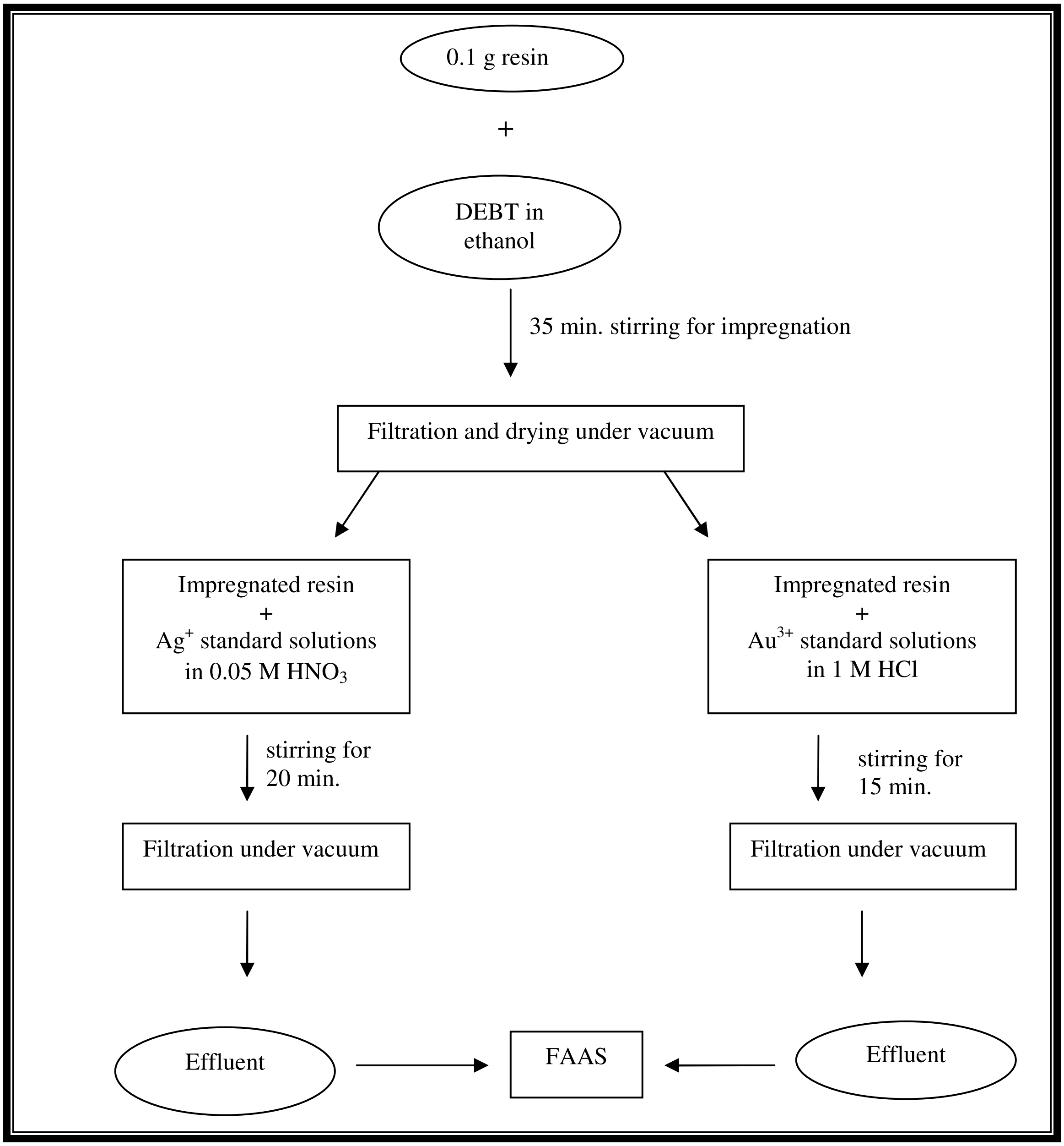


Figure 2.3 Flow chart for batch processes.

Column Process:

2.8 Optimization of Column Conditions for Preconcentration PM's Using DEBT Impregnated Resin

Since the kinetic and equilibrium aspects of column process are different than batch process, optimization of column conditions is needed.

2.8.1 Effect of DEBT Impregnated onto Different Amounts of Resin and Breakthrough Capacities

0.1 mmol DEBT alcoholic solutions were stirred with 0.2 g, 0.5 g and 1.0 g of resin for 35 minutes. Then they were filtered under vacuum. After drying in air and under vacuum, columns were prepared as mentioned in Section 2.2.

5 mL aliquots of 0.5 mg/L of silver ions solutions were successively passed through both of the columns having of 0.2 g and 0.5 g resins at a flow rate of 0.5 mL/min.

Totally, 65 mL aliquots of 0.5 mg/L of silver ions solutions were passed through the column containing 1.0 g resin at a flow rate of 0.5 mL/min and then the experiment was continued with percolation of totally 95 mL of 1 mg/L solutions at a flow rate of 0.5 mL/min.

Totally, 25 mL aliquots of 1.5 mg/L of gold ions solutions were passed through the column containing 1.0 g resin at a flow rate of 0.5 mL/min and then the experiment was continued with the percolation of totally 60 mL of 3 mg/mL of the solution at the same flow rate.

During the experiment, metal ion concentrations initially present and that in the effluent after percolation were determined by FAAS. The amounts of metals sorbed on resin were calculated according to difference in metal ion concentrations.

Breakthrough curves were prepared by plotting concentrations of metal ions (μg/mL) in the effluents versus sum of volumes the sample solution (mL) added at the end of each loading (see Figure 3.11).

2.8.2 Sample Flow Rate

10 mL of 0.5 µg/mL silver standard solutions in 0.05 M HNO_3 were passed through the columns containing 1.0 g resin at flow rates from 1 mL/min to 2 mL/min. Then the metal concentrations in the effluent were determined by FAAS.

2.8.3 Eluent Concentration, Volume and Flow Rate

10 mL of 0.5 µg/mL silver standard solutions in 0.05 M HNO_3 were passed through the columns at a flow rate of 0.5 mL/min. In order the find minimum eluent volume, 5 mL aliquots of 0.1 M $Na_2S_2O_3$ in water were successively passed through the columns until the maximum desorption percentage could be achieved. The same experiments were repeated at flow rates from 1 mL/min to 0.3 mL/min.

2.9 Optimization of Sorption of Metal Chelates on Amberlite XAD-16 (non-impregnated resin)

2.9.1 Effect of Flow Rate for Impregnation of DEBT on Amberlite XAD-16

In order to determine the optimum flow rate range for DEBT molecules to have a retention on resin efficiently, a series of columns were prepared (having 0.5 g resin in each). 3 mL of 3.75×10^{-4} M DEBT solution were passed through the columns at flow rates changing from 0.3 mL/min to 2.5 mL/min. DEBT concentrations before percolation and in the effluents were determined by UV spectrophotometry. The difference between the two values was taken as the amount of DEBT retained on resin

2.9.2 Effect of Ligand Solution Volume on Impregnation onto Amberlite XAD-16

In order to find maximum applicable ligand solution volume that will be used during formation of metal chelates in metal standard solutions, keeping the ligand concentration constant (3.75×10^{-4} M), 3 mL of the solution were passed through the column (0.5 g resin) for 4 times at optimized flow rates given in Section 2.9.1. Then DEBT concentration in the effluent was determined by UV spectrophotometry.

2.9.3 Effect of Optimized Ligand Concentration on Amount of Metal Chelates

In order to demonstrate that an amount of 3 mL of 2×10^{-3} M DEBT solution is in excess as compared to amounts of analyte metals, keeping ligand amount constant; 3 mL of 2×10^{-3} M, 10 mL of 0.5 µg/mL, 10 µg/mL, 50 µg/mL silver and gold standard solutions were prepared. They were passed through the columns at flow rate 0.5 mL/min. Then the metals in the effluents were determined by FAAS.

2.10.1 Optimum Column Conditions for Preconcentration of Silver

First of all, 10 mL of silver chelates solution (0.5 µg/mL Ag^+ and 3 mL of 2×10^{-3} M DEBT) were passed though the column (1.0 g pure resin) at a flow rate of 0.5 mL/min. Then metal ions can be eluted with 13 mL of 0.1 M $Na_2S_2O_3$ in water, quantitatively $\geq$95 %.

Then 50 mL of silver chelates solution (0.5 µg/mL Ag^+ and 3 mL of 2×10^{-3} M DEBT) were passed through the column at the same flow rate. The preconcentration could be achieved with 13 mL of 0.1 M $Na_2S_2O_3$ in water at 0.3 mL/min with a 90 % desorption.

Finally, 100 mL of silver chelates solution were prepared similarly and the same procedure above was applied. Preconcentration was achieved with 88.1 ± 1.8 % desorption. This experiment was repeated three times.

2.10.2 Optimum Column Conditions for Preconcentration of Gold

Here, 25 mL of gold chelates solution (1.5 µg/mL Au^{3+} and 3 mL of $2x10^{-3}$ M DEBT) were passed though the column (1.0 g pure resin) at a flow rate of 0.5 mL/min. Then metal ions can be eluted with 15 mL of 0.2 M $Na_2S_2O_3$ in water, quantitatively ≥104 % at a flow rate of 0.3 mL/min.

Finally, 100 mL of gold chelates solution were prepared similarly and the same procedure above was applied. Preconcentration was achieved with 97.6 ± 2.3 % desorption. This experiment was repeated two times.

2.11 Interference Studies

In order to observe the interference effect of copper on silver determination by FAAS, standard solutions with Ag/Cu mass ratios of 1:1, 1:10 and 1:50 were prepared in 10 mL of 0.05 M HNO_3. Percent variations in Ag signal were calculated based on the signal of pure analyte solution of 0.5 µg/mL Ag in 10 mL of 0.05 M HNO_3.

In order the observe interference effect of copper during preconcentration and determination of silver in geological samples by the proposed method, 50 mL of 0.1 µg/mL, 1 µg/mL and 5 µg/mL standard copper solutions were prepared in 0.05 M HNO_3. Then solutions were percolated through the columns at a flow rate of 0.5 mL/min. Desorption was followed with 13 mL of 0.1 M $Na_2S_2O_3$ in water at a flow rate of 0.3 mL/min and copper ions concentrations in the effluents were determined by FAAS.

In case of gold studies, interference effect of copper was expected during the retention of both copper and gold chelates on resin hence gold ions may not be retained quantitatively in the presence of excess copper. For this purpose, 50 mL of 300 μg/mL of copper standard solution was prepared in 1 M HCl. (1000-fold of analyte metal amount). Initial metal ion concentration was determined by FAAS. Then the solution was percolated through the column at a flow rate 0.5 mL/min. The copper ions concentration in the effluent was determined by FAAS.

2.12 Decomposition of Geological Samples

In this study, considering differences in the natural occurrences and the distributions of gold and silver in ore samples, two different sample preparation procedures have been applied.

2.12.1 Microwave Digestion Procedure for Samples Containing Silver

The sample was dried at 80^{o}C for 4 hours. Then Microwave-assisted digestion of this material was performed according to a procedure by Boch K. and coworkers [50] and Orhan Acar [51] with some modifications. A microwave sample preparation system (MILESTONE MICROWAVE Laboratory Systems, ETHOS PLUS Microwave Labstation equipped with Lab Terminal 800 Controller) was used in this study. This system is pressure and temperature controlled, so that reaching maximum pressure or temperature the microwave energy input is restricted automatically.

The vessels of the microwave system were charged with 0.2 g for Mining Research Institution (MTA) samples and 0.3 g for Cyprus Mining Corporation (CMC) Cu-ore sample, 7 mL of HNO_3 (65 % w/w) and 3 ml of H_2O_2 (31 % w/w). Solid particles attached to the wall of the vessel line should be rinsed down with the digestion reagents. After 10 min, when the first vigorous reaction has taken place, the pressure vessels were closed and the first microwave step was performed. When the vessels are opened, nitrogen gases escaped and a precipitation of silicate was observed.

For the second step, 4 mL of hydrofluoric acid (38-40 % w/w) were added. The vessels were closed and heated according to step 2. After they have cooled down, the bomb cap was withdrawn and the digested solutions were transferred to other Teflon vessels. The vessels were placed on a hot plate. 4 mL of concentrated H_2SO_4 (95-97 % w/w) were added and gently boiled near to dryness in order to evaporate excess acids such as HF. The microwave energy programs used for the two-step digestion are summarized in Table 2.2.

The dried material was diluted with 50 mL of 0.05 M HNO_3 and filtered through Whatman white band filter paper into 100-mL glass flasks, finally with the addition of 3 mL of 2×10^{-3} M DEBT, final volume was completed to 100 mL with 0.05 M HNO_3. Then the proposed method for preconcentration of silver was applied.

Table 2.2 Energy Programs and Reagents for the Microwave-Assisted Digestion Procedure.

Procedure number	**Energy (W)**	**Time (min)**	**Temperature (°C)**
First step: 7 mL HNO_3, 3 mL H_2O_2			
1	500	5	0-150
2	500	10	150
3	500	5	150-180
4	500	15	180
Cooling	0	5	Room temperature (RT)
Second step: 4 mL HF			
1	500	5	0-150
2	500	10	150
3	600	5	150-180
4	600	20	180
Cooling	0	10	RT

2.12.2 Acid Digestion Procedure for Samples Containing Gold

Acid digestion procedure was applied to Cu-ore and Gold Ore (MA-1b) samples as suggested elsewhere [52]. For this reason, two parallel 10.0 g of Cu-ore sample and 1.0 g of Gold Ore (MA-1b) were transferred into Teflon beakers. Few milliliters of deionized water were added to moist the sample. 0.15 µg/mL of gold ions solution was spiked to one of the Cu-ore samples. 20 mL of concentrated HCl were added to each; the beakers were covered and placed on a warm hot plate. After 15 minutes digestion, 15 mL of concentrated nitric acid were added cautiously and the contents were digested for 20 min.; then 25 mL of concentrated HCl and 25 mL of deionized water were added. The beakers were covered and the contents were boiled to expel nitric acid digestion gases and to dissolve all soluble salts. After cooled, they were diluted successively with small amounts of water and filtered through Whatman white band filter paper into 100-mL PTFE flasks. Then 3 mL of $2x10^{-3}$ M DEBT solution was added, final volume was completed to 100 mL with water. Later, the proposed procedure for preconcentration of gold was applied.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Decomposition of Geological Samples

3.1.2 Microwave Digestion Procedure for Samples Containing Silver

For precious metals determination, apart from the considerable reduction of the decomposition time, microwave decomposition shows some advantages such as:

1- Greater completeness of dissolution, avoiding additional fusion in specific cases (such as carbonaceous slimes).

2- The use of nitric acid or its mixtures with hydrochloric acid instead of high-boiling acids, yielding low–solubility compounds with matrix components.

3- Significant decrease in acid volumes and improvement of detection limits due to the absence of losses and contamination and

4- Compatibility with preconcentration techniques and instrumental determination methods [53].

3.1.3 Acid Digestion Procedure for Samples Containing Gold

It is known that the constituent of gold mineral is complicated, in which the gold content is very low and the distribution is heterogeneous. Therefore, 10 g or more amounts of samples are necessary to obtain accurate data [4]. Microwave digestion method was not employed because it can digest 0.5 g amounts of geological sample per vessel (and in practice usually 0.1-0.2 g). This requires many vessels to dissolve 10 g amount of geological sample which is not practical and is time consuming.

3.2 Pretreatment of Resin

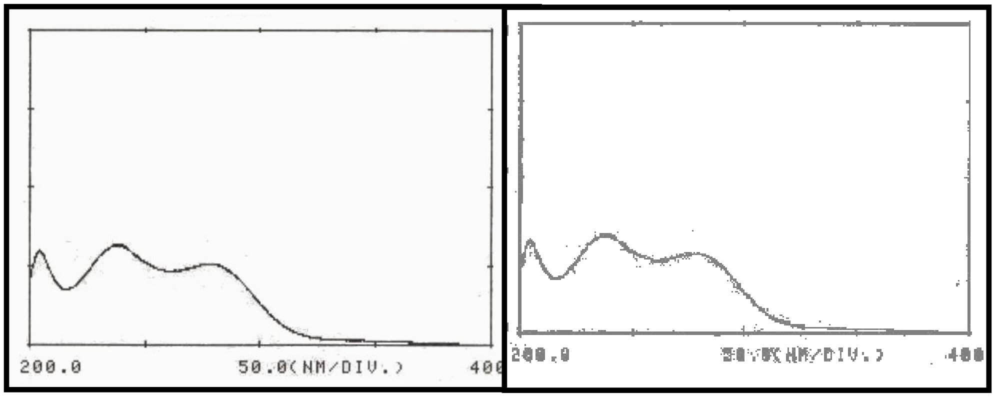
Although some sorbents have been used without a pretreatment step, it is not recommended. It is mentioned that, this step will at least remove possible remaining contaminants and air from the sorbent bed. Additionally, in some cases this step is crucial for successful retention of the analytes. The nature of the conditioning solvent must be appropriate to the nature of solid sorbent to ensure good wettability of the functional groups.

In the study, since Amberlite XAD-16 is one of the members of hydrophobic PS-DVB supports, quite polar organic solvent such as ethanol was used. Since highly acidic metal solutions were to be used for further studies, resin was preconditioned by 4 M HCl similar to the nature of the sample.

3.3 Confirmation of DEBT, Its Impregnation and Retention of Metal Chelates on Resin

3.3.1 UV –Absorption Studies of DEBT

UV-absorption bands of DEBT show close similarity to those given in literature. (Figure 3.1)



In this study **Literature (Merdivan 1994)**

Figure 3.1 UV-Absorption spectra of DEBT ($2x10^{-5}$M DEBT in ethanol).

DEBT has a very weak absorption above 300 nm. However; it has strong but broad absorption bands at 237 and 278 nm. All UV experiments related with DEBT were carried out at 237 nm, throughout the study.

3.3.2 IR Studies of Amberlite XAD-16, DEBT and Impregnated Resin

FTIR spectra of DEBT given in the literature [47] and that of the synthesized reagent in this study are given in Figures 3.2a. and 3.2b. The characteristic absorption bands for N-H, C-H and amide I (C=O), amide II and amide III at 3276, 3066-2936, 1656, 1537 and 1306 cm^{-1} respectively appearing in both of the spectra support the formation of DEBT.

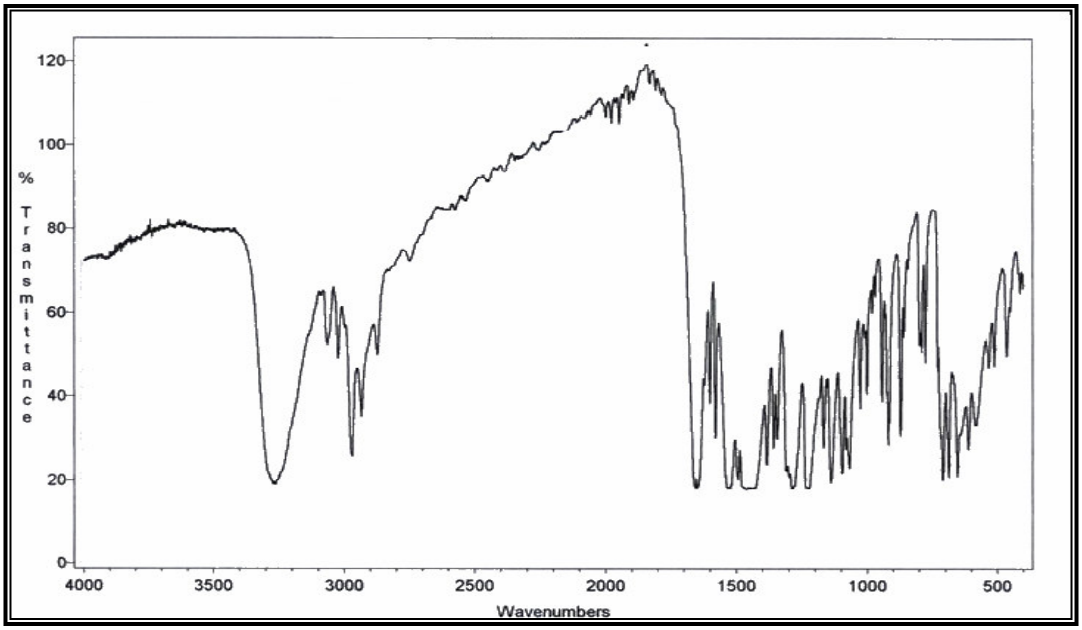


Figure 3.2a Infrared Spectra of DEBT (This Study).

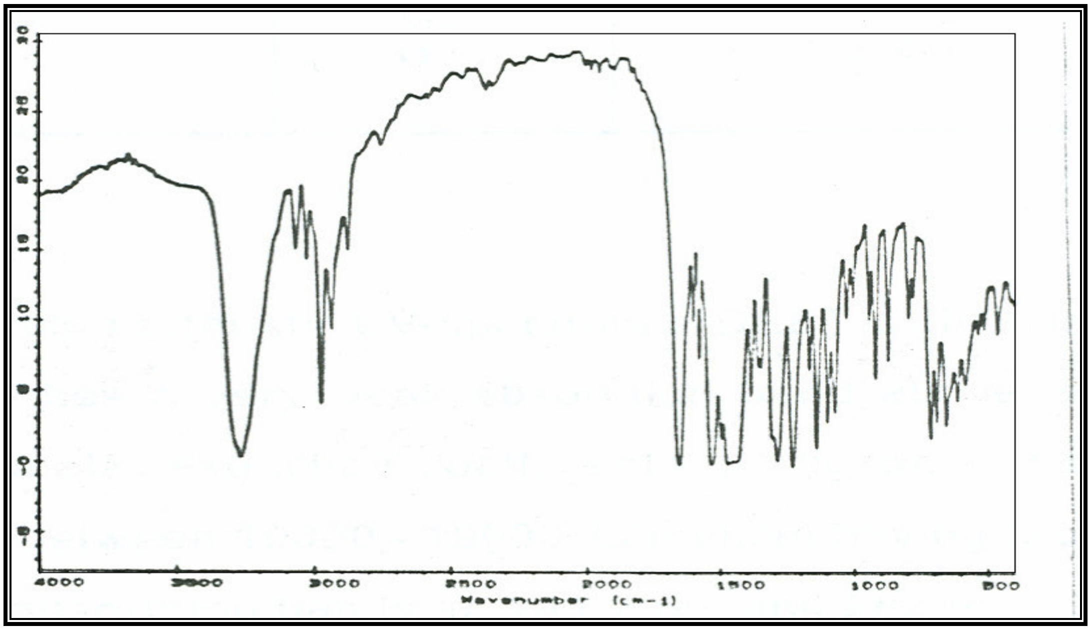


Figure 3.2b Infrared Spectra of DEBT [47].

In order to confirm the impregnation of DEBT on to resin, IR spectra of impregnated resin is studied as well. The IR spectrum of Amberlite XAD-16 is available in literature [48]. The IR absorption frequency assignments for Amberlite XAD-16, DEBT molecule and DEBT-XAD-16 resin are given in Table 3.1. The characteristic absorption bands for C-H and amide I (C=O), amide II and amide III at 3276, 3066-2936, 1656, 1537 and 1306 cm^{-1} respectively appear only in the spectra of DEBT and impregnated resin. Some modifications of the characteristic normal modes of DEBT on resin compared with the spectrum of the free reagent. Small shifts (~ 10 cm^{-1}) either positive or negative are observed upon impegnation.

Table 3.1 Some fundamental frequencies (in cm^{-1}) of Amberlite XAD-16, DEBT and DEBT impregnated resin.

Amberlite XAD-16	DEBT	DEBT-XAD-16	Assignments
3047	3066	3052	Aromatic C-H stretching
2856	2875	2872	Aliphatic C-H stretching
-	1656	1680	Amide I, C=O stretching
-	1537	1539	Amide II, N-H bending
-	1463	1452	Amide II, -CS-N
1510	-	1504	C=C ring stretching
-	1366	1370	Amide I
-	1306	1298	Amide I
-	1027	1020	C=S stretching

3.3.3 IR Studies of Metal Chelates Retained on Resin

The IR spectral bands corresponding to C=N, C-H, N-H and C=O bands of DEBT and metal complexes are given in Table 3.2.

Table 3.2 IR spectral bands of DEBT and metal chelates.

	DEBT	$Au(DEBT)_3$	Ag(DEBT)
ν N-H	3276	-	-
ν C=O	1656	-	-
ν CH_3	2875,2885	2872,2882	2869,2879
ν CH_2	2936	2930	2929
ν C-H	3020, 3052	3052,3090	3051,3086
ν C=N	-	1588	1587

The metal chelates have similar IR spectra, which indicate that they have similar structures and there is no significant dependence on the central metal ion. The characteristic IR bands of $–N(CH_2CH_3)_2$ group , appearing at 2875 and 2885 cm^{-1} (ν CH_3) and 2936 cm^{-1} (ν CH_2) in the spectrum of the ligand, remain almost unchanged in the spectra of the complexes. In complexes of DEBT, $-N(CH_2CH_3)_2$ group and aromatic ring displayed slight shifts on complexation. The small change in the $-N(CH_2CH_3)_2$ band indicates that this group does not take part in coordination. In the aromatic ring upon the formation of the metal-ligand bond the C-H vibration is shifted to higher frequencies.

The position of the amide I, amide II and III bands of DEBT (1656, 1537, 1306 cm^{-1}), arising from the carbonyl of the benzamide moiety, disappeared in the complexes. The vibration band of the secondary amide at 3276 cm^{-1}also disappeared in the complexes. Similar discussion is valid for IR spectrum of Ag-DEBT chelate.

3.4 Optimization Parameters for Impregnation of DEBT

3.4.1 Determination of Optimum Stirring Time

During determination of optimum stirring time, 0.025 M DEBT solution was used with 0.1 g of resin. Referring to Figure 3.3, it can be said that within 30 minutes, 95 % of DEBT was impregnated on resin. However, in order to be on safer side; 35 minutes in which 100 % impregnation is achieved is used as optimum stirring time for further experiments.

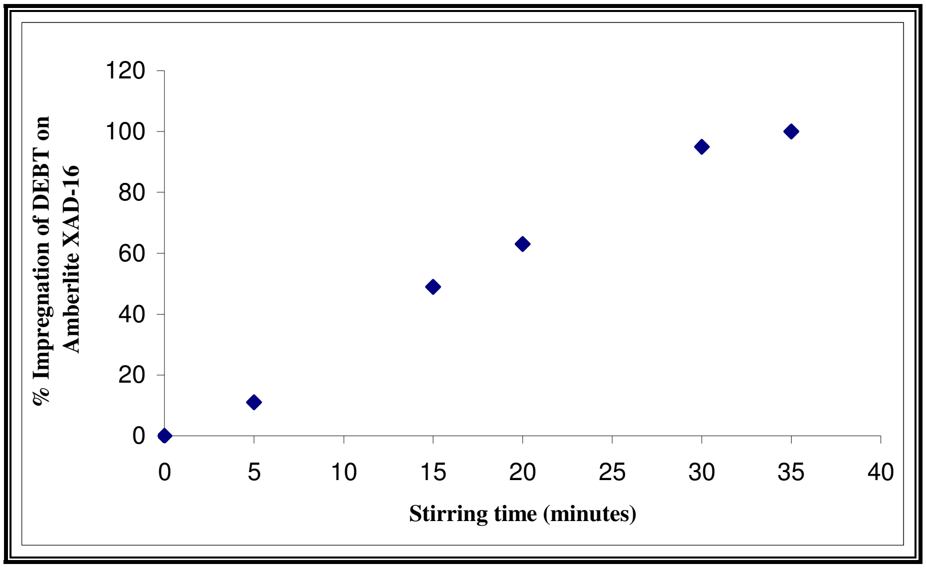


Figure 3.3 Stirring time for impregnation of DEBT.

Initial DEBT concentration; 0.025M, amount of resin; 0.1 g.

3.4.2 Determination of Chelating Agent Capacity of Resin

In literature; it is possible to find different procedures for impregnation of a chelating agent on solid support by batch process. In the first part of the study, impregnation is carried out according to procedure described Section 2.6.1 by batch process. We aimed to saturate adsorbent surface with DEBT so that all take-up of metals would be a result of selective chelation mechanism between precious metals and DEBT. Accordingly, in order to find chelating agent capacity of resin, a series of impregnation experiments were performed. When DEBT content of the filtrate was determined by absorbance measurements, at the end of the optimized stirring time (35 minutes) as it was shown in Figure 3.4. no saturation was observed even up to a value of 0.027 M DEBT solution. However, when the resin was dried in air under vacuum, some precipitated DEBT particles were observed. When we could not reach to saturation during impregnation, first, we thought that the reason was the macroporous nature and large surface area of Amberlite XAD-16. However, when the precipitation of some DEBT particles on resin was observed upon drying, this implied that excess amount of DEBT was impregnated. According to the procedure [48], 0.1 g sample of resin was stirred continuously with DEBT in its ethanolic solutions. Because of the kinetic effect, even excess DEBT was dissolved and attached on resin. This may be the reason why we could not find any critical amount of DEBT remained in the filtrate to confirm an end point for saturation. For the following experiments, we started to study with 2.5 mmol DEBT/ g resin as a ligand amount.

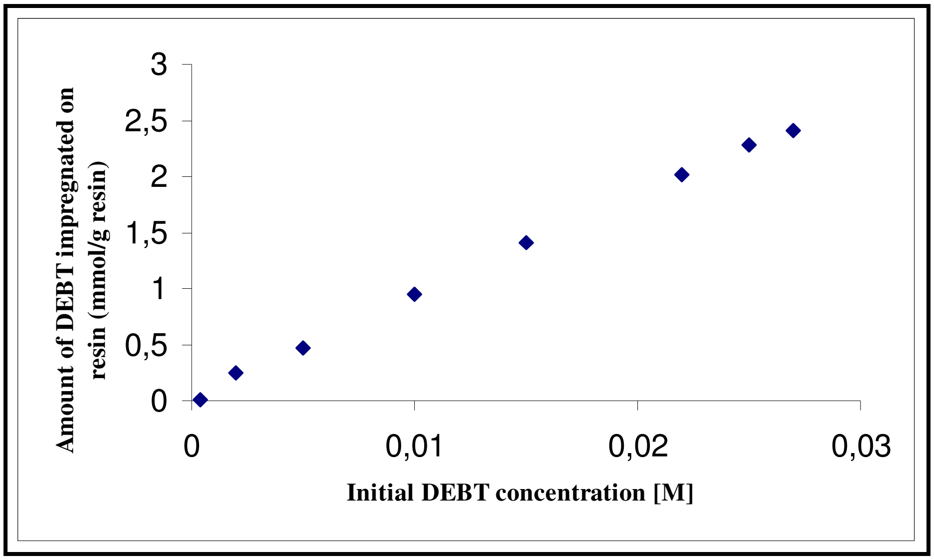


Figure 3.4 Chelating agent capacity of resin.

DEBT concentrations; (0.0001-0.027 M). Volume of ethanol; 10 mL. Stirring time; 35 minutes.

3.5 Optimization Parameters for Sorption of Silver Ions on Impregnated Resin in Batch Process

3.5.1 pH Effect

The pH effect on chelation of silver ions with DEBT is investigated through the pH range from 1 to 4. This range is intentionally investigated because DEBT has ability to form stable and selective complexes with noble metals only in acidic or strongly acidic media [54]. Schuster and Schwarzer 1996, suggested pH range as 0-4 in one of their studies related with liquid-liquid extraction of precious metals with DEBT [25].

When silver standard solutions were prepared in 0.5 M nitric acid solutions and experiments for sorption of silver ion onto DEBT impregnated resin were carried out, a color change (from colorless to grey) on impregnated resin was observed. This is probably because of the oxidizing effect of nitric acid at that concentration on DEBT. Therefore, the lowest pH (~ 1) adjustment was achieved when standard solutions were prepared by 0.05 M HNO_3.

In Figure 3.5, it can be seen that maximum percent sorption is obtained at approximate pH 1. For further sorption studies of silver, standard solutions were prepared by diluting AAS standard stock solution with 0.05 M HNO_3.

In addition, the nature of DEBT forming metal chelates in strongly acidic or acidic media is an advantage such that it is not necessary to adjust the acidity of sample solutions exactly in their analysis.

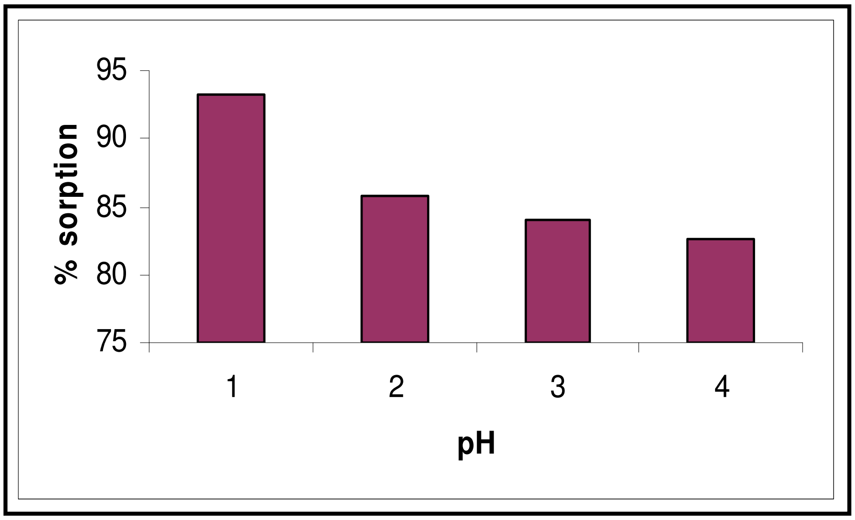


Figure 3.5 Effect of pH on silver sorption.

Amount of resin; 0.1 g, amount of DEBT; 2.5 mmol/g resin, stirring time; 30 minutes.

3.5.2 Effect of Stirring Time

Referring to Figure 3.6, it can be said that 20 minutes of stirring is sufficiently good enough to achieve sorption equilibrium for three different concentrations of silver ion. Actually, fast kinetics can be expected in applications of macroporous resins.

In addition, high ligand concentration; 2.5 mmol/g resin used in impregnation thus increasing selectivity of the resin can also be a reason for fast sorption rate.

Three different silver ion concentrations were studied during determination of stirring time effect. As it is observed, there is no effect of higher silver ion concentration on the optimum time for sorption. By this way, 20 minutes of stirring can be accepted as a compatible stirring time during loading of resin with higher concentrations of silver ions to determine silver ion capacity of the resin (see Section 3.5.3).

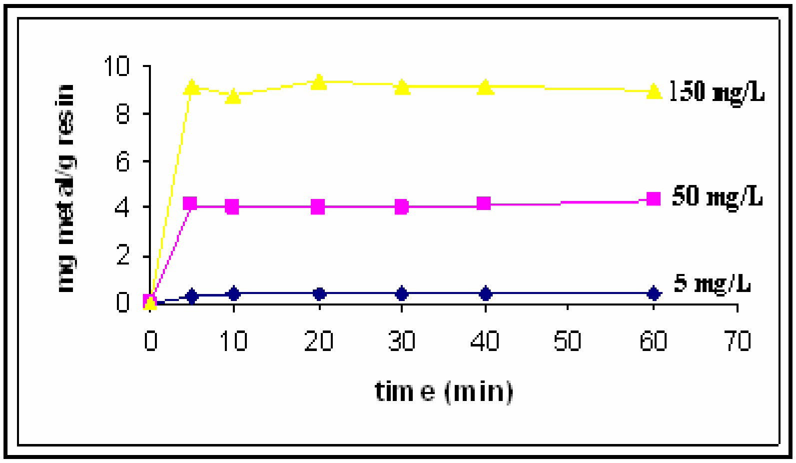


Figure 3.6 Effect of stirring time on silver sorption.

Amount of resin; 0.1 g, amount of DEBT; 2.5 mmol/g resin.

3.5.3 Silver Ion Capacity of Resin

The resin seems to reach saturation after a concentration of 250 mg/L silver ion solution (see Figure 3.7). Using the Equation 3.1 [14];

$$Q = \frac{(C_o - C_A) \times V}{W} \qquad \text{(Equation 3.1)}$$

Where, Q= metal ion capacity (mg/g)

C_o = initial concentration of metal ion (mg/L)

C_A=equilibrium concentration of metal ion (mg/L)

V= volume of the solution (L)

W= weight of the resin (g)

Silver ion capacity of the resin is calculated as 11.22 mg Ag^+/g resin (0.104 mmol Ag^+/g resin).

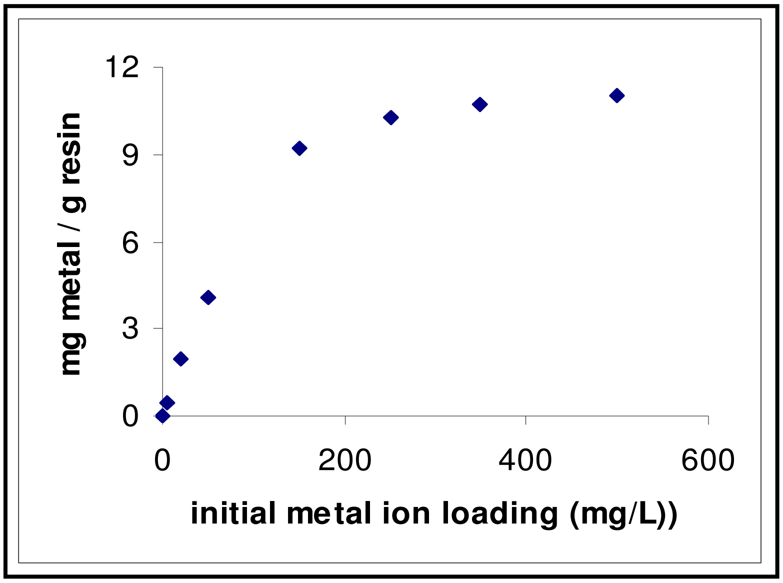


Figure 3.7 Silver ion capacity of resin.

Amount of resin; 0.1 g, amount of DEBT; 2.5 mmol/g resin, stirring time; 20 minutes.

3.5.4 Desorption of Silver Ions from Impregnated Resin

Pu et. al. [27] mentioned that 0.05% thiourea (TU) solution can quantitatively desorb Ag^+ from 2-mercaptobenzothiazole-modified silica gel. Finally, they pointed out that dilute HNO_3 had no influence on desorption but high concentrations of HNO_3 (>3 M) oxidized thioureas seriously.

Considering all, we started with 0.1 % TU (w/v) in 0.05 M HNO_3 as eluent. After 10 minutes stirring, 58% desorption was obtained. Approximately, 100 % desorption was achieved at the end of 20 minutes stirring. This showed that 0.1 %TU in 0.05 M HNO_3 was dilute to achieve a fast and quantitative desorption. So, TU concentration is increased to 0.5% TU keeping acid concentration constant and after 10 minutes stirring a 100 % desorption was obtained.

As a conclusion, it can be stated that 0.5% TU in 0.05 M HNO_3 can quantitatively desorb Ag^+ from DEBT- impregnated resin within 10 minutes of stirring (see Table 3.3).

Table 3.3 Desorption studies of silver.

Stripping agent Thiourea (TU)	Desorption (%)	Stirring time (min.)
0.1% TU in 0.05 M HNO_3	58	10
0.5%TU in 0.05 M HNO_3	≥100	10
0.1% TU in 0.1 M HNO_3	33	10
0.1% TU in 0.05 M HNO3	≥100	20
0.5% TU in 0.05 M HNO_3	≥100	20

Average of two parallels, deviation from the mean ±5 %.

3.6 Optimization Parameters for Sorption of Gold Ions on Impregnated Resin

3.6.1 pH Effect

The pH effect on chelation of gold ions with DEBT impregnated resin is investigated through the pH range from 1 to 5. This range is intentionally investigated because in literature, as it is mentioned before DEBT forms stable and selective complexes with noble metals only in acidic or strongly acidic media [25]. Also Schuster et al. in their studies mentioned before, suggested the pH range as 0-5 for liquid-liquid extraction of gold with DEBT [54].

In Figure 3.8, it can be seen that maximum percent sorption is obtained at pH ~ 1. For further studies of gold, standard solutions were prepared by diluting AAS standard stock solutions with 1 M HCl. In further experiments (under all optimum conditions), higher percent sorption is achieved with 1 M HCl.

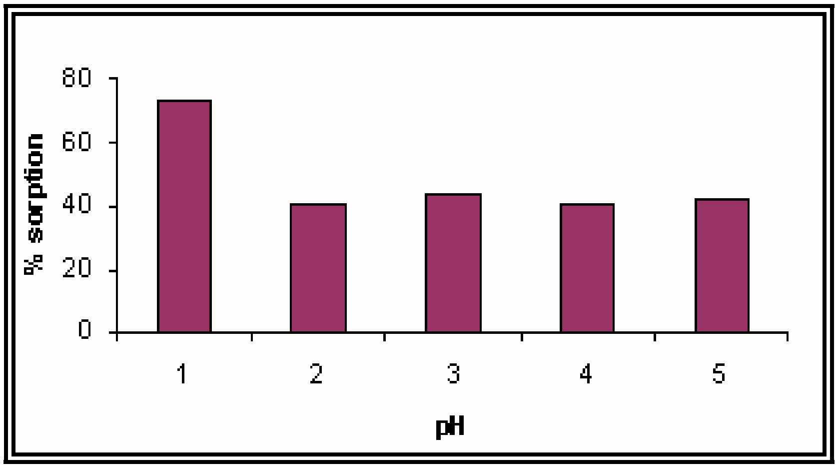


Figure 3.8 Effect of pH on gold sorption.

Amount of resin; 0.1 g resin, amount of DEBT; 1mmol/g resin, stirring time; 50 minutes.

3.6.2 Effect of Stirring Time

Referring to the Figure 3.9, we can say that 15 minutes is good enough to reach to sorption equilibrium for three concentrations of gold ions. The discussion in section 3.5.2 is valid here. In literature, it is mentioned that if the selectivity of the sorbents is determined mainly by the chelating group (nature of the functional group and/or donor atom able to form complexes with metal ions) other analytical properties of the sorbent such as kinetic features, mechanical and chemical strength and degeneration depend on the polymeric matrix, resin [29]. We can say that silver and gold show similar sorption kinetics as long as the same polymeric matrix, close ligand concentrations and low pH's for sorption media are supplied.

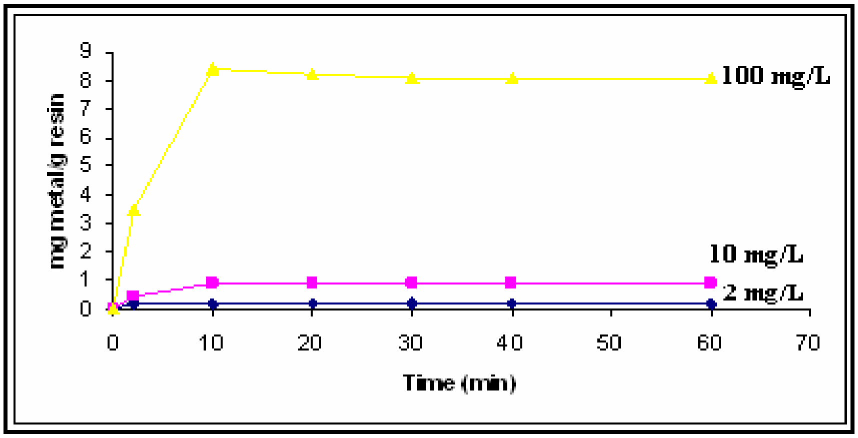


Figure 3.9 Stirring time effect on gold sorption.

Amount of resin; 0.1 g, amount of DEBT; 1 mmol/g resin.

3.6.3 Gold Ion Capacity of Resin

Referring to Figure 3.10, after 500 mg/L of gold ions solutions, the resin reaches saturation. Using the Equation 3.1 the metal ion capacity of the resin is calculated as 33.48 mg Au^{3+}/g resin (0.17 mmol Au^{3+} /g resin).

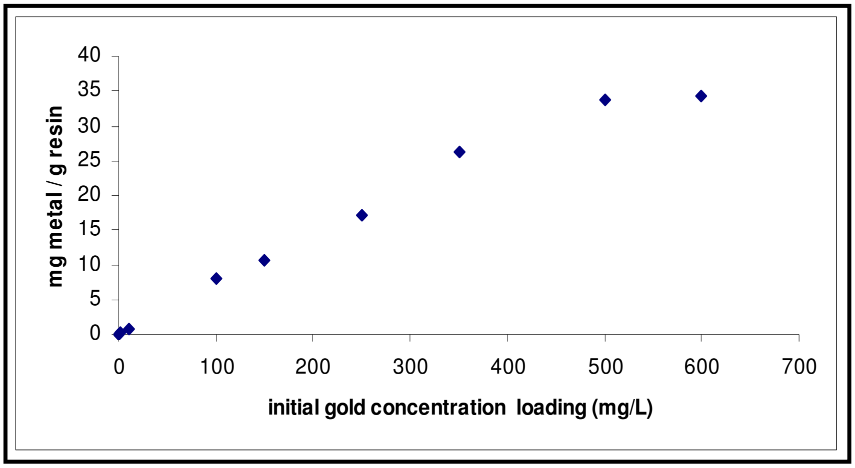


Figure 3.10 Gold ion capacity of resin.

Amount of resin; 0.1 g, amount of DEBT; 1 mmol/g resin, stirring time; 15 minutes.

3.6.4 Desorption of Gold Ions from Impregnated Resin

Since we observed similar sorption behavior for silver and gold, we expected the same behavior during desorption. Considering this, we carried out desorption studies starting with the same thiourea concentrations that were used during silver desorption but in hydrochloric acid solutions.

As it is given in Table 3.4, maximum desorption of 30 % was obtained even if the stirring time was increased to 30 minutes. Any better results could not be obtained when desorption in only 4 M HCl was carried out. Actually, low percent desorption in the presence of high HCl concentration proves that chelation mechanism governs the metal sorption-desorption process, [55] not the formation of a charged complex such as $AuCl_4^-$. This means, according to hard and soft acid-base theory (HSAB), a ligand stronger than DEBT can result in higher percent desoption of gold. During silver desorption, we have already observed that TU being a stronger ligand than DEBT could desorp silver ions quantitatively. Therefore, for a higher percent desorption of gold, we should either increase TU concentrations together with the concentration of acid or use another stronger ligand such as sodium thiosulfate. Actually, at this stage we did not try to improve desorption of gold as this could be used as an advantage for the separation of silver and gold ions where both metals occur together in real samples.

Table 3.4 Desorption studies of gold.

Stripping agent	Au (III) Desorption (%)	Stirring time (min.)
0.1%TU in 1 M HCl	28	10
0.5%TU in 1 M HCl	27	10
0.1% TU in 4 M HCl	30	10
0.1% TU in 0.1 M HCl	31	10
0.1% TU in 0.1 M HCl	29	30
4 M HCl	~ 0	10
4 M HCl	29	30

Average of two parallels, deviation from the mean: ±3 %.

3.7 Conclusion of the Experiments Carried Out by Batch Processes

During the first part of this thesis, we successfully synthesized DEBT in our laboratory. UV-absorption and FTIR analyses have been used for its characterization. In UV absorption analysis, absorption bands of DEBT coincided with those given in literature, indicating the formation of pure DEBT. The verification of formation of the chelating agent was also obtained from the IR spectrum.

Impregnation of DEBT on Amberlite XAD-16 was also confirmed such that; IR spectrum of impregnated resin show characteristic absorption bands of DEBT which also appeared in the spectrum of pure DEBT but not in the spectrum of pure Amberlite XAD-16.

Selection of Amberlite XAD-16 (macroporous resin) as solid support supplied fast sorption kinetics for each metal ion. Metal ion capacites were found as 0.17 mmol/g resin and 0.104 mmol/g resin for gold and silver respectively. Considering such high resin capacities of each metal, this method could be applicable for separation and purification of relatively high concentrations of gold and silver from highly interfering matrices as well.

It is well known that preconcentration with chelating agent impregnated sorbent improves the sensitivity and reliability of the determination of elements. DEBT is a very good reagent for selective extraction of PM's due to its high extraction values with these metals. The ligand provides an extraordinary chemical resistance against oxidation and hydrolysis and most probably will provide a striking selectivity for PM's in geological samples which are our concern.

In addition, we can conclude that SPE of PM's is feasible in a batch-equilibrium mode. However, considering the low concentrations of precious metals especially in highly interfering matrix of geological samples and larger sample volumes for preconcentration, it is expected for PM's to show slow kinetics for sorption. Therefore, it is advantageous to use a column packed with solid extractant. Passing the liquid sample through such a column provides intimate contact with the solid particles, and there are multiple equilibria as the sample passes through the column and comes into contact with fresh solid extractant particles. In this mode the completeness of extraction will depend on the number of separate equilibrations with fresh solid extractant in the column as well as the mass distribution ratio [19].

Considering all, we have decided to carry out separation and preconcentration of PM's by DEBT impregnated resin using column process.

3.8 Optimization of Column Parameters for Preconcentration of Gold and Silver Using DEBT Impregnated Resin in Column Process

In the second part of the thesis, we aimed to preconcentrate PM's selectively using DEBT impregnated resin by using column process. For this reason, some critical parameters which are valid for column process such as the type and concentration of eluent, the pH of eluent, the effect of sample and eluent flow rates on the extraction efficiency have been studied for each metal ion. The optimization procedure was carried out by varying a parameter while the others were kept constant. In addition, the breakthrough capacities for each metal have already been obtained.

3.8.1 Effect of DEBT Impregnated onto Different Amounts of Resin and Breakthrough Capacities for Metal Ions

In order to demonstrate the effect of DEBT when impregnated on different amounts of resin, so to plot the breakthrough curves for each metal ion, a series of sorption experiments with three different amounts of resin, namely 0.2, 0.5 and 1.0 g were performed (each of which impregnated with same amount of DEBT; 0.1 mmol). Besides detection limits of the instrument, breakthrough capacities which are derived from breakthrough curves are also important to decide about the amount of metals to be studied for preconcentration.

From the curves given in Figure 3.11a and 3.11b, it is not possible to calculate breakthrough capacities and to use these columns for preconcentration studies. Even in first loading cycle of 2.5 μg silver ion, only 1.2 μg metal ions could be retained.

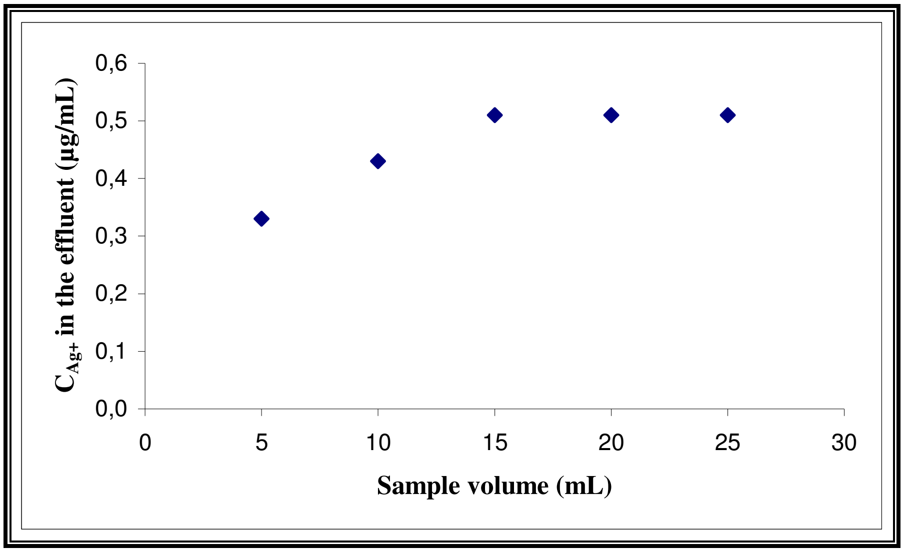


Figure 3.11.a Breakthrough curve of silver.

Amount of resin; 0.2 g. Amount of DEBT; 0.1 mmol, initial silver ion concentration; 0.5 µg/mL.

In case of 0.5 g resin, as observed from Figure 3.11b, loading of 2.5 µg silver ion was retained with first cycle but it almost reached saturation with the following loading cycles.

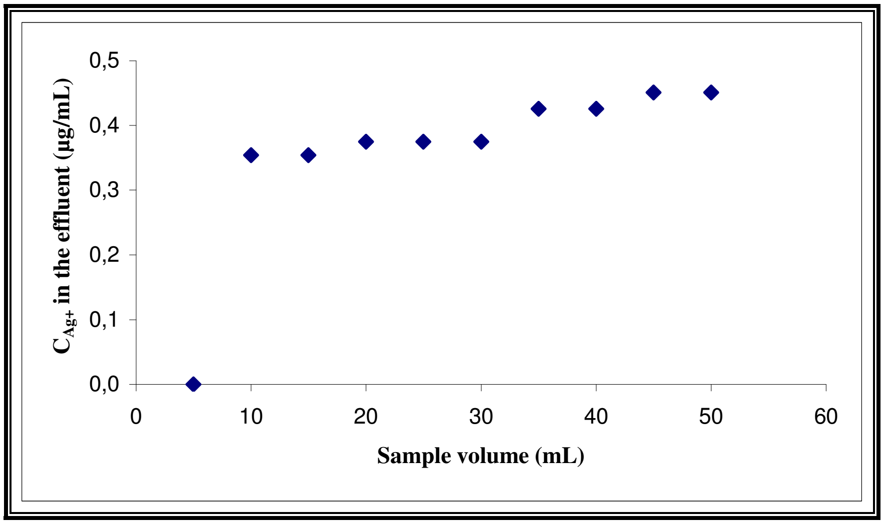


Figure 3.11b Breakthrough curve of silver.

Amount of resin; 0.5 g. Amount of DEBT; 0.1 mmol, initial silver ion concentration; 0.5 µg/mL.

The proper condition, so the best breakthrough curve is obtained by impregnation of 0.1 mmol DEBT on 1.0 g resin as depicted in Figure 3.11c (below). Breakthrough capacity of silver ion is calculated as 32.4µg. Resin was able to retain that much metal ions. After that value it was possible to observe meaningful signals in the effluents which show that resin is going to reach saturation.

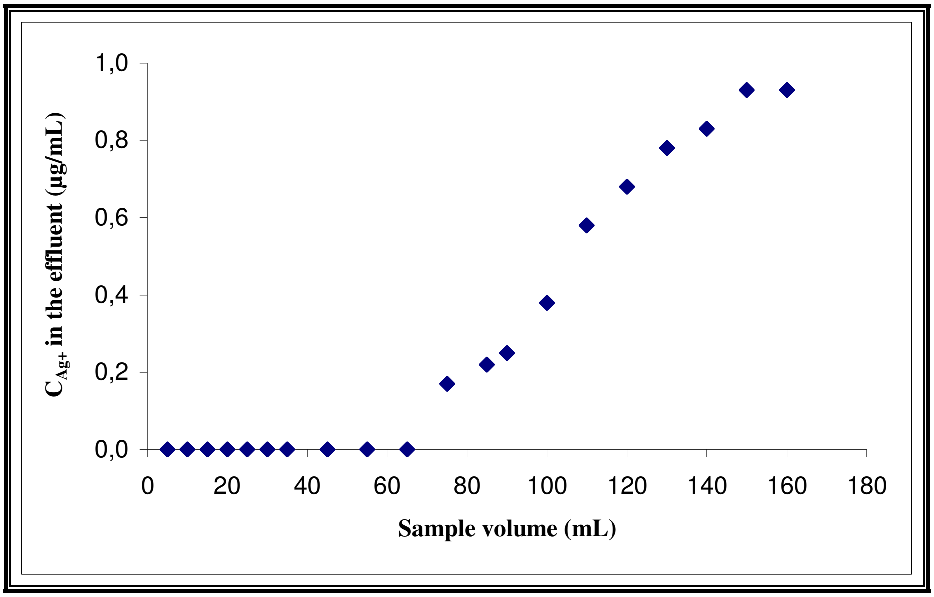


Figure 3.11.c Breakthrough capacity of silver (32.4 µg/g resin).

Amount of resin; 1.0 g. Amount of DEBT; 0.1mmol/g resin, initial Ag^+ concentrations; 0.5 µg/mL for the first 65 mL and 1 µg/mL for the next 95 mL of the sample solution.

Since we obtain better results with 1.0 g resin with a ligand amount of 0.1mmol DEBT during silver studies, we used the same amount of DEBT and resin for gold studies. As shown in Figure 3.11d, up to 94 µg gold ions were retained completely on resin. After that point, we obtained a detectable signal in the effluents which implied that resin was going to reach saturation.

Considering the capacities we obtained for each metal, we decided to study with 5 µg of silver and 15 µg of gold in the further experiments.

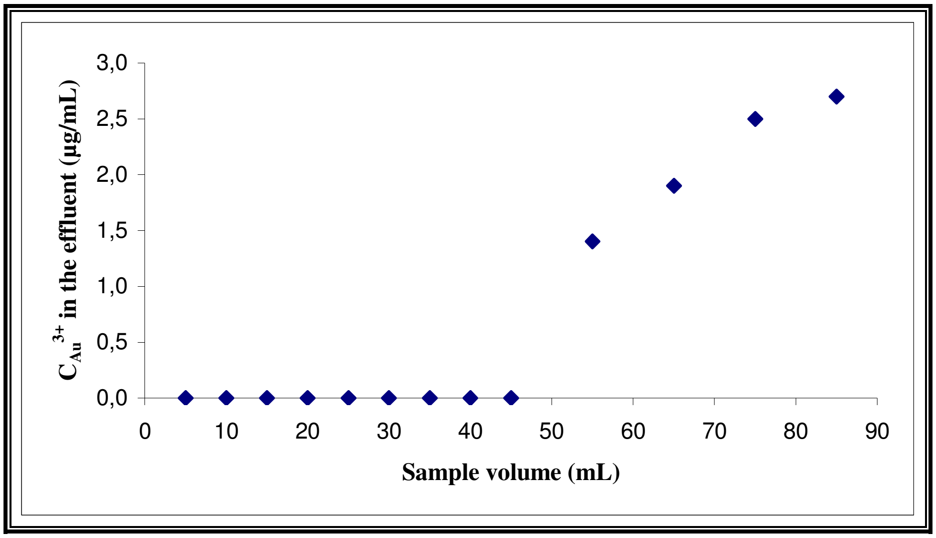


Figure 3.11.d Breakthrough capacity of gold (94.04 µg/g resin).

Amount of resin; 1g. Amount of DEBT; 0.1mmol, initial Au^{3+} concentrations; 1.5 µg/mL for the first 25 mL and 3 µg/mL for the next 60 mL of the sample solution.

3.8.2 Effect of pH on Sorption

In batch studies, it was observed that maximum silver ion sorption on DEBT impregnated resin was achieved when standard solutions were prepared in 0.05 M HNO_3. Therefore, another pH study for silver ion sorption was not repeated in case of column process. All the sample solutions for silver were prepared in 0.05 M HNO_3 during column studies.

In case of gold similarly, during studies on column, pH we kept constant at the optimized value given in Section 3.6.1. Accordingly, all gold solutions were prepared in 1 M HCl.

3.8.3 Effect of Sample Flow Rate

For low analyte concentrations, low kinetics is expected. For this purpose, percent sorption of (10 mL of 0.5 mg/L) silver ion on the sorbent surface was examined at different sample solution flow rates such as 2 mL/min, 1.5 mL/min and 1 mL/min. As indicated in Table 3.5, at flow rates greater than 1 mL/min, decreasing in percent sorption was observed. This may be due to the insufficient equilibration of sample ion with the sorbent. For further studies, considering application of larger volume of sample solutions for preconcentration, to be on safe 0.5 mL/min was accepted as optimum sample flow rate.

Table 3.5 Effect of sample solution flow rate on Ag^+ sorption.

Flow rate (mL/min)	**% Ag^+ sorption**
1.0	98
1.5	93
2.0	70

1.0 g resin; 0.1 mmol DEBT/g resin

3.8.4 Choice of Eluent

In batch studies, thiourea seemed to be a good eluent for silver ions. However, in the study of deposition of silver by immobilized DDTC on surfactant-coated alumina and its determination, S. Dadfarnia et. al. suggested that interference effect of copper during silver determination could be removed by the addition of thiourea at a concentration of twice the concentration of copper [56]. Considering that real sample is supplied from copper ore, we may suffer from serious interference effect of copper. More details are given during interference studies.

Taking this into account, we surveyed the literature to find the most suitable eluent for desorbing silver ions. A. Safavi et al. used a series of selected eluent solutions such as sodium acetate, ammonia, sodium thiocyanate, sodium cyanide, sodium thiosulfate and thiourea in order to desorb silver ions from 2-mercaptobenzothiazole-silica gel [8]. Percent recoveries of silver ions are given in Figure 3.12.

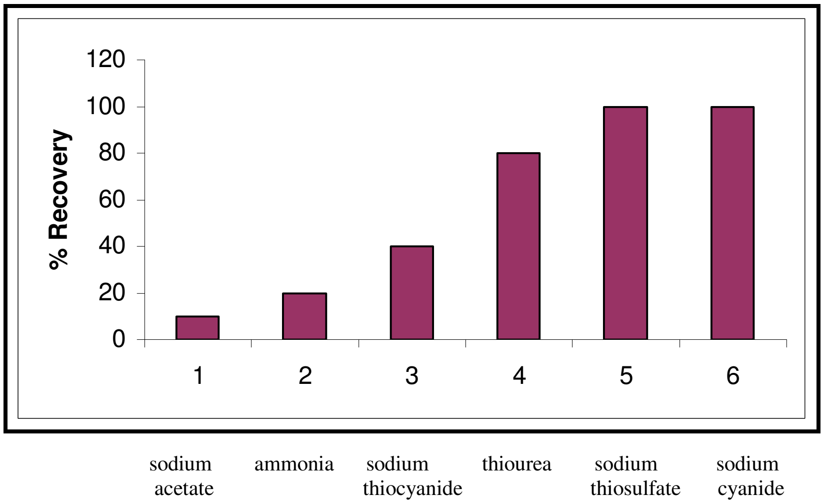


Figure 3.12 Effect of nature of eluent on percent recovery of silver ion [8]

It can be seen that sodium thiosulfate or sodium cyanide solution gives the best recovery under optimized conditions better than thiourea. It was indicated that sodium thiosulfate was less toxic and it also showed better selectivity compared to sodium cyanide for desorption of silver ion in the presence of foreign ions [8].

In addition, we already mentioned that sorption of silver ions was governed by chelation mechanism that is silver ions (belong to class of soft acids) have affinity for (S-O) chelating group of DEBT. During desorption, (S-S) chelating groups of $Na_2S_2O_3$ provides a stronger complex formation as silver has a higher affinity for (S-S) than (S-O) chelating group.

Since selective preconcentration of PM's cannot be carried out only with selective retention of metals but also it should be followed with a selective eluent, we decided to use sodium thiosulfate as eluent in further experiments.

3.8.5 Nature of Eluent, Concentration and Effect of Eluent Flow Rate

It is mentioned that when sodium thiosulfate is added to strongly acidic medium, a cloudiness develops almost immediately as a consequence of elemental sulfur [43]. It is also known that silver precipitates as silver hydroxide when pH>7.5 [56].

Considering all we decided to prepare sodium thiosulfate solutions in water and accordingly to optimize its concentration, flow rate and volume.

It is well known that the flow rates of eluent are generally lower than the flow rates of sample solutions. Considering this, flow rate range from 1.0 mL/min to 0.3 mL/min was surveyed. 10 mL of 0.5 µg/mL Ag^+ standard solutions in 0.05 M HNO_3 were previously passed through the columns at 0.5 mL/min. 5 mL of 0.1M $Na_2S_2O_3$ in water was passed in two portions at flow rates of 1.0 mL/min to 0.3 mL/min. The maximum percent desorption was achieved with sum of 10 mL of eluent at 0.3 mL/min. Higher percent desorption could not be further increased although different eluent volumes were tried.

Table 3.6 Effect of flow rate on desorption.

Flow Rate (mL/min)	**% Ag^+ Desorption**
0.3	84
0.5	79
1.0	70

Sample solution; 10 mL of 0.5 µg/mL, flow rate; 0.5 mL/min.
Eluent volume; 10 mL.

In order to check if higher percent desorption was not achieved because of the inadequate concentration of 0.1M $Na_2S_2O_3$ in water, 5 mL of 3 µg/mL Ag^+ standard solution was similarly passed through the column, 80 % desorption (~ 12µg metal) could be achieved with 10 mL of 0.1M $Na_2S_2O_3$ in water at 0.3 mL/min. Here also, further percent desorption could not be achieved. This implied that although 0.1M $Na_2S_2O_3$ in water was strong enough to desorb up to 12µg silver ions under optimized conditions, it could only desorb ~ 4 µg of 5µg silver ions, initially loaded. As a result, the eluent concentration was sufficient to remove 5µg silver ions if desorption could have been 100%.

When sample volume was increased to 50 mL, no satisfactory results were obtained with 10 mL of 0.1M $Na_2S_2O_3$ in water at 0.3 mL/min. This was most probably because the silver ion concentration was beyond the limit of quantitation.

3.9 Stability of Impregnated Resin During Preconcentration

During the application of the proposed method for preconcentration, it was realized that excess volume of sample solutions during sorption leaches the impregnated DEBT together with analyte losses occurred. This resulted in poor desorption percentages and limited sample volume hence very low preconcentration factor and sometimes no preconcentration can be achieved and also this reduced the life time of resin which could be used only for once. Leaching of DEBT may start with procedure given in Section 2.2 for preparation of columns and then leaching of analytes together with DEBT may also happen when 15 mL of blank solution such as 0.05 M HNO_3 for Ag^+ and 1 M HCl for Au^{3+} was passed through the column at a flow rate of 1 mL/min. before sample solution and 15 mL water were passed through the column before eluent. However, the analyte in such blank solutions can not be determined by FAAS because its concentration is under the limit of quantitation for each metal. (See Table 3.11). This leaching process is actually the main drawback of impregnation as impregnation deals with physical interactions between the chelating agent and solid support by either inclusion in the pores of the support material or adhesion process or electrostatic interaction and no chemical bond formation [20].

The leaching process, at the beginning was not significantly obvious during optimization experiments of column for metal sorption because during optimization separate identical columns were used for once. It was not also realized during the determination of breakthrough capacities of each metal. This may be because of low sample volume and relatively higher sample concentrations which reduced the leaching effect of sample solution.

Another serious problem introduced by leaching of impregnated ligand is partial exhaustion of available chelating sites which caused irreproducible results of sorption percentages of metal ions.

As a result, unfortunately further experiments for preconcentration with DEBT impregnated resins could not be carried out.

Since we have obtained optimum pH for sorption of each metal, optimum flow rates of sample solutions and eluent and mass of solid in our previous experiments, we decided to continue experiments preparing metal chelates with addition of DEBT solution to aqueous solution. This time, DEBT-metal chelates in solution will be passed through the column (pure resin).

3.10 Optimization of Sorption of Metal Chelates on Amberlite XAD-16 (non-impregnated resin)

Before the formation of metal chelates and followed with the application of solid phase extraction, it was needed to check some parameters related with DEBT and resin.

3.10.1 Effect of Ligand Solution Volume

In literature, people dealing with similar studies mentioned the importance of applicable maximum volume and ligand solution concentration on analyte sorption [39, 42]. Therefore, before forming metal chelates and their further application for SPE, maximum applicable ligand volume on retention is found. In Figure 3.13, it can be seen maximum amount of DEBT retained on Amberlite XAD-16 was achieved with the first 3 mL of DEBT solution. Following additions of 3 mL of 3.75×10^{-4} M DEBT solution showed a decrease in amount of DEBT retained on resin. This may be because of the leaching effect of ethanol on DEBT retained.

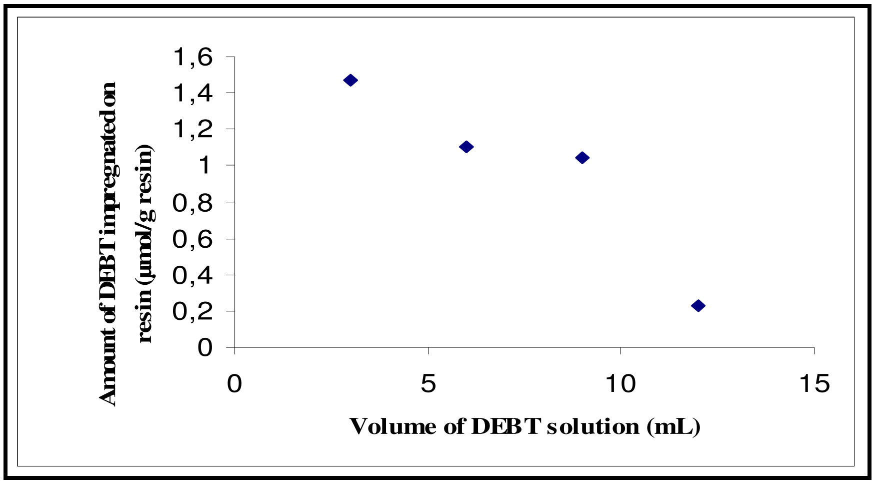


Figure 3.13 Effect of ligand volume on impregnation.

Initial DEBT concentration; 3.75×10^{-4} M.

3.10.2 Effect of Flow Rate on Retention of DEBT

In further sections, it will be mentioned that metal chelate solutions are prepared always in the presence of excess DEBT and that flow rate of metal chelates solutions is accepted as 0.5 mL/min which was previously optimized (see Section 3.8.3). For a selective preconcentration application in real samples, excess DEBT is also required to be retained on resin. When 3 mL of 3.75×10^{-4} M DEBT solution were passed through the columns at flow rates from 0.3 mL/min to 2.5 mL/min, it was observed that retention of DEBT was almost the same. The range of the flow rates is observed to be compatible with the flow rate of sample solution for excess DEBT to be retained on resin quantitatively.

3.10.3 Effect of Ligand Concentration on Its Retention

As it is given in Table 3.7, as the concentration of DEBT increases, higher percent retention of DEBT is achieved.

Table 3.7 Effect of ligand concentration on its impregnation.

Initial DEBT concentration [M]	$1.3x10^{-4}$	$2.4x10^{-4}$	$3.7x10^{-4}$
% DEBT impregnated on resin	75	81	85

Mass of resin ; 0.5 g, volume of DEBT solution; 3 mL.

Ligand concentration is also important because if it is not excessively present, metal ions may not be selectively retained on resin. However, excess DEBT (in case of inadequate amount of resin) may prevent retention of metal chelates because of the competition for sorption on resin between excess DEBT and metal chelates.

Considering the further applications of the proposed method to a real sample and limitations related with ligand mentioned above, it was decided to use again 1.0 g of resin, and amount of DEBT as 3 mL of $2x10^{-3}$M. This amount of DEBT is always in excess considering the amounts of analyte metals that are studied (5 µg for Ag and 15 µg for Au) (see Table 3.8).

3.10.4 Flow Rate of Metal Chelate Solutions

Sample flow rate that was optimized in Section 3.8.3 kept constant as 0.5 mL/min. This flow rate is actually compatible with the optimum range of flow rate for DEBT in Section 3.10.2.

During batch studies, we concluded that DEBT showed similar kinetics on chelation with silver and gold as long as DEBT concentration is kept the same or close and/or optimum pH for sorption is maintained. Since we decided to use the same ligand concentration which was in excess compared to amount of analyte metals and the same sorption media at the previously optimized pH (see Sections 3.5.1 and 3.6.1), the optimum sample flow rate as 0.5 mL/min for gold sorption was also accepted.

3.10.5 Effect of Optimized Ligand Concentration on Amount of Metal Chelates

It is mentioned that DEBT concentration should be in excess considering the stoichiometric ratios of DEBT and metal ions. We wanted to confirm this and find out the maximum amount of metal ions that can form metal chelates with 3 mL of 2×10^{-3} M DEBT safely. As it is indicated in Table 3.8, up to 100 μg silver ions and 100 μg gold ions can be safely retained on 1.0 g of resin as metal chelates. When 10 mL of 50 μg/mL metal chelate solutions were passed through the columns, some metal ions in the effluents could be determined thus a decrease in percent retention was observed; 75 % and 94 % for silver and gold respectively. Accordingly, 370 μg silver ions and 470 μg gold ions were retained on columns, each 1.0 g resin.

During this study, we studied with quite low amounts of metal ions and carried out the optimizations accordingly. However, results in Table 3.8 indicate that with higher amounts of metals up to 100 μg silver and gold ions, one can study safely under the same conditions (such as amount of resin, sample flow rate, pH of sorption media and ligand volume) as long as the concentration of eluent and its volume are reoptimized.

Table 3.8 Effect of ligand concentration of retention of metal chelates.

Amount of DEBT	**Amount of Ag^+ in sample solution (µg)**	**% sorption of silver chelates on resin**	**Amount of Au^{3+} in sample solution (µg)**	**% sorption of gold chelates* on resin**
3mL of $2x10^{-3}$ M	5	100	15	100
3mL of $2x10^{-3}$ M	100	100	100	100
3mL of $2x10^{-3}$ M	500	74	500	94

Mass of resin; 1.0 g, sample volume; 10 mL, sample flow rate 0.5 mL /min.

* when 10 mL of 100 µg/mL of gold chelate solution was passed through the column, metal chelates precipitated (yellowish color) both on resin and in effluent.

3.11.1 Optimum Conditions for Preconcentration of Silver

During desorption studies, the nature of eluent, its concentration and its flow rate (0.1 M $Na_2S_2O_3$ in water, 0.3 mL/min respectively) were kept constant. However, in order to find minimum volume required for desorption, further studies on of eluent volume were carried out in two portions. It was found that ≥ 95% desorption could be achieved with 13 mL of 0.1 M $Na_2S_2O_3$ in water at 0.3 mL/min when the sample volume was 10 mL. When sample volumes of 50 mL and 100 mL were passed through the columns, 90 % and 88.1 ± 1.8 % desorption and preconcentration were achieved respectively with 13 mL of 0.1 M $Na_2S_2O_3$ in water at a flow rate of 0.3 mL/min. In Figure 3.14, a summary of optimized method for preconcentration of silver was depicted.

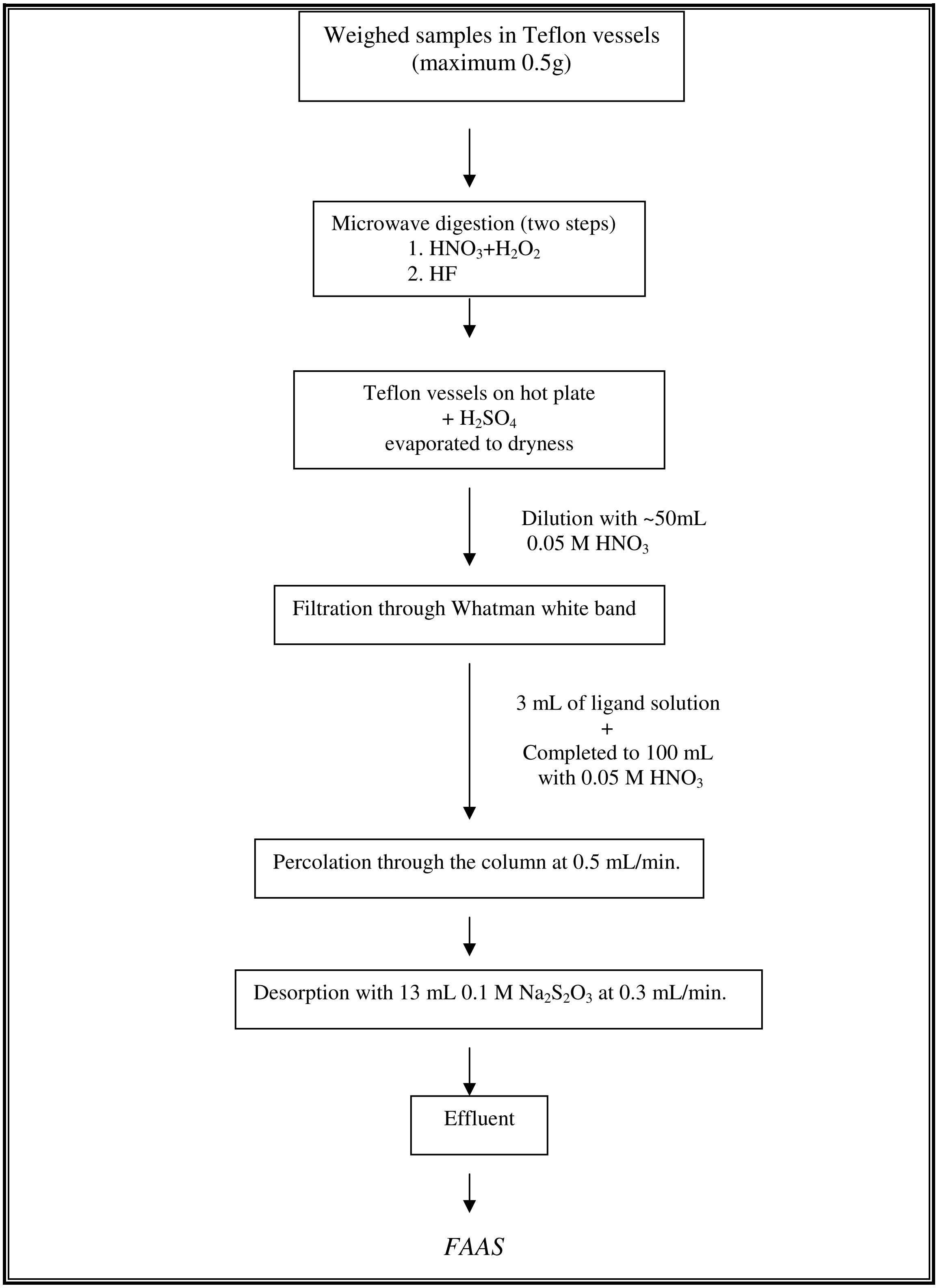


Figure 3.14 Flow chart of preconcentration of silver.

3.11.2 Optimum Conditions for Preconcentration of Gold.

In case of gold, firstly 0.1 M $Na_2S_2O_3$ in water was used as an eluent at flow rate of 0.3 mL/min and only 65% desorption was achieved. Therefore, we decided to increase $Na_2S_2O_3$ amount in water to 0.2 M $Na_2S_2O_3$ in water and we obtain $\geq$ 95% desorption with 15 mL. In case of 25 ml and 100 mL of sample solution, 104 % and 97.6 ± 2.3 % desorptions were achieved respectively.

In Figure 3.15, it is possible to find an overall summary of optimized method for preconcentration of gold.

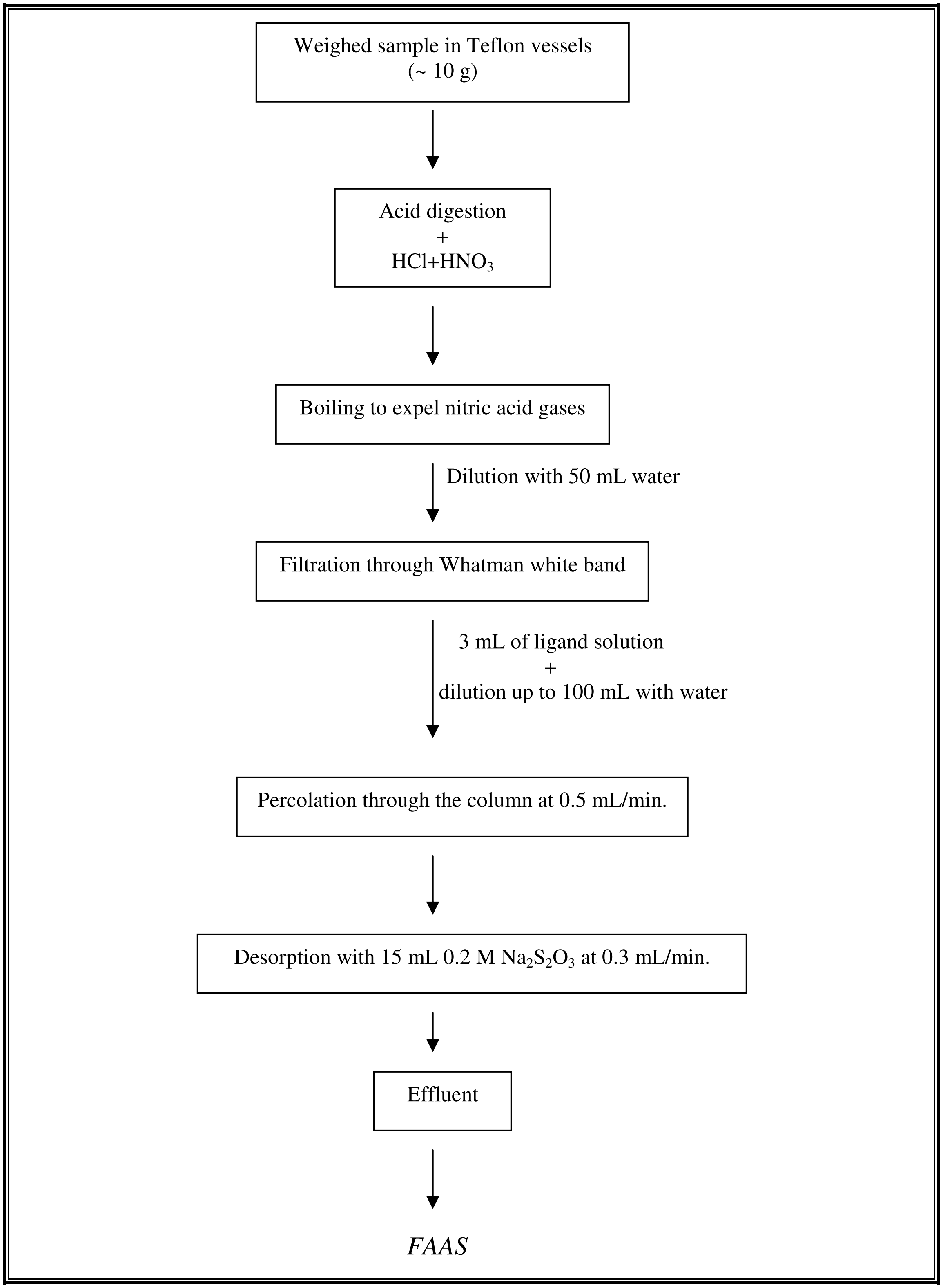


Figure 3.15 Flow chart of preconcentration of gold.

3.12 Interference Studies

In 2003, Schuster et. al. studied selective separation and recovery of heavy metal ions from aqueous solutions using water-soluble N-benzoylthiourea modified PAMAM (polyamidoamine dendrimers) polymers. It was mentioned that N-benzoylthiourea are bidentate chelating ligands with S and O as donor atoms. The low NH-acidity, as well as the possibility of increasing the electron density at the sulfur atoms by means of resonance effect, lead to a selective complexing behavior, which can be influenced by adjustment of the pH of the aqueous solution. Ubiquitous elements such as alkaline and alkaline earth metals as well as Fe (III) or Al (III) are not bound to these ligands. During the study, they observed that mercury strongly bound to the benzoylthiourea modified polyamidoamine dendrimers (BTUPAMAM) and can be retained quantitatively even in strongly acidic media. The release of Hg (II) bound to BTUPAMAM can only be achieved by thiourea solution in dilute HCl. [57].

In 2002, Zhang et al. carried out synthesis of amidinothioureido-silica gel and studied its application by FAAS to determine silver and gold in ore samples. They investigated the effect of the metal ions co-existing with noble metals and the anions Cl^-, NO^-, SO_4^{2-}, PO_4^{3-} and ClO_4^-, which may be present in sample solutions. They mentioned that 2.0 mg/mL of Ca^{2+}, Mg^{2+}, Cu^{2+}, Fe^{3+}, Al^{3+}, Ni^{2+}, Pb^{2+}, Mn^{2+}, Zn^{2+} and Cr^{3+}, 1.0 mg/mL of Co^{2+} and Cd^{2+} and 20 mg/mL of the anions mentioned above (added as sodium salts) did not interfere with the determination of silver and gold. In addition, they investigated the effect of other noble metal ions and the effects of Ag and Au on each other. They mentioned that 100-fold excesses of other noble metal ions did not interfere with the determination of Ag and Au [7].

In 1997, Tunçeli et. al. studied on determination of gold in geological samples by FAAS after preconcentration with Amberlite XAD-16. They investigated the effect of some accompanying elements such as Na, Fe, Ni and Cu on determination of gold.

They observed that the recovery of gold did not decrease when the matrix elements were studied individually. Even 5000-fold excess of iron over gold did not interfere; the recovery of gold was almost constant. However, when the matrix elements were used altogether, the recovery of gold decreased by about 22.5%. The reason for decrease was attributed to the insufficient column capacity [36].

In 2000, Tunçeli et. al. studied on determination of silver in tin base alloys by FAAS after preconcentration with Amberlite XAD-16. Investigated matrix elements were Cu, Ni, Fe, Na, K, Mg and Ca at 1000-fold excess of silver ions. They observed that silver signal was increased by ≤ 8% [38].

In Table 3.9, a summary of some metals that are mostly found in geological samples and metals that form chelates with DEBT are given.

Table 3.9 Summary of some metals in geological samples and metals forming chelates with DEBT.

Metal ions co-existing in geological samples	**Main metal ions forming chelate with DEBT [49]**	**pH for metal-DEBT chelates**
Na^+, K^+	***Au^{3+}***	***0-5****
Cu^{2+}, Ni^{2+}	***Ag^+***	***0-4****
Pb^{2+}, Mn^{2+},	Pt^{2+}	1-7
Fe^{3+}, Zn^{2+}	Rh^{3+}	1-5
Al^{3+}, Cr^{3+}	Pd^{2+}	1-7*
	Ru^{3+}	1-3
	Ir^{3+}	2-7
	Cu^{2+}	***0-7****
	Fe^{3+}	*2-4**

* Complexation takes place at room temperature.

According Table 3.9, besides gold and silver, copper is also expected to form chelates with DEBT at our working pH. However, formation of copper chelates is not desired. Since our geological sample is Cu-ore, inevitably copper is always in excess.

In order to observe the interference effect of copper on silver determination by FAAS, standard solutions with Ag/Cu mass ratios of 1:1, 1:10 and 1:50 were prepared in 10 mL of 0.05 M HNO_3. Variations in silver signal were calculated based of the absorbance of pure analyte solution of 0.5 µg/mL Ag^+ in 0.05 M HNO_3.

Table 3.10a Effect of copper on Ag signal.

Copper/silver (m/m)	1	10	50
Variation in Ag Absorbance (%)	- 4	+ 948	+ 1233

Mass of silver ions; 5 µg, sample volume; 10 mL

Number of replicates; N=3

Relative error of less than 5 % was considered to be within the range of experimental error [56]. Referring to Table 3.10a, in the presence of copper ions with 1:1 mass ratio, there is no significant change in silver signal. However, in case of 10-fold and more, copper ions severely increased the analyte signal.

In order observe the interference effect of copper on silver determination by the proposed method, considering the amount of analyte metal that is 5 µg, standard solutions containing only copper in the concentrations of Ag/Cu mass ratios of 1:1, 1:10 and 1:50. According to this, 50 mL of 0.1 µg/mL, 1 µg/mL and 5 µg/mL copper ions solutions in 0.05 M HNO_3 were percolated through the columns at a flow rate of

0.5 mL/min. Desorption was followed with 13 mL of 0.1 M $Na_2S_2O_3$ in water at a flow rate of 0.3 mL/min. Results are given in Table 3.10b.

Table 3.10b Interference effect of copper during preconcentration and determination of silver.

Amount of copper in sample solutions (μg)	5	50	250
% desorption of copper ions with 13 mL of 0.1 M $Na_2S_2O_3$ in water	0	0	1.1

Mass of resin; 1 g, amount of DEBT; 3 mL of $2x10^{-3}$M, sample volume; 50 mL.

Although copper ion formed complex with DEBT and retained on the resin, referring to Table 3.10b, it was observed that no copper ions could be eluted with 13 ml of 0.1 M $Na_2S_2O_3$, eluent. When the amount of copper ions was increased to 250 μg, only 1.1 % desorption was obtained which could be accepted as negligible. In addition, after desorption, it was still possible to observe green precipitates of copper-DEBT complexes on the resin.

After all, when the proposed method used for preconcentration and determination of silver in real samples by FAAS (see Section 3.11.1), only the analyte signal was observed which means that there is no copper in the effluent (see Table 3.12a). By this way, completely interference free method is proposed for the determination of silver ions especially in highly interfering matrix such as geological sample.

Considering the sample amount weighed according to gold digestion procedure (at least 10.0 g), so much excess copper may compete with gold for DEBT and it may limit ligand capacity which may result in low % sorption of gold. Therefore, during gold studies, first ligand capacity was tried to be increased. It was observed that when 1-3 mL of 0.2 M DEBT solution was added to 1 M HCl solution, DEBT crystallizes as it was happening during its synthesis (see Section 2.4.). So the ligand concentration was kept constant at 3 mL of 2 x10^{-3} M. However, competition between excess copper ions and gold and silver may result in complex formation mostly with copper and retention of gold ions may be affected. In such cases, it will be inevitable to mask copper and enable complex formation only with gold.

Considering all, 50 mL of 300 µg/mL of copper standard solution was prepared in 1 M HCl. Initial metal ion concentration was determined by FAAS. Then the solution was percolated through the column at a flow rate 0.5 mL/min. The metal ion concentration in the effluent was determined by FAAS. Initial metal ion concentration was found to be 292 µg/mL and the metal ion concentration in the effluent was found as 288 µg/mL. As a result, only 1.37 % of copper ions were adsorbed on resin. Although it is known that copper ion forms complexes with DEBT in pH range of 0-7, this result showed it does not form complexes with DEBT in 1 M HCl medium.

After all, with the proposed method, we successfully obtained the analyte signal suggesting an interference free media for the preconcentration and determination of gold in geological samples (see Table 3.12b).

We did not study interference effects of gold and silver on each other. Although they are found to be together, considering their low concentrations in Cu ore samples, there will not be significant amount of either Au or Ag that would compete for ligand in the medium.

The amount of gold weighed according to its digestion procedure is considerably large. Therefore, it may be thought that silver ions would be present in that much ratio. For gold studies, we are preparing 1 M HCl solution for sorption medium. Referring to Figure 3.16 depicted in literature, it is possible to say that formation of unextractable silver chloro complexes accounts for silver's negligible extraction at high hydrochloric acid concentrations.

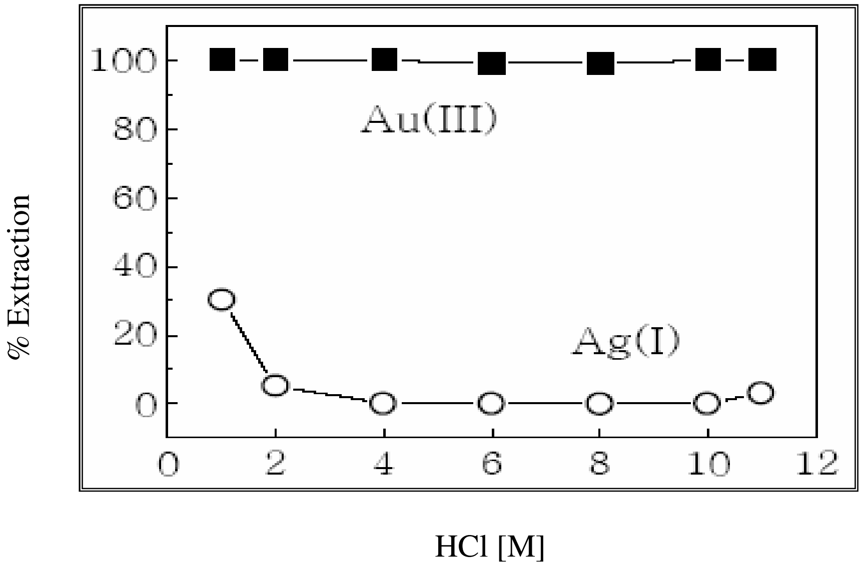


Figure 3.16 Effect of hydrochloric acid on the extraction of gold (III) ■ and silver (I) o by 0.05 mol/dm^3 18-crown-6 (18C6) oxonium cation in 1,2-dichloroethane [58].

According to digestion procedure applied for silver containing samples (see Section 2.12.1) maximum applicable sample is only 0.5 g. Since very small amounts of sample are taken, the amount of gold will not be at interfering level.

3.13 Analytical Figures of Merit

The detection limit and limit of quantitation for Ag and Au ions were determined employing the standard solutions giving absorbance signal slightly recognizable than blank (0.05 M nitric acid and 1 M HCl for Ag and Au respectively, in appropriate concentration). The limit of detection is calculated based on 3s/slope of 10 measurements of the blank, where s is the standard deviation of the sample solution. The limit of quantitation was calculated based on 10s/slope of 10 measurements of the sample. The results of the LOD, LOQ and precision (RSD %) for each metal and in addition, the concentrations of the metals which can be determined after preconcentration by the proposed method together with preconcentration factors are given in Table 3.11.

Table 3.11 Analytical figures of merit.

Parameters	Silver	Gold
Sample volume	100 mL	100 mL
Concentration of solution	0.30mg/L	0.75mg/L
Detection limit (3s)	0.04 mg/L	0.17 mg/L
Limit of quantitation	0.13 mg/L	0.57 mg/L
Precision (RSD %)	4.44 %	7.56 %
Number of replicates (N)	10	10
Concentration of solution preconcentrated by the proposed method	0.05 mg/L	0.15 mg/L
Preconcentration factor	7.7	6.7

3.14 Application to the Analysis of Real Samples

In order to demonstrate the accuracy of the proposed method, it was applied for the analysis of two real samples; one of which was supplied by MTA and the other one was supplied from CMC Cu-ore (see Table 3.12a and 3.12b) and a Gold Ore (MA-1b) as a standard reference material.

Calibration plots given in Figure 3.17 and 3.18 are used during the determination of silver and gold in real samples by FAAS.

In Table 3.13 and 3.14, it is possible to find approximate chemical compositions of residue pile Cu-ore supplied from CMC and Gold Ore (MA-1b).

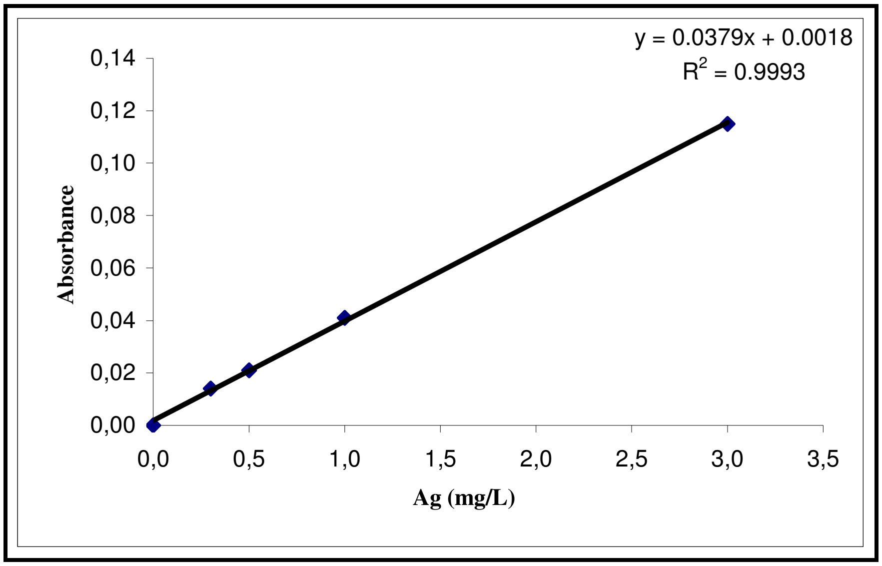


Figure 3.17 Calibration graph for determination of silver by FAAS during real sample applications. (All standard solutions were prepared in 100 mL of 0.1 M $Na_2S_2O_3$ in water).

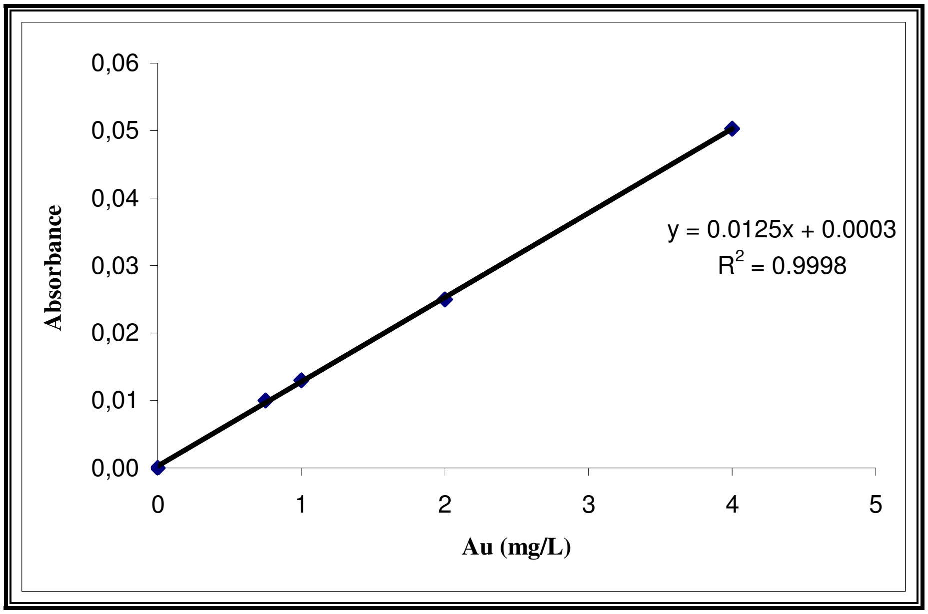


Figure 3.18 Calibration graph for determination of gold by FAAS during real sample applications (All standard solutions were prepared in 100 mL of 0.2 M $Na_2S_2O_3$ in water).

Table 3.12a Determination of Ag in geological samples.

Samples	**Ag Concentration (mg/kg)**	**Corrected values according to 88% desorption**
MTA sample		
Ag (found)* N	29.7 ± 2.5	33.7 ± 2.5
Ag (given)	37.5	37.5
CMC sample		
Ag (found)* N	17.9 ± 1.0	20.4 ± 1.0
Ag (given)	24	24

* Values are given as mean ± standard deviation (SD)

N= 3 (number of replicates).

When we look at the Table 3.12a, corrected values according to 88 % desorption (see Section 2.10.1) are in good agreement with the given values.

Table 3.12b Determination of Au in CMC ore and Gold Ore (MA-1b) samples.

Samples	Au Concentration (mg/kg)	Corrected values according to 97 % desorption
CMC sample		
Au (found) * N	0.48 ± 0.06	0.49 ± 0.06
Au (given)	1.34	1.34
Au (spiked found) * N	13.64 ± 0.62	14.06 ± 0.62
Au (spiked)	15	15
Gold Ore (MA-1b)		
Au (found) * N	14.95 ± 0.99	15.41 ± 0.99
Au (certified value)	17.0 ± 0.3	17.0 ± 0.3

* Values are given as mean ± SD

N= 3 (number of replicates)

The corrected value, 0.49 ± 0.06 according to 97 % (see Section 2.10.2) was not in good agreement with the given value. This is because the concentration of gold in the Cu-ore sample was below the limit of quantitation so the results may not be reliable. The value found for the spiked sample was in good agreement with the spiked amount.

In case of Gold Ore (MA-1b); standard reference material, although it is suggested to study with 10.0 g of sample (because of the hetereogenous distribution of gold in geological samples) to obtain correct data, we studied with 1.0 g of the sample. The certified value of Gold Ore (MA-1b) is given as 17.0 ± 0.3 mg/kg and the use of 10.0 g of the sample could exceed the resin capacity causing poorer results. Since the found value was in good agreement with the certified value, 1.0 g of sample was sufficient to study with SRMs.

Table 3.13 Approximate chemical composition of residue pile supplied by CMC*.

Constituent	mg/kg
Cu	970.80
Pb	692.30
Zn	991.00
Ni	2.00
Co	9.00
Mo	58.60
V	61.00
Au	1.34
Ag	24.00
Pt	0.02

* From the report prepared for Doba Investments LTD.

Table 3.14 Approximate chemical composition of Gold Ore (MA-1b) *

Constituent	wt %	Constituent	mg/kg
Si	24.5	Cr	200
Al	6.11	Pb	200
Fe (total)	4.62	Rb	160
Ca	4.60	Zr	140
K	4.45	Cu	100
Mg	2.56	Zn	100
C (total)	2.44	Bi	100
Na	1.49	Ni	90
S (total)	1.17	Mo	80
Ti	0.38	Te	40
Ba	0.18	Co	30
P	0.16	Y	20
Mn	0.09	W	15
H_2O	0.1	Sc	13
		As	8
		Ag	3.9
		Sb	3

* MA-1b Gold Ore (Certified Reference Materials at Canmet-MMSL).
MA-1b was prepared from mill feed from Lac Minerals Limited,
Macassa Division, Kirkland Lake, Ontario.

3.15 Future Work

In this study, high selectivity of DEBT for gold and silver has been shown with the results obtained, so it can be concluded that use of DEBT as ligand was a good choice. But in order to investigate the sorption behaviour of impregnated resin, a lot of work has been carried out. If the atomic absorption spectrometer could be solely devoted for this work so, the system could be constructed as an on-line system, experiments could be carried out continuously. By this way, higher breakthrough capacities using less amounts of resin and improved detection limits are expected to be achieved.

Also as it is stated in the discussion, more reproducible results could be obtained if Amberlite XAD-16 modified chemically with DEBT had been used instead of DEBT impregnated resin.

CHAPTER 4

CONCLUSION

In this study, although the aim was to separate and preconcentrate two of the precious metals; gold and silver using DEBT impregnated resin, no satisfactory results could be obtained. The resin selected which is a hydrophobic, nonionic resin and has a large surface area is expected to have large capacity for the ligand (DEBT), so for the metal ions. Besides these favorable properties of the resin, the selected ligand DEBT is well known for being a highly selective chelating agent for precious metals. Combining these two features, it is expected to develop a successful preconcentration method for the determination of PM's.

The expectations were realized in batch process which was the first step of this study performed to investigate the sorption behavior of DEBT impregnated resin with Ag (I) and Au (III) in highly acidic medium. However, during optimizations of impregnated resins for preconcentration in column process, partial leaching of DEBT and sometimes together with analyte made the method not applicable for preconcentration. In addition, leaching of impregnated ligand resulted in partial exhaustion of available chelating sites which caused irreproducible results of sorption of metal ions.

However, we succeeded in preconcentration of PM's by first forming metal chelates and then applying to SPE. The proposed method provided high selectivity for PM's during preconcentration. The addition of excess DEBT to aqueous media could allow chelation with the metals that might form chelates with DEBT only at our working pH. In the absence of DEBT, some metal ions that would be able to retain on adsorbent resin as their chloro complexes were not sorbed. Sorption of precious metal chelates and excess DEBT on resin most probably prevented or reduced the sorption of other interfering metals seriously. By this way, gold and silver have been selectively separated from highly interfering matrices namely geological samples.

In order to demonstrate the accuracy of the proposed method, two geological samples (one supplied from MTA and the other from CMC Cu-ore) and Gold Ore (MA-1b) as a standard reference material were analyzed. The results are in good agreement with the given values.

Comparisons of the proposed method with some similar studies in literature are given in Table 4.1a and 4.1b. By the proposed method; we can determine PM's by preconcentration of lower concentrations such as 0.15 μg/mL for gold and 0.05 μg/mL for silver compared to similar studies. Therefore, this method appears to be more sensitive and in addition, it is highly selective for gold and silver considering the highly interfering matrix of geological samples.

Table 4.1.a Comparison of this study with other similar studies in literature* for gold

Amount of gold studied (μg)	Concentration of sample solution (μg/mL)	Interfering metal(s)	Preconcentration factor	LOD (μg/mL)	Determination method	Ref.
25	0.25	None**	10	0.046	FAAS	36
5	0.2	Pb^{2+}, AsO^{3-}_4	3.1	0.032	FAAS	39
15	0.15	None	6.7	0.17	FAAS	This Study

* Matrix; geological samples.

** When individually studied, no metals interfered but when all used, gold recovery decreased due to insufficient column capacity.

Table 4.1.b Comparison of this study with other similar studies in literature* for silver.

Amount of silver studied (µg)	Concentration of sample solution (µg/mL)	Interfering metal(s)	Preconcentration factor	LOD (µg/mL)	Determination method	Ref.
25	0.25	Cu^{2+} , Fe^{3+}	10	0.047	FAAS	38
5	0.05	None	7.7	0.04	FAAS	This Study

* Matrix; geological samples.

In literature, it is possible to find more sensitive determination methods for PM's such as ICP-MS, NAA etc. However, low cost and rapidness of FAAS make it available in most of the routine and research laboratories. As a result, our proposed method is inexpensive, easily applied and can be widely applicable in most of the laboratories.

As a final conclusion a suggestion can be made. It is mentioned that mass of pile of CMC Cu-ore is approximately 300.000 tones. We also know that it is highly rich in Cu content. In addition, according to our results, we confirmed the presence of silver and gold. However, the ore has not been run for 31 years. If the residue pile were to be processed, it would probably have some economical value and its income may be small but can be a contribution to TRNC's budget as a newly developing country.

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