

**DOKUZ EYLUL UNIVERSITY GRADUATE SCHOOL OF
NATURAL AND APPLIED SCIENCES**

**SORPTION OF URANIUM USING SILICA GEL
IMPREGNATED WITH
BENZOYLTHIOUREA DERIVATIVES**

by

Sinem AYDINCI

January, 2010

İZMİR

**SORPTION OF URANIUM USING SILICA GEL
IMPREGNATED WITH
BENZOYLTHIOUREA DERIVATIVES**

**A Thesis Submitted to the
Graduate School of Natural and Applied Sciences of
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In Partial Fulfillment of
the Requirements for the Degree of Master of Science
in Chemistry**

**by
Sinem AYDINCI**

**January, 2010
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M. Sc. THESIS EXAMINATION RESULT FORM

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ABSTRACT

Benzoylthiourea derivatives (N,N-diphenyl-N-(3-methylbenzoyl)thiourea and diphenyl-N-(4-methylbenzoyl)thiourea) were impregnated onto silica gel. The preconcentration of uranium(VI) from aqueous solution was investigated. Extraction conditions were optimized in batch method prior to determination by uv-visible absorption spectrometry. The optimum pH for quantitative adsorption is 3- 7. Quantitative recovery of uranium (VI) was achieved by stripping with 0.1 molar HCl. The effects of sorption time was studied. The contact time was studied in the range of 5 to 120 min. Equilibration time was determined as 30 min for 99% sorption of U(VI). The effects of common electrolytes and diverse ions on the recovery of U(VI) was studied. Under optimal conditions, dynamic linear range of for U (VI) was found as 0.25–10 ppm.

Keywords: Benzoylthiourea, Solid Phase Extraction, Uranium, Preconcentration.

BENZOİLTİYOÜRE TÜREVLİ SİLİKA JELLE URANYUM TUTUNMASI

ÖZ

Benzoiltiyöüre türevlerinin (N,N-difenil-N-(3-metilbenzoil) tiyöüre ve difenil-N-(4-metilbenzoil)tiyöüre) silikajele emdirilmesi ile sorbentler hazırlandı. U(VI)'nın hazırlanan bu sorbentler ile önderiştirilmesi incelendi. UV-görünür absorbsiyon spektrometresi ile tayin öncesi özütleme şartları kesikli özütleme yöntemi kullanılarak optimize edildi. Nicel adsorpsiyon için optimum pH aralığı 3 ile 7 arasında belirlenmiştir. Uranium (VI)'nın nicel geri kazanımı 0.1 molar HCl ile sıyırma yapılarak sağlanmıştır. Uranyumun tutulma zamanı 5 ila 120 dakika zaman aralığında çalışıldı. Uranyumum %99 tutunması için denge zamanı 30 dakika olarak belirlendi. Uranyumum geri kazanımında elektrolitlerin ve çeşitli iyonların etkisi incelendi.. Optimum çalışma şartları altında U(VI) için dinamik doğrusal çalışma aralığı 0.25–10 ppm olarak belirlenmiştir.

Anahtar Kelimeler: Benzoiltiyöüre, Katı Faz Özütleme, Uranyum, Önderiştirme

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CHAPTER ONE

INTRODUCTION

Uranium is a hard, dense, malleable, ductile, silver-white, radioactive metal. Uranium metal has very high density. When finely divided, it can react with cold water. In air it is coated by uranium oxide, tarnishing rapidly. It is attacked by steam and acids. Uranium can form solid solutions and intermetallic compounds with many of the metals (Zoellner, 2009).

1.1 Uranium Properties

Uranium is a radioactive element that occurs naturally in low concentrations (a few parts per million) in soil, rock, and surface and groundwater. It is the heaviest naturally occurring element, with an atomic number of 92. Uranium in its pure form is a silver-colored heavy metal that is nearly twice as dense as lead and is pyrophoric when finely divided.

Uranium exhibits three crystallographic modifications as follows: alpha -- (688°C)→ beta --(776°C)→ gamma. It is a little softer than steel, and is attacked by cold water in a finely divided state. It is a slightly paramagnetic. In air, the metal becomes coated with a layer of oxide. Acids dissolve the metal, but it is unaffected by alkalis.

Table 1.1 Properties of uranium

Atomic number	92
Atomic mass	238.03 g.mol ⁻¹
Electronegativity according to Pauling	1.7
Density	18.95 g.cm ⁻³ at 20°C
Melting point	1132 °C
Boiling point	3818 °C
Vanderwaals radius	0.121 nm
Ionic radius	nm (+3) nm 0.103 0.093 (+4)
Isotopes	16
Electronic shell	[Rn] 5f ³ 6d ¹ 7s ²

1.2 The History of Uranium

The name derives from the planet Uranus, which in Roman mythology was "Father Heaven". Uranium was found to be first used in yellow-colored glass, which contained more than 1% uranium oxide, dating back to 79 A.D. found near Naples, Italy. The metal was first isolated in 1841 by the French Chemist Eugene-Melchior Peligot, who reduced the anhydrous chloride with potassium. The German Chemist Martin Heinrich Klaproth discovered the element in 1789 when he recognized an unknown element in the mineral pitchblende, following the German/English astronomer William Hershel's discovery of the planet in 1781.

Uranium was apparently formed in super novae about 6.6 billion years ago, a decay product of elements with higher atomic weight, which may have once been present on Earth or elsewhere in the universe. It occurs in most rocks in concentrations of 2 to 4 parts per million, and in much lower concentrations in seawater. Its radioactive decay provides the main source of heat inside the Earth, causing convection and continental drift.

1.3 Uranium Resources

Uranium, not as rare as once thought, is now considered to be more plentiful than mercury, antimony, silver, or cadmium, and is about as abundant as molybdenum or arsenic. It occurs in numerous minerals such as pitchblende, uraninite, carnotite, autunite, uranophane, and tobernite. It is also found in phosphate rock, lignite, monazite sands, and can be recovered commercially from these sources.

The United States Department of Energy purchases uranium in the form of acceptable triuranium octaoxide (U_3O_8) concentrates. This incentive program has greatly increased the known uranium reserves. Uranium can be prepared by reducing uranium halides with alkali or alkaline earth metals or by reducing uranium oxides by calcium, aluminum, or carbon at high temperatures. The metal can also be produced by electrolysis of KUF_5 or uranium tetrafluoride (UF_4), dissolved in a molten mixture of calcium chloride ($CaCl_2$) and sodium chloride ($NaCl$). High-purity uranium can be prepared by the thermal decomposition of uranium halides on a hot filament.

1.4 Uses of Uranium

Uranium is of great importance as a nuclear fuel. Uranium-238 (^{238}U) can be converted into fissionable plutonium by the following reactions:

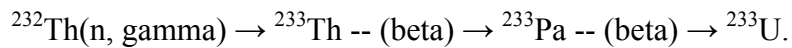


This nuclear conversion can be brought about in breeder reactors where it is possible to produce more new fissionable material than the fissionable material used in maintaining the chain reaction.

Uranium-235 (^{235}U) is of even greater importance because it is the key to utilizing uranium. ^{235}U , while occurring in natural uranium to the extent of only 0.71%, is so fissionable with slow neutrons that a self-sustaining fission chain reaction can be

made in a nuclear reactor constructed from natural uranium and a suitable moderator, such as heavy water or graphite, alone.

Uranium-235 can be concentrated by gaseous diffusion and other physical processes, if desired, and used directly as a nuclear fuel, instead of natural uranium, or used as an explosive. Natural uranium, slightly enriched with ^{235}U by a small percentage, is used to fuel nuclear power reactors to generate electricity. Natural thorium can be irradiated with neutrons as follows to produce the important isotope ^{233}U :



While thorium itself is not fissionable, ^{233}U is, and in this way may be used as a nuclear fuel. One pound of completely fissioned uranium has the fuel value of over 1500 tons of coal.

The uses of nuclear fuels to generate electrical power, to make isotopes for peaceful purposes, and to make explosives are well known. The estimated worldwide capacity of the 429 nuclear power reactors in operation in January 1990 amounted to about 311,000 megawatts. Uranium in the U. S. is controlled by the U. S. Nuclear Regulatory Commission. New uses are being found for depleted uranium, i.e., uranium with the percentage of ^{235}U lowered to about 0.2%.

Uranium is used in inertial guidance devices, in gyro compasses, as counterweights for aircraft control surfaces, as ballast for missile reentry vehicles, and as a shielding material. Uranium metal is used for X-ray targets for production of high-energy X-rays; the nitrate has been used as a photographic toner, and the acetate is used in analytical chemistry.

Crystals of uranium nitrate are triboluminescent. Uranium salts have also been used for producing yellow "vaseline" glass and glazes. Uranium and its compounds

are highly toxic, both from a chemical and radiological standpoint (Hore, Lacy & Ian, 2009).

1.5 Uranium Isotopes

Uranium has sixteen isotopes, all of which are radioactive. Naturally occurring uranium nominally contains 99.28305% by weight ^{238}U , 0.7110% ^{235}U , and 0.0054% ^{234}U . Studies show that the percentage weight of ^{235}U in natural uranium varies by as much as 0.1%, depending on the source. The U.S. Department of Energy has adopted the value of 0.711 as being their official percentage of ^{235}U in natural uranium. Natural uranium is sufficiently radioactive to expose a photographic plate in an hour or so. Much of the internal heat of the Earth is thought to be attributable to the presence of uranium and thorium.

Table 1.2 Radioactive properties of uranium isotopes

Radioactive Properties of Key Uranium Isotopes				
Isotope	Half-Life yr	Natural Abundance (%)	Specific Activity (Ci/g)	Decay Energy (MeV)
^{234}U	248,000	0.0055	6.2×10^{-3}	4.8 α
^{235}U	700 million	0.72	2.2×10^{-6}	4.4 α 0.21 γ
^{238}U	4.5 billion	99.27	3.3×10^{-7}	4.2 α

Uranium is naturally radioactive, which means that atoms of uranium are unstable and decay by emitting particles and energy. Uranium decays very slowly by emitting an alpha particle. The half-life of uranium-238 is about 4.5 billion years, which means it is not very radioactive. In fact, its very long half-life (and thus low radioactivity) is the reason uranium still exists on the Earth. Three additional isotopes of uranium are not naturally present but can be produced by nuclear transformations. These are uranium-232, uranium-233, and uranium-236. Like the natural uranium isotopes, these three also decay by emitting an alpha particle.

The isotope ^{235}U is important because under certain conditions it can readily be split, yielding a lot of energy. When the nucleus of a ^{235}U atom captures a neutron it splits in two (fissions), releases energy in the form of heat, and emits two or three neutrons. If enough of these expelled neutrons cause the nuclei of other ^{235}U atoms to split, releasing further neutrons, a fission ‘chain reaction’ can be achieved. This is the process that occurs in a nuclear reactor where the heat is used to make steam to produce electricity. Each fission of a ^{235}U atom releases about 200 MeV (3.2×10^{-11} joule)—about 50 million times as much energy as burning an atom of carbon. In other terms, a kilogram of natural uranium used in a typical reactor yields around 20,000 times as much energy as a kilogram of coal, and a kilogram of enriched nuclear fuel yields 160,000 times as much. Fission produces hundreds of different kinds of fission products (isotopes of much lighter elements), most of which are radioactive. In addition, a uranium atom may capture a neutron without splitting, leading the formation of a number of radioactive transuranic elements. These byproducts comprise nuclear waste (Hore, Lacy & Ian, 2009).

1.6 Chemical Forms of Uranium

Uranium can take many chemical forms. In nature, uranium is generally found as an oxide, such as in the olive-green-colored mineral pitchblende, which contains triuranium octaoxide (U_3O_8). Uranium dioxide (UO_2) is the chemical form most often used for nuclear reactor fuel. Uranium-fluorine compounds are also common in uranium processing, with uranium hexafluoride (UF_6) being the form used in the gaseous diffusion enrichment process. Uranium tetrafluoride (UF_4) is frequently produced as an intermediate in the processing of uranium. As noted above, in its pure form, uranium is a silver-colored metal. Because several of these compounds might be used or produced during the conversion process, a brief description of the physical and chemical properties of each is provided below.

Table 1.3 Chemical forms of uranium

Physical Characteristics of Uranium Compounds				
Compound	Melting Point (°C)	Crystal Particle [Density (g/cm ³)]	Bulk [Density (g/cm ³)]	Solubility in Water at Ambient Temperature
UF ₆	64.1	4.68	4.6	Decomposes to UO ₂ F ₂
UF ₄	960 ± 5	6.7	2.0 - 4.5	Very slightly soluble
UO ₂ F ₂	Decomposes to U ₃ O ₈ at 300	6.37	~2.6	Soluble
U ₃ O ₈	Decomposes to UO ₂ at 1,300	8.30	1.5 - 4.0	Insoluble
UO ₂	2.878 ± 20	10.96	2.0 - 5.0	Insoluble
Uranium metal	1.132	19.05	19	Insoluble

1.7 Uranium in the Environment

Although uranium is radioactive, it is not particularly rare. It is widely spread throughout the environment and so it is impossible to avoid uranium. Uranium can be found naturally in the environment in very small amounts in rocks, soil, air and water. Humans add uranium metals and compounds, because they are released during mining and milling processes.

In air the uranium concentrations are very low. Even at higher than usual concentrations in air, there is so little uranium present per cubic meter that less than one atom transfers every day.

In water most of the uranium is dissolved uranium that derives from rocks and soil that the water runs over. Some of the uranium is suspended, so that the water gets a

muddy texture. Only a very small part of uranium in water settles from air. The amounts of uranium in drinking water are generally very low.

Uranium is found in soils in varying concentrations that are usually very low. Humans add uranium to the soil through industrial activities.

Erosion of tailing from mines and mills may cause larger amounts of uranium to be released into the environment.

1.7.1 Effects of Uranium on the Environment

Uranium is a radioactive material that is very reactive. As a result it cannot be found in the environment in its elemental form. Uranium compounds that have consisted during reactions of uranium with other elements and substances dissolve in water to their own extent. The water-solubility of a uranium compound determines its mobility in the environment, as well as its toxicity.

While uranium itself is not particularly dangerous, some of its decay products do pose a threat, especially radon, which can build up in confined spaces such as basements.

Uranium in air exists as dust that will fall into surface water, on plants or on soils through settling or rainfall. It will then sink to the sediment in water or to the lower soil layers, where it will mix with uranium that is already present.

Water containing low amounts of uranium is usually safe to drink. Because of its nature, uranium is not likely to accumulate in fish or vegetables and uranium that is absorbed will be eliminated quickly through urine and faeces.

The compounds in the soil will combine with other compounds, which can stay in the soil for years without moving towards the groundwater. Uranium concentrations are often higher in phosphate-rich soil, but this does not have to be a problem, because concentrations often do not exceed normal ranges for uncontaminated soil.

Plants absorb uranium through their roots and store it there. Root vegetables such as radishes may contain higher than usual concentrations of uranium as a result. When the vegetables are washed the uranium will be removed (Zoellner, 2009).

1.7.2 Health Effects of Uranium

People always experience exposure to a certain amount of uranium from food, air, soil and water, as it is naturally present in all these components. Food, such as root vegetables, and water will provide us with small amounts of natural uranium and we will breathe in minimal concentrations of uranium with air. The concentrations of uranium in seafood are usually so low that they can be safely ignored.

People that live near hazardous waste sites, people that live near mines, people that work in the phosphate industry, people that eat crops grown on contaminated soil or people that drink water from a uranium waste disposal point may experience a higher exposure than other people. Uranium glazes are banned, but some artists that still use them for glasswork will experience a higher-than-usual exposure.

Because uranium is a radioactive substance health effects have been researched. Scientists have detected no harmful radiation effects of natural levels of uranium. However, chemical effects may occur after the uptake of large amounts of uranium and these can cause health effects such as kidney disease. When people are exposed to uranium radionuclides that are formed during radioactive decay for a long period of time, they may develop cancer. The chances of getting cancer are much higher when people are exposed to enriched uranium, because that is a more radioactive form of uranium. This form of uranium gives off damaging radiation, which can cause people to develop cancer within a few years. Enriched uranium may end up in the environment during accidents in nuclear power plants. Whether uranium can cause reproductive effects in people is currently unknown.

1.8 Separation Methods for Uranium

Numerous methods have been described for their effective separation and preconcentration; procedures based on ion exchange (Walton & Rocklin, 1990; Keim & Gmelin, 1983), solvent extraction (Sekine & Hasegawa, 1977) and solid phase extraction (Merdivan, Buchmeiser & Bonn, 1999; Lee, Suh, Joe, Eom & Lee, 1997) are among them. Solid phase extraction is now widely used for the preconcentration and clean up of various chemicals and for applications such as the removal of toxic or valuable substances from a variety of predominantly aqueous solutions. Chelating resins are of immense value for selective trace metal analysis. Appropriate chelating reagents can be chemically bonded to (Prasad & Sundd, 1995) or impregnated onto support matrices (Merdivan, Duz & Hamamci, 2001), thus providing complexing or chelating solid phases.

1.8.1 Solvent Extraction

Solvent extraction separation is based on differences in the solubility of elements and their compounds in two immiscible liquid phases. Usually, the initial phase is an aqueous solution and second phase is an organic solvent immiscible with water (Marczenko, 1986).

1.8.2 Ion-Exchange

Separation and concentration of trace elements can be achieved by using synthetic organic ion-exchangers. Ion exchange processes are based on the reversible exchange of ions between the solid ion-exchange resin and a liquid eluent. Separation depends on the differences in stability of complexes, and the associated differences in distribution coefficients (Marczenko, 1986).

Solvent Extraction and Ion Exchange techniques have been mostly applied to the recovery and separation of metal ions. However, recovery and separation by solvent extraction requires multiuse extraction and back-extraction in order to get successful

separation. Also, ion exchange resins have lower extraction selectivity for transition metals with respect to alkali metals (Polkowska-Motrenko, & Dybczynski, 1980).

1.8.3 Solid Phase Extraction

1.8.3.1 Principle

Solid phase extraction is currently being used as a preconcentration or separation technique whenever complex matrices or low concentration analytes have to be analyzed. It is now the most common sampling technique in many areas of chemistry, including environmental, pharmaceutical, clinical food and industrial chemistry. The basic principle of SPE is the transfer of analyte from the aqueous phase to achieve sites of three major components: water (liquid phase); analyte; and, sorbent. Either the analyte after sorption on the solid phase is desorbed with a suitable eluate or the analyte along with the sorbent is dissolved in a suitable solvent and further analyzed (Martinez, Cugat, Borrull & Callul, 2000).

1.8.3.2 Normal Phase SPE

A selection of solid phase extraction cartridges, available in many sizes, shapes, and types of stationary phase.

A typical solid phase extraction involves four basic steps. First, the cartridge is equilibrated with a non-polar solvent or slightly polar, which wets the surface and penetrates the bonded phase. Then water, or buffer of the same composition as the sample, is typically washed through the column to wet the silica surface. The sample is then added to the cartridge. As the sample passes through the stationary phase, the analytes in the sample will interact and retain on the sorbent while the solvent, salts, and other impurities pass through the cartridge. After the sample is loaded, the cartridge is washed with buffer or solvent to remove further impurities. Then, the analyte is eluted with a non-polar solvent or a buffer of the appropriate pH.

A stationary phase of polar functionally bonded silicas with short carbon chains frequently makes up the solid phase. This stationary phase will adsorb polar molecules which can be collected with a more polar solvent.

1.8.3.3 Reversed phase SPE

Reversed phase SPE separates analytes based on their polarity. The stationary phase of a reversed phase SPE cartridge is derivatized with hydrocarbon chains, which retain compounds of mid to low polarity due to the hydrophobic effect. The analyte can be eluted by washing the cartridge with a non-polar solvent, which disrupts the interaction of the analyte and the stationary phase.

A stationary phase of silicon with carbon chains is commonly used. Relying on mainly non-polar, hydrophobic interactions, only non-polar or very weakly polar compounds will adsorb to the surface (Supelco, 1998).

Several SPE materials, such as the alkyl- or aryl-bonded silicas are in the reversed phase category. Here, the hydrophilic silanol groups at the surface of the raw silica packing (typically 60Å pore size, 40µm particle size) have been chemically modified with hydrophobic alkyl or aryl functional groups by reaction with the corresponding silanes (Figure 1.2.).

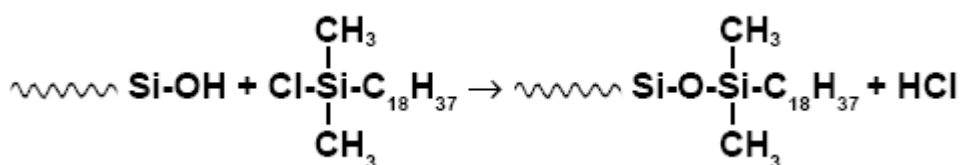





Figure 1.2 Silica Packing

Retention of organic analytes from polar solutions (e.g. water) onto these SPE materials is due primarily to the attractive forces between the carbon-hydrogen bonds in the analyte and the functional groups on the silica surface. These nonpolar-nonpolar attractive forces are commonly called van der Waals forces, or dispersion forces. To elute an adsorbed compound from a reversed phase SPE tube or disk, use a nonpolar solvent to disrupt the forces that bind the compound to the packing.

Table 1.4 Characteristic of solvents commonly used in SPE

Polarity			Solvent	Miscible in Water
Nonpolar  Polar	Strong Reversed Phase	Weak Normal Phase	Hexane	No
	 Weak Reversed Phase	 Strong Normal Phase	Isooctane	No
			Carbon tetrachloride	No
			Chloroform	No
			Methylene chloride	No
			Tetrahydrofuran	Yes
			Diethyl ether	No
			Ethyl acetate	Poorly
			Acetone	Yes
			Acetonitrile	Yes
			Isopropanol	Yes
			Methanol	Yes
			Water	Yes
Acetic acid	Yes			

1.8.3.4 Ion Exchange Solid Phase Extraction

Ion exchange SPE can be used for compounds that are charged when in a solution (usually aqueous, but sometimes organic). Anionic (negatively charged) compounds can be isolated on LC-SAX or LC-NH₂ bonded silica cartridges. Cationic (positively charged) compounds are isolated by using LC-SCX or LC-WCX bonded silica cartridges. The primary retention mechanism of the compound is based mainly on the electrostatic attraction of the charged functional group on the compound to the charged group that is bonded to the silica surface. In order for a compound to retain by ion exchange from an aqueous solution, the pH of the sample matrix must be one at which both the compound of interest and the functional group on the bonded silica are charged. Also, there should be few, if any, other species of the same charge as the compound in the matrix that may interfere with the adsorption of the compound of

interest. A solution having a pH that neutralizes either the compound's functional group or the functional group on the sorbent surface is used to elute the compound of interest. When one of these functional groups is neutralized, the electrostatic force that binds the two together is disrupted and the compound is eluted. Alternatively, a solution that has a high ionic strength, or that contains an ionic species that displaces the adsorbed compound, is used to elute the compound.

1.8.3.4.1 Anion Exchange Solid Phase Extraction. Anion exchange sorbents are derivatized with positively charged functional groups that interact and retain negatively charged anions, such as acids. Strong anion exchange sorbents contain quaternary ammonium groups that have a permanent positive charge in aqueous solutions, and weak anion exchange sorbents use amine groups which are charged when the pH is below about 9. Strong anion exchange sorbents are useful because any strongly acidic impurities in the sample will bind to the sorbent and usually will not be eluted with the analyte of interest; to recover a strong acid a weak anion exchange cartridge should be used. To elute the analyte from either the strong or weak sorbent, the stationary phase is washed with a solvent that neutralizes the charge of either the analyte, the stationary phase, or both. Once the charge is neutralized, the electrostatic interaction between the analyte and the stationary phase no longer exists and the analyte will elute from the cartridge.

1.8.3.4.1 Cation Exchange. Cation exchange sorbents are derivatized with functional groups that interact and retain positively charged cations, such as bases. Strong cation exchange sorbents contain aliphatic sulfonic acid groups that are always negatively charged in aqueous solution, and weak cation exchange sorbents contain aliphatic carboxylic acids, which are charged when the pH is above about 5. Strong cation exchange sorbents are useful because any strongly basic impurities in the sample will bind to the sorbent and usually will not be eluted with the analyte of interest; to recover a strong base a weak cation exchange cartridge should be used. To elute the analyte from either the strong or weak sorbent, the stationary phase is washed with a solvent that neutralizes ionic interaction between the analyte and the stationary phase.

1.8.3.5 Secondary Interactions

The primary retention mechanisms for compounds on the SPE materials are described above. For the bonded silicas, it is possible that secondary interactions will occur. For reversed phase bonded silicas, the primary retention mechanism involves nonpolar interactions. However, because of the silica particle backbone, some polar secondary interactions with residual silanols — such as those described for normal phase SPE — could occur. If a nonpolar solvent does not efficiently elute a compound from a reversed phase SPE packing, the addition of a more polar solvent (e.g. methanol) may be necessary to disrupt any polar interactions that retain the compound. In these cases, methanol can hydrogen-bond with the hydroxyl groups on the silica surface, thus breaking up any hydrogen bonding that the analyte may be incurring (Supelco, 1998).

1.8.3.6 The Role of pH in Solid Phase Extraction

Solutions used in SPE procedures have a very broad pH range. Silica-based packings, such as those used in HPLC columns, usually have a stable pH range of 2 to 7.5. At pH levels above and below this range, the bonded phase can be hydrolyzed and cleaved off the silica surface, or the silica itself can dissolve. In SPE, however, the solutions usually are in contact with the sorbent for short periods of time. The fact that SPE cartridges are disposable, and are meant to be used only once, allows one to use any pH to optimize retention or elution of analytes. If stability of the SPE cartridge at an extreme pH is crucial, polymeric or carbon based SPE materials may be used. These materials are stable over the pH range of 1-14.

For reversed phase SPE procedures on bonded silicas, if trapping the analyte in the tube is desired, the pH of the conditioning solution and sample (if mostly or entirely aqueous) should be adjusted for optimum analyte retention. If the compound of interest is acidic or basic you should, in most cases, use a pH at which the compound is not charged. Retention of neutral compounds (no acidic or basic functional groups) usually is not affected by pH. Conversely, you can use a pH at which the unwanted compounds in the sample are retained on the SPE packing, but

the analyte of interest passes through unretained. Secondary hydrophilic and cation exchange interactions of the analyte can be used for retention at a proper pH (Thurman, Mills, 1998).

1.9 Adsorption Processes

Adsorption is the accumulation of atoms or molecules on the surface of a material. This process creates a film of the adsorbate (the molecules or atoms being accumulated) on the adsorbent's surface. It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term sorption encompasses both processes, while desorption is the reverse process of "adsorption" (Henderson, Seetohul, Dean, Russell & Pruneanu, 2009). Simply adsorption is defined the accumulation of matter at the solid-liquid interface (Rytwo, 2004).

Absorption phenomena are operative in most natural physical, biological, and chemical system, and adsorption operations employing solids such as activated carbon and synthetic resins are used widely in industrial applications and for purification of waters and wastewaters (Marczewski, 2002).

Adsorption, ion exchange, and chromatography are sorption processes in which certain adsorbates are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column (Henderson, Seetohul, Dean, Russell & Pruneanu, 2009).

1.9.1 Factors Influencing Adsorption

1.9.1.1 Nature of the Adsorbent

The physicochemical nature of the adsorbent can have profound effects on both rate and capacity for adsorption. The rate of adsorption increases with in surface area of the adsorbent.

1.9.1.2 Nature of the Adsorbate

1.9.1.2.1 Solubility of Adsorbate. Adsorption of a solute is inversely proportional to its solubility in the solvent. The greater is the solubility, the stronger the solute-solvent bond and the smaller the extent of adsorption (Lundelius's rule)

On the other hand, the solubility of any organic compound in water decreases with increasing chain length, because the compound becomes more hydrocarbon-like as the number of carbon atoms becomes greater (Traube's rule).

1.9.1.2.2 Molecular Sizes. If the rate is controlled by intraparticle transport, the reaction generally will proceed more rapidly the smaller the adsorbate molecule, within given class of compound.

1.9.1.2.3 Degree of Ionization. As long as the compounds are structurally simple, adsorption is at minimum for the charged species and at a maximum for the neutral species. As compounds become more complex, the effect of ionization becomes of decreasing importance (Tournassat, Greneche, Tisserand & Charlet, 2004; Sposito, 1984).

1.9.1.2.4 pH. Because hydrogen and hydroxide ions are adsorbed strongly, the adsorption of other ions is influenced by the pH of the solution. In general, adsorption of typical organic pollution from water is increased with decreasing pH. We should also take care of the ionization equilibrium of the adsorbate.

1.9.1.2.5 Experimental Conditions. Temperature (Adsorption reactions are normally exothermic, thus the extent of adsorption generally increases with decreasing temperature), air flow velocity and relative humidity (Gereli, 2006).

1.10 Desorption Process

An adsorbed species present on a surface at low temperatures may remain almost indefinitely in that state. As the temperature of the substrate is increased, however,

there will come a point at which the thermal energy of the adsorbed species is such that one of several things may occur :

1. A molecular species may decompose to yield either gas phase products or other surface species.
2. An atomic adsorbate may react with the substrate to yield a specific surface compound, or diffuse into the bulk of the underlying solid.
3. The species may desorb from the surface and return into the gas phase.

The last of these options is the desorption process. In the absence of decomposition the desorbing species will generally be the same as that originally adsorbed but this is not necessarily always the case (Gereli, 2006).

1.11 Silica Gel

Silica gel is a granular, vitreous, highly porous form of silica made synthetically from sodium silicate. Despite its name, silica gel is a solid.

Silica gel is most commonly encountered in everyday life as beads packed in a semi-permeable plastic. In this form, it is used as a desiccant to control local humidity in order to avoid spoilage or degradation of some goods. Because of poisonous dopants (see below) and their very high adsorption of moisture, silica gel packets usually bear warnings for the user not to eat the contents. If consumed, the pure silica gel is unlikely to cause acute or chronic illness, but would be problematic nonetheless. Food-grade desiccant should not include any poisons which would cause long-term harm to humans if consumed in the quantities normally included with the items of food. A chemically similar substance with far greater porosity is aerogel.

1.11.1 Silica Gel Properties

Silica gel's high surface area (around 800m²/g) allows it to absorb water readily, making it useful as a desiccant (drying agent). Once saturated with water, the gel can be regenerated by heating it to 120 °C (250 °F) for two hours.

1.11.2 Preparation of Silica gel

A solution of sodium silicate is acidified to produce a gelatinous precipitate that is washed, then dehydrated to produce colorless silica gel. When a visible indication of the moisture content of the silica gel is required, ammonium tetrachlorocobaltate (II) (NH₄)₂CoCl₄ or cobalt chloride CoCl₂ is added. This will cause the gel to be blue when dry and pink when hydrated (Greenwood, Norman Earnshaw, 1997)

1.11.3 Applications of Silica Gel in Chemistry

In chemistry, silica gel is used in chromatography as a stationary phase. In column chromatography the stationary phase is most often composed of silica gel particles of 40-63 μm. Different particle sizes are used for achieving a desired separation of certain molecular sizes. In this application, due to silica gel's polarity, non-polar components tend to elute before more polar ones, hence the name normal phase chromatography. However, when hydrophobic groups (such as C18 groups) are attached to the silica gel then polar components elute first and the method is referred to as reverse phase chromatography. Silica gel is also applied to aluminium, glass, or plastic sheets for thin layer chromatography.

The hydroxy (OH) groups on the surface of silica can be functionalized to afford specialty silica gels that exhibit unique stationary phase parameters. These so-called functionalized silica gels are also used in organic synthesis and purification as insoluble reagents and scavengers.

Chelating groups have also been covalently bound to silica gel. These materials have the ability to remove metal ions selectively from aqueous media. Chelating groups can be covalently bound to polyamines that have been grafted onto a silica gel surface producing a material of greater mechanical integrity. Silica gel is also combined with alkali metals to form a M-SG reducing agent.

Silica gel is not thought to biodegrade in either water or soil (Environmental Health and Safety, 2007).

1.12 Related Studies on Preconcentration of Uranium by Solid Phase Extraction

In recent years, solid phases modified with the immobilised organic compounds are attracting great interest because of high selectivity, high enrichment capacity and operational simplicity. In solid phase extraction (SPE), (Lee, Suh, Joe, Eom, & Lee, 1997) immobilisation of organic ligands on the surface of inorganic or organic solid supports is aimed to modify the surface with certain target functional groups that can be exploited for further analytical purposes. A number of solid sorbents such as polymer- Amberlite series, silica, octadecyl silica membrane discs, activated silica gel, controlled pore glass polyurethane foam activated carbon and cationic or anionic exchange resins have been reported for the enrichment of uranium(VI) from dilute solutions prior to determination by a variety of analytical techniques (Farhadi, Abdollahnezhad & Maleki, 2008).

In 2004, Starvin and coworkers studied Solid phase extractive preconcentration of uranium(VI) onto diarylazobisphenol modified activated carbon. Diarylazobisphenol (DAB) 1 and diarylazobisphenol modified carbon 2 were synthesized and characterised. The latter has been used for solid phase extractive preconcentration and separation of trace amounts of uranium(VI) from other inorganics. The accuracy of the developed preconcentration method in conjunction with the Arsenazo III procedure was tested by analysing MESS-3, a marine sediment certified reference

material. Further, the above procedure has been successfully employed for analysis of uranium(VI) in soil and sediment samples(Starvin & Rao, 2004).

In 2005, Praveen and coworkers studied solid phase extractive preconcentration of uranium (VI) using quinoline-8-ol anchored chloromethylated polymeric resin beads. A new chelating polymeric sorbent has been developed using Merrifield chloromethylated resin anchored with quinoline-8-ol (HQ). The modified polymeric resin was characterized by FT-IR spectroscopy and elemental analysis. The HQ anchored resin showed superior binding affinity for U(VI) over Th(IV) and La(III). The influence of various physicochemical parameters on the recovery of U(VI) were optimized by both static and dynamic methods. The phase exchange kinetic studies performed for U(VI) revealed that <5 min was sufficient for reaching equilibrium metal ion sorption (Praveen, Metilda, Daniel & Rao, 2005).

In 2006, Seyhan and coworkers studied solid phase extractive preconcentration of trace metals using *p-tert*-butylcalix[4]arene-1,2-crown-4-anchored chloromethylated polymeric resin beads. 5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,26-dihydroxy-27,28-crown-4-calix[4]arene in the cone conformation was synthesized. This *p-tert*butylcalix[4]arene-1,2-crown-4 compound was then anchored with Merrifield chloromethylated resin beads. The modified polymeric resin was characterized by ¹H NMR, FT-IR and elemental analysis and used successfully for the separation and preconcentration of Cu(II), Cd(II), Co(II), Ni(II) and Zn(II) prior to their determination by FAAS. Effective extraction conditions were optimized in both batch and column methods (Seyhan, Colak, Merdivan, Demirel, 2006).

In 2007, Seyhan and coworkers studied solid phase extraction. Amberlite XAD-2000 resin was impregnated with *o*-phenylene dioxydiacetic acid to investigate the separation and preconcentration of U(VI) and Th(IV) by column and batch experiments. The impregnation of *o*-phenylene dioxydiacetic acid (OPDA) into a polymeric matrix, Amberlite XAD-2000, is reported and was characterized by infrared spectroscopy. The impregnated resin exhibits a high chemical stability, reusability and fast equilibration. The method was used for the determination of

U(VI) and Th(IV) in model solutions and rock samples (Seyhan, Merdivan & Demirel, 2007).

In 2007, Dutta and coworkers studied solid phase extraction. A procedure for the pre-concentration and separation of trace amounts of Eu and U by solid phase extraction using Tulsion CH-90 resin (with imino diacetate functional group) has been developed. The determinations of europium and uranium have been carried out by a radiotracer technique using $^{152,154}\text{Eu}$ and ^{233}U radionuclides. The experiments were carried out using both batch and column techniques. Parameters such as equilibration rate, effect of pH, sorption and desorption of metal ions have been studied (Dutta, Mohapatra, Dhekane, Das, Manchanda, 2007).

In 2009, Yousefi and coworkers synthesized modified mesoporous silica (MCM-41) using 5-nitro-2-furaldehyde (fural) was applied as an effective sorbent for the solid phase extraction of uranium (VI) and thorium (IV) ions from aqueous solution for the measurement by inductively coupled plasma optical emission spectrometry (ICP OES). The influences of some analytical parameters on the quantitative recoveries of the analyte ions were investigated in batch method. The sorbent exhibited good stability, reusability, high adsorption capacity and fast rate of equilibrium for sorption/desorption of uranium and thorium ions. The applicability of the synthesized sorbent was examined using CRM and real water samples (Yousefi, Ahmad, Shemirani, Jamali, Niasari, 2009).

In 2009, Daneshvara and coworkers used on-line solid phase extraction method. The aim of this study was to develop an on-line SPE-ICP-OES method to analyze U and Th in aqueous samples using C18silica cartridge modified with 2,3-dihydro-9,10-dihydroxy-1,4-anthracenedion. The retention and elution conditions for preconcentration and sequential determination of U and Th using ICP-OES have been optimized. Finally, the developed method was also verified by determination of these elements in various natural as well as seawater samples (Daneshvar, Jabbari, Yamini & Paki, 2009).

In 2009, Sadeghi and coworkers used silica gel modified with murexide for preconcentration of uranium (VI) ions from water samples by solid phase extraction. Murexide was chemically bonded to silica gel surface immobilized 3-aminopropyl trimethoxysilane (APMS) to produce the new sorbent. A solid phase extraction method using the new sorbent has been developed to separate and concentrate trace amount of uranium (VI) from aqueous samples for the measurement by spectrophotometry method using Arsenazo III reagent. The influences of some analytical parameters on the quantitative recoveries of the analyte were investigated both in batch and column methods (Sadeghi, Sheikhzadeh, 2009).

In 2009, Sadeghi and coworkers studied solid phase extraction using silica gel functionalized with Sulfasalazine for preconcentration of uranium(VI) ions from water samples. Silica gel surface was chemically functionalized by reaction the silanol from the silica surface with 3-chloropropyltrimethoxysilane followed by reaction with Sulfasalazine. This new sorbent has been used for the preconcentration of low levels of U(VI) ions from an aqueous phase. Parameters involved in extraction efficiency such as pH, weight of the sorbent, volume of sample and eluent were optimized in batch and column methods prior to determination by spectrophotometry using arsenazo(III) reagent (Sadeghi, Sheikhzadeh, 2009).

1.13 Solid Phase Extraction with Benzoylthiourea

Benzoylthiourea is known to have strong tendencies to form complexes with transition metals, especially with platinum group metals and uranium(VI) ions through the N–CS–NH–CO–Ph chelating group. Benzoylthiourea-modified mesoporous silica gel is a potential adsorbent for mercury(II) ion from aqueous solutions. Also, determination of palladium in gasoline and airborne particulate matter have been achieved by sorbent extraction using N,N-diethyl-N0-Benzoylthiourea as a chelating agent (Merdivan, Seyhan & Gok, 2006).

In 2006, Merdivan and coworkers studied separation and preconcentration of U (VI). Benzoylthiourea immobilized on silica gel was prepared by two-step post-

synthesis modification. The capacity of the chelating silica gel, which was characterized by FTIR, The separation and enrichment of uranium(VI) from solutions was investigated. Effective extraction conditions were optimized in both batch and column methods prior to determination by spectrophotometry using arsenazo(III). The method was used for the determination of uranium in synthetic samples and a soil sample (Merdivan, Seyhan & Gok, 2006).

In 2008, Ayata and coworkers studied solid phase extractive preconcentration of silver from aqueous samples. *N,N*-dibutyl-*N*-benzoylthiourea (DBBT) impregnated onto a polymeric matrix, Amberlite XAD-16 was prepared. The separation and enrichment of Ag(I) from solution was investigated. Effective extraction conditions were optimized in column methods prior to determination by atomic absorption spectrometry (Ayata, Kaynak & Merdivan, 2008).

In 2008, Merdivan and coworkers studied Sorption behaviour of uranium(VI) with *N,N*-dibutyl-*N*-benzoylthiourea (DBBT) Impregnated in Amberlite XAD-16. DBBT impregnated resin was prepared by direct adsorption of chelating ligand onto macroporous support, Amberlite XAD-16. The adsorption of DBBT on the macroporous support is shown by FTIR spectroscopy to be the result of only weak chelating ligand-support interactions. Parameters such as the pH effect on the sorption of uranium, the sorption capacity of the impregnated resin, the stripping of uranium and the effect of coexisting ions were investigated by batch experiments (Merdivan, Zahir & Hamamci, 2001).

1.14 Objective This Work

Determinations of uranium are important from the point of view of their technological applications, especially in metallurgy, ceramic and nuclear industry. For all these purposes, the development of analytical methodologies for the sorption and desorption behavior of U(VI) by batch experiments is important.

The aim of this study was development a solid phase extraction procedure with benzoylthiourea as chelating agent impregnated resin for enrichment and separation of U(VI) from soil samples. To achieve this goal, we aimed at: (1) preparing of benzoylthiourea derivatives impregnated silica gel resin; (2) characterization of benzoylthiourea derivatives impregnated silica gel resin using FT-IR; (3) examination of parameters such as pH, sorption capacity, sorption times for preconcentration of U(VI); (4) controlling the effects of diverse ions; (5) applying the proposed method to soil samples.

CHAPTER TWO

EXPERIMENTAL

2.1 Materials and Methods

2.1.1 Reagents and Chemicals

Stock solution of U(VI) was prepared by dissolving an appropriate amount of uranyl acetate dihydrate in doubly distilled water. N,N-diphenyl-N'-(3-methylbenzoyl)thiourea (o-DPMBT) and N,N-diphenyl-N'-(4-methylbenzoyl)thiourea (p-DPMBT) were supplied from Prof. Dr. Nevzat Külcü. The stock ion solutions were prepared by dissolving analytical reagent-grade metal nitrates, chlorides, carbonates, sulfates and phosphates in doubly deionized water. A 0.1% Arsenozo III solution was prepared in deionized water. Potassium bromide (Merck, for spectroscopy) was used for the preparation of pressed discs for the Fourier Transform Infrared (FT-IR) spectrometer. All other reagents and solvents used were of analytical reagent grade. The water used throughout the study had been deionized by means of a Millipore Milli-Q system. The silica resin (styrene–divinylbenzene copolymer, surface area: $800\text{m}^2\text{ g}^{-1}$, pore diameter: 10nm and bead size: 20–60 mesh) was supplied by Sigma. The silica gel was dried in vacuum oven at 60°C and stored in a polyethylene bottle.

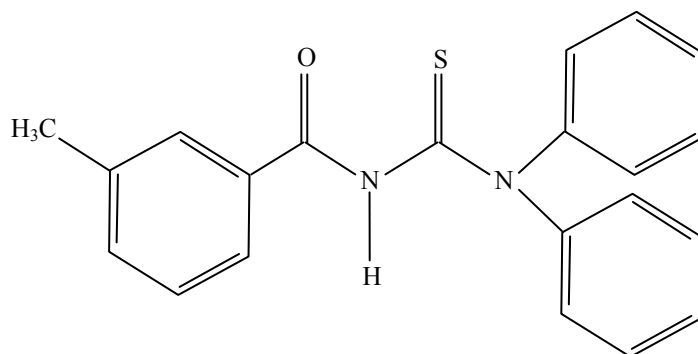


Figure 2.1 Molecule structure of N,N-diphenyl-N'-(3-methylbenzoyl)thiourea.

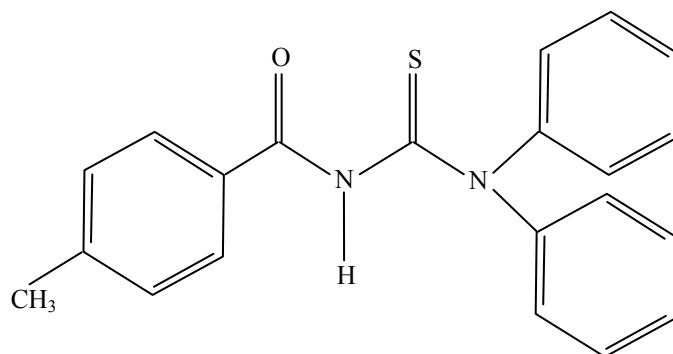


Figure 2.2 Molecule structure of N,N-diphenyl-N'-(3-methylbenzoyl)thiourea.

2.2 Apparatus

FT-IR spectra of silica, benzoylthiourea derivatives (N,N-diphenyl-N'-(3-methylbenzoyl)thiourea and N,N-diphenyl-N'-(4-methylbenzoyl)thiourea impregnated silica were recorded with a Perkin Elmer Spectrum BX Fourier Transform IR spectrometer using KBr discs in the range of $4000\text{--}700\text{ cm}^{-1}$, 30 co-added interferograms were scanned at 2 cm^{-1} resolution. pH measurements were made on a Lab WTW model digital pH-meter. For solid phase experiments, a gooch crucible connected the outlet tip of the syringe barrel to a Watson Marlow peristaltic pump. U(VI) Shimadzu UV-1601 model UV spectrometer was used for the determination of uranium (VI) as U(VI)-arsenazo III complex at 654 nm.

2.3 Preparation of Resin

A 5 g of dry silica gel was placed in 50 mL of 0.1 gram benzoylthiourea derivative (N,N-diphenyl-N'-(3-methylbenzoyl)thiourea or N,N-diphenyl-N'-(4-methylbenzoyl)thiourea) ethanol solution and the final mixture was stirred for 24 h at room temperature. The mixture was separated by filtration through a gooch. The resin was dried in air and kept in desiccator. The amount of o- and p-DPMBT attached to the silica were found as 0.053 mmol g^{-1} .

2.4 Sorption by Batch Technique

A sample solution containing 100 μg U(VI) ion in a volume of 10 mL was taken and pH was adjusted to optimum pH for metal ion. 0.05 g of DPMBT impregnated silica was used at batch experiments. After filtration and stripping of sorbed uranium from impregnated silica, the determination of uranyl ion was carried out by visible absorption spectrophotometer after diluting to necessary ratio.

2.5 Determination of Uranium.

0.1 % (w/v) Arsenazo III {3,6-bis [(2- arsonophenyl)-azo]-4,5-dihydroxy-2,7-nphthalenedisulphonic acid} solution was prepared from an Aldrich sample (Figure 2.3). Standard stock solutions ($1000 \mu\text{mL}^{-1}$) of uranium was prepared by dissolving the required amount of their $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in doubly distilled water. Calibration standard solutions of U(VI) 0.25 to 3 $\mu\text{g mL}^{-1}$ was prepared. KCl/HCl buffer solution having pH 2 was prepared by mixing 8.1 mL of 0.2 mol L^{-1} HCl and 41.9 ml of 0.2 mol L^{-1} KCl solutions and diluting to 100 mL with doubly distilled water. Reagent blank solution containing Arsenazo III and buffer solution was freshly prepared at each measurement.

Calibration solutions and sample solutions containing 1 mL of standard/sample solution + 0.2 ml of Arsenazo III solution + 1 ml buffer solution were diluted to 5 mL with distilled water and measured at 654 nm for U(VI).

Calibration curves of U(VI) was linear and correlation coefficient were 0.998. At each measurement, new calibration curve was used.

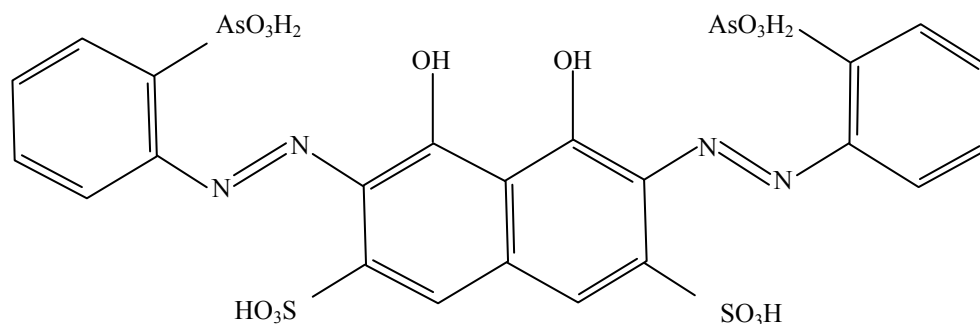


Figure 2.3 Molecular structure of arsenazo III

2.6 Optimization of the Stripping Procedure for Loaded Ions

For the complete desorption of studied ions, type of eluting solution and its concentration were tested.

For these propose, different concentration of HCl and HNO₃ solutions were used. HCl solutions were varried from 0.01 to 0.2 mol L⁻¹ and HNO₃ solutions were varied from 0.01 to 1 mol L⁻¹.

2.7 Preparation Electrolytes of Diverse Ion Solution

The effects of common electrolytes and diverse ions on the recovery of U(VI) was studied. For this purpose NaCl (0.5-1 mol L⁻¹), NaNO₃ (0.5-1 mol L⁻¹), Na₂SO₄ (0.2-0.3 mol L⁻¹), Na₃PO₄ (0.1-0.2 mol L⁻¹), Na₂CO₃ (0.001-0.01 mol L⁻¹, Merck) and Cd(II), Co(II), Cu(II), Zn(II), Ni(II) (1-5-10 µg L⁻¹), Th(IV), Ce(III), La(III) (5-10 µg L⁻¹, Merck) were used to prepare their working solutions.

2.8 Analysis of Soil samples

To checked the applicability of the proposed method was tested by determining uranium in soil samples collected from Gunesli Town, Gordes (Manisa) and Dogancay Town, Bigadic(Balikesir) (located in the Agean region of Turkey).

About 1 g of the soil samples were treated with 10 mL conc. H₂SO₄ and 25 mL distilled water, and the mixtures were stirred for 3 h. After filtration of the mixtures, the amount of uranium in the samples were determined by applying the batch method.

CHAPTER THREE

RESULTS AND DISCUSSION

3.1 Characterization of Sorbent

Characterization studies of infrared spectrum of *o*- and *p*-DPMPT, silica gel and benzoylthiourea derivatives impregnated silica gel have been evaluated. The IR absorption frequencies assignments for *o*- and *p*-DPMPT/silica sorbent show small modifications on the characteristic normal modes compared with the spectrum of the silica (Fig.3.1 and 3.2). The IR absorption frequencies assignments *o*-DPMPT/silica and *p*-DPMPT/silica resin show similar modifications of the characteristics normal modes of *o*-DPMPT and *p*-DPMPT compared with the spectrum of the free reagent as before. It was found that benzoylthiourea derivatives have similar features.

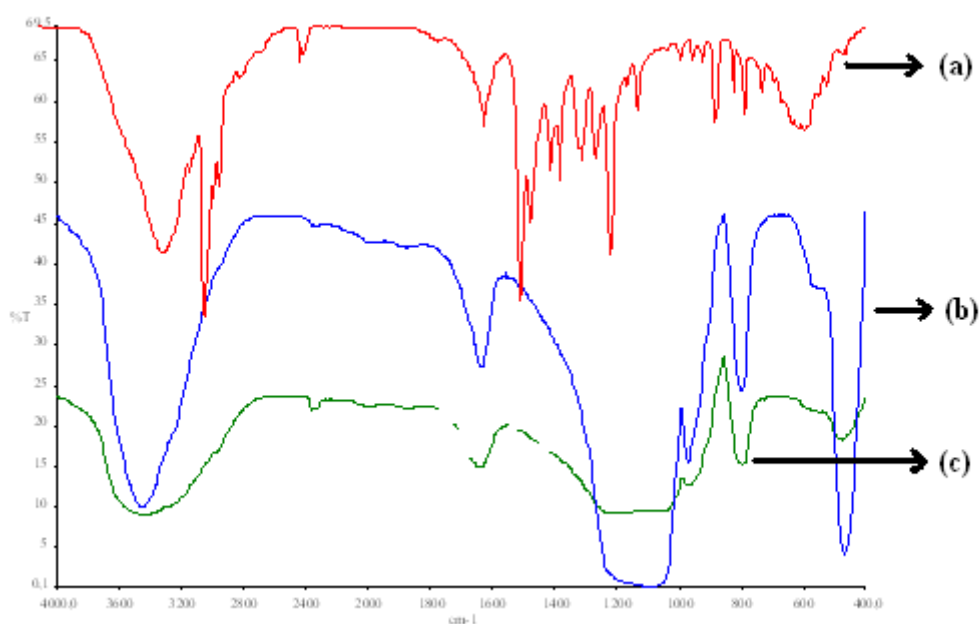


Figure 3.1 FT-IR spectrum of a) *o*-DPMBT; b) silica gel; (c) *o*-DPMBT/silica impregnated silica

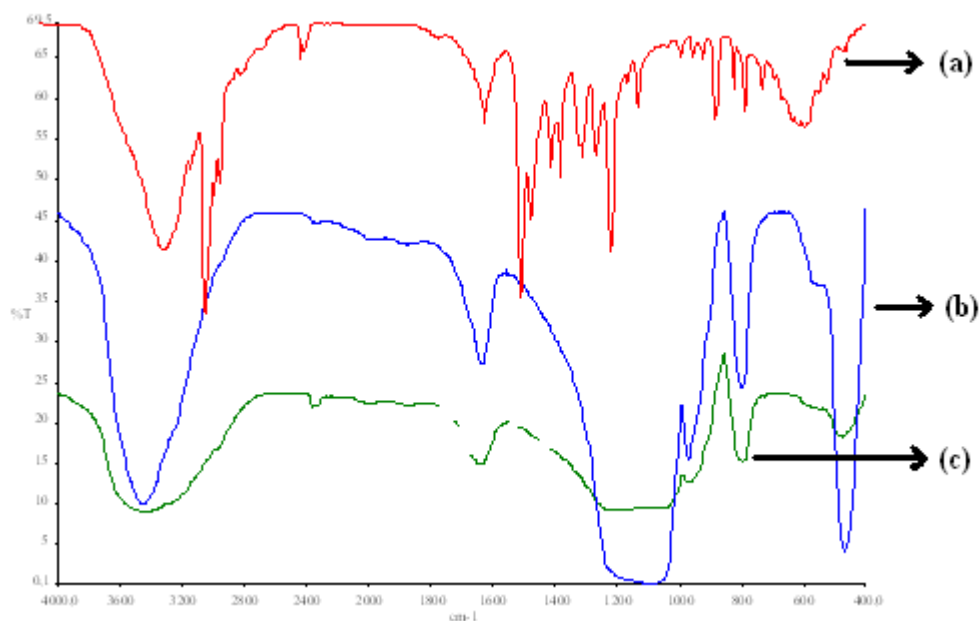


Figure 3.2 FT-IR spectrum of a) p-DPMT; b) silica gel; c) p-DPMT/silica impregnated silica

3.2 Effect of pH on Metal Sorption

Extraction experiments were carried out to investigate the effects of pH for sorption of U(VI). A 50 mL solution at various pH values (3, 4, 5, 6, and 7) containing $10 \mu\text{g U(VI) mL}^{-1}$ was added to 50 mg of o- and p-DPMBT/silica. The sorption behaviour of U(VI) depending on pH was demonstrated in Figure 3.3. Sorption percentage was found between 90 and 95 from pH 3 to 7 in both derivatives Table 3.1. Although there is not so big differences in sorption percentage of U(VI) for o- and p-DPMBT in range of pH 3-7, p-DPMBT as sorbent and pH 5 was preferred to further studies. The sorption experiments were carried out in triplicate.

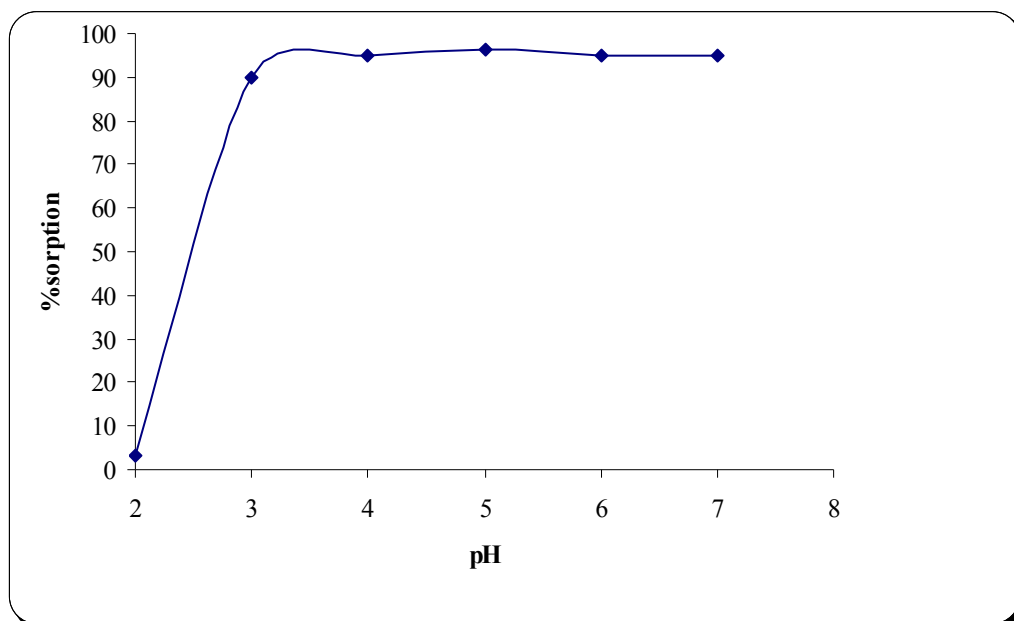


Figure 3.3 Effect of pH on the sorption of U(VI) on o- and p-DPMBT /silica

Table 3.1 Sorption of U(VI) depending on sorbents at different pH

pH	% Sorption	
	o-DPMBT	p-DPMBT
3	90	87
4	95	94
5	96	96
6	95	95
7	95	95

3.3 Effect of time on Sorption Capacity

To determine the rate of loading of uranium on the sorbent, batch experiments were carried out under the following conditions: 0.05 g of sorbent was stirred with 10 mL of feed solution containing uranium at room temperature. The studied contact times are: 5, 10, 15, 30, 45, 60 and 120 min as shown in (Figure 3.4). The concentration of uranyl ion in the filtrate solution and the amount uranyl ion loaded on the resin phase was calculated by mass balance as $\mu\text{g g}^{-1}$ resin. Uranium was observed equilibration

time of about 30 min U(VI) was required for 99% sorption. The faster uptake of this metal ion on benzoylthiourea reflects a better accessibility of the metal ion to chelating sites in the resin.

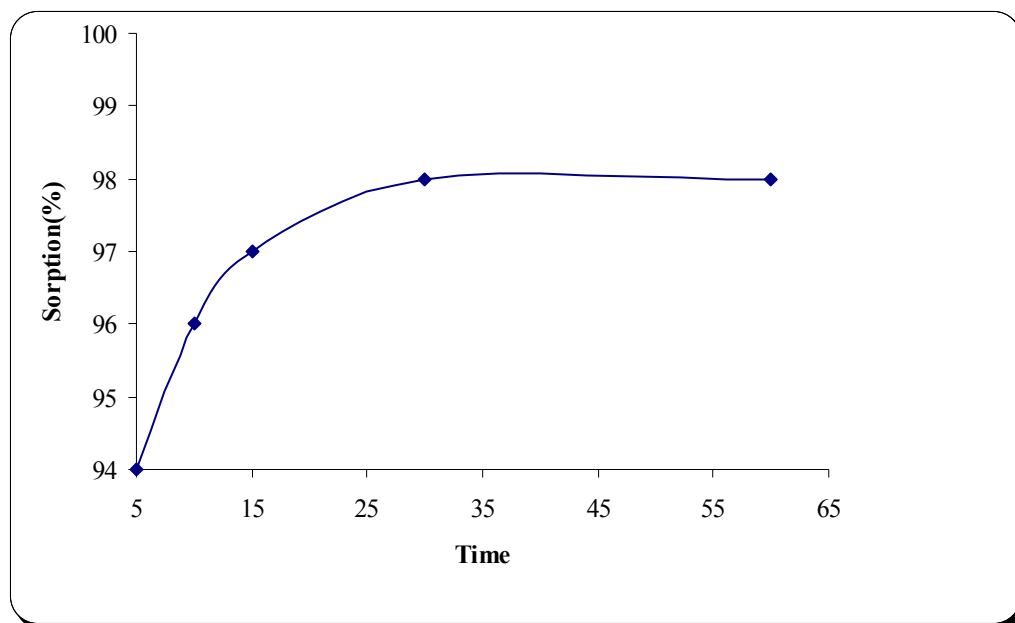


Figure 3.4 Effect of time on sorption of U(VI)

3.4 Sorption Capacity

The sorption capacity of the silica loaded with DPMBT for the extraction of uranium was also determined. Increasing amounts of uranium were added to 0.05 g of loaded sorbent. The sorption curve appears to be linear in the range of 0.25 – 10 μg of U(VI) per mL and it reaches a plateau at maximum sorption capacity, that is, 0.005 mmol U(VI) g^{-1} at pH 5. This indicates that DPMBT/silica could be used as a sorbent for preconcentration of uranium in the trace concentration range (Figure 3.5).

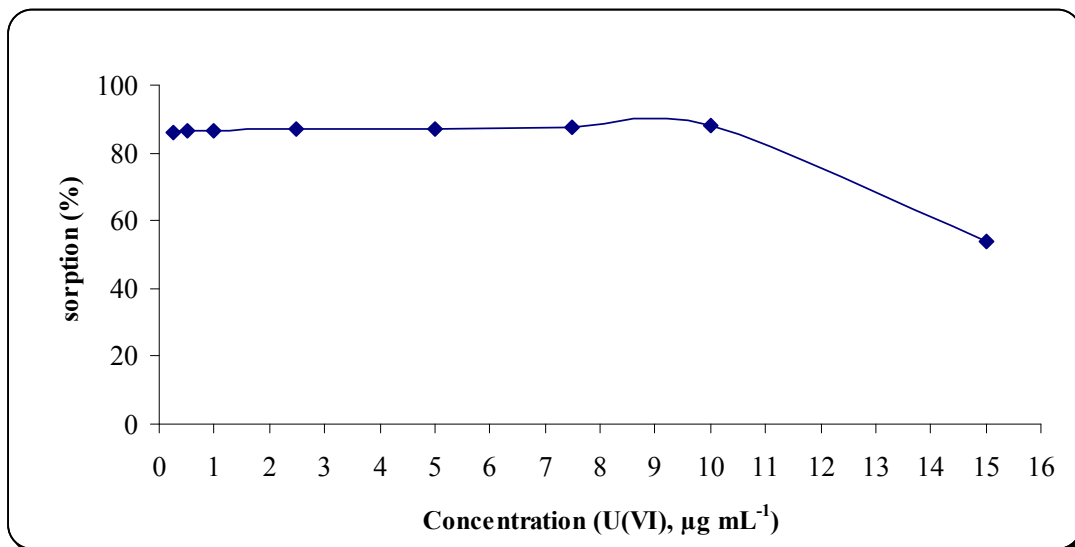


Figure 3.5 Effect of concentration on the sorption of U(VI) on benzoylthiourea /silica

3.5 Effect of Concentration of Stripping Agents

Desorption experiments were carried out to investigate the effects of HCl and HNO_3 in concentration range of 0.01, 0.05, 0.1, 0.2 M and 0.01, 0.05, 0.1, 0.2 M, respectively (Figure 3.6). The uranium (VI) ion was eluted successively with 5 mL of 0.1 M HCl by maximum recovery.

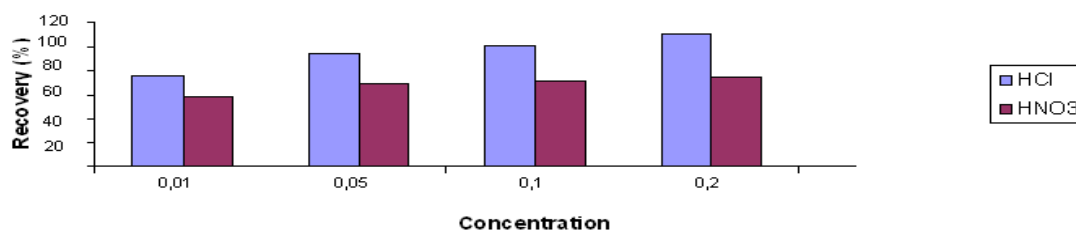


Figure 3.6 Elution values using different concentration of HCl / HNO_3

3.6 Effect of Electrolytes and Diverse Ions

The results of the uranium desorption in the presence of coexisting metal ions in combination are presented in terms of their influence on recovery percentage in (Table 3.2. and Table 3.3.). The effects of various electrolytes like NaNO_3 , NaCl , Na_2SO_4 , Na_3PO_4 and Na_2CO_3 on the sorption of U(VI) with benzoylthiourea resin was studied. It was found that all the electrolytes were tolerable within the range of $0.15 - 0.5 \text{ mol L}^{-1}$ except carbonate ion. The sorption of U(VI) was considerably reduced in the carbonate concentration range exceeding 1.0 mM due to formation of the stable tricarbonato complex of U(VI) .

Since the metal ions are at the same concentrations and in excess of the loaded resin at pH 5, a competitive sorption will exist among the metal ions for the available loaded ligand. U(VI) was preferentially sorbed over the other metal ions tested. The result suggests that Ni(II) , Co(II) , Cd(II) , Cu(II) and Zn(II) do not seriously interfere with the sorption of U(VI) .

Table 3.2 Tolerance limits of electrolytes on the sorption of U(VI) on the sorbent.

Electrolytes (mol L^{-1})					
	NaNO_3	NaCl	Na_2SO_4	Na_3PO_4	Na_2CO_3
$5 \mu\text{g mL}^{-1}$ U(VI)	0.5	0.3	0.3	0.15	0.001

Table 3.3 Tolerance limits of cation on the sorption of U(VI) * on the sorbent.

Multiple metal ion solution	Metal ion ($\mu\text{g mL}^{-1}$)	Sorption of U(VI) (%)
$\text{Cd(II), Co(II), Cu, Zn(II), Ni(II)}$	5	50
$\text{Cd(II), Co(II), Cu, Zn(II), Ni(II)}$	1	100

* $c_{\text{U(VI)}} = 5 \mu\text{g mL}^{-1}$

3.7 Figures of Merit

Calibration curves were obtained by the preconcentration of 10 mL of U(VI) sample solution in the presence of 0.05 g sorbent at pH 5. The samples were determined as U(VI)-arsenazo(III) complex by absorption spectrometry following the stripping with 5 mL of 0.1 mol L⁻¹ HCl solution. In this case, linear relationships between the absorbance measured and the concentration of metal placed in solution were obtained. (Table 3.4) gives the summary of analytical features of the method. The relative standard deviation (R.S.D.) obtained for ten replicates determination of 10 µg mL⁻¹ of U(VI) was 0.05 % and limit of detection (LOD) calculated, as three times the standard deviation of the blank signals was 8.7 ng mL⁻¹. The calibration graph for U(VI) is linear up to 10 µg mL⁻¹.

Table 3.4 Analytical characteristics of the method

Parameter	Analytical feature
Linear range, µg mL ⁻¹	0.25-10
Limit of detection, ng mL ⁻¹	8.7
Sample volume, mL	10
Precision (U(VI), 10 µg mL ⁻¹ , n: 10)	0.05
RSD%	

3.8 Application of the Method

Proposed method was applied to the determination of U(VI) in soil and water samples. Accuracy of the proposed method was proved by spike-recovery test. Aliquots of 10 mL of tap water was spiked with concentration of uranium(VI) at 2 µg mL⁻¹ and recovery experiments were conducted as well for that sample. The results are summarized in Table 3.5. A good agreement was obtained between the added and measured analyte amounts. The percentage recovery (R) was determined by using the equation: $R = \{100(C_m - C_o)/m\}$. Where C_m is a value of metal in a spiked sample, C_o is a value of metal in a sample and m is the amount of metal spiked. The recovery values calculated for the added standards were always higher than 96%,

thus confirming the accuracy of the procedure and its independence from the matrix effects.

Table 3.5 Results obtained for uranium determination in geothermal water samples (n:3)

Sample	Added (ng mL⁻¹)	Given (ng mL⁻¹)	Found (ng mL⁻¹)	Recovery (%)
Tap water	0		0	
	200		198±4.0	99
Soil 1	0	384	374±1.0	98
Soil 2	0	336	322±2.0	96

CHAPTER FOUR

CONCLUSION

N,N-diphenyl-N'-(3-methylbenzoyl)thiourea (o-DPMBT) and N,N-diphenyl-N'-(4-methylbenzoyl) thiourea (p-DPMBT) were immobilized on silica gel yielding a sorbent and benzoylthiourea/silica gel has high mechanical and chemical strength. The novel immobilized silica gel sorbent could be used in acidic solutions. Several optimum conditions; sorption pH, sorption time, stripping solvent, common electrolytes and diverse ions on the recovery of U(VI) were determined. Also, sorption capacity of proposed silica sorbent was investigated by batch method. In addition, characterization of novel sorbent was realised by IR spectroscopy. By using DPMBT/silica gel sorbent, separation and preconcentration of U(VI) could be possible.

The advantages of this procedure are; easiness and fastness, using of non-organic solvent in the desorption step, high percentage recovery of uranium from the resin, reusing of resin for several times, probably easy adaptation to a column technique for preconcentration and determination of uranium.

The use of DPMBT/silica for the selective extraction and recovery of uranium could possibly be extended to uranium recovery from geological, biological and radioactive wastes.

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