PRECONCENTRATION OF RARE EARTH ELEMENTS (REEs) USING SILICA GEL MODIFIED WITH SEVERAL FUNCTIONAL GROUPS

A Thesis Submitted to the Graduate School of Engineering and Sciences of İzmir Institute of Technology in Partial Fulfillment of the Requirements for the Degree of

MASTER OF SCIENCE

in Chemistry

by
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July 2007
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ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my supervisor, Assoc. Prof. Dr. Ahmet EROĞLU, for his supervision, guidance, support, and encouragement throughout my study. I am also grateful to my co-supervisors Assoc. Prof. Dr. Talal SHAHWAN and Assist. Prof. Dr. Ali ÇAĞIR for their valuable recommendations.

I specially express thanks to members of the thesis committee, Prof. Dr. Emür HENDEN, Assoc. Prof. Dr. Nusret ERTAŞ and Assoc. Prof. Dr. Durmuş ÖZDEMİR for their valuable comments.

I would like to thank to research specialists Oya ALTUNGÖZ and Sinan YILMAZ for their contributions during the ICP-MS and ICP-OES analyses. Special thanks to Evrim YAKUT and Duygu OĞUZ at Material Research Center for their help in performing SEM/EDX and TGA analyses.

Also I deeply appreciate the support of my friend Rsch. Assist. Kader REYHAN. Special thanks to my friends Ayşegül ŞEKER, Ezel BOYACI, Nazlı EFECAN, Özge TUNUSOĞLU, Elif KUMRAL and Meral KARACA for their helps during laboratory studies.

Finally, I would like to thank to my family for their support, encouragement, and understanding.

ABSTRACT

PRECONCENTRATION OF RARE EARTH ELEMENTS (REEs) USING SILICA GEL MODIFIED WITH SEVERAL FUNCTIONAL GROUPS

Determination of rare earth elements (REEs) in environmental samples can be performed by inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS), in addition to other spectrometric and chromatographic methods. Although these plasma-based techniques offer a good quality data for the determination of REEs, an efficient separation/preconcentration technique prior to instrumental measurements may still be required due to low concentrations and the presence of heavy matrix, in order to achieve accurate and reliable results.

In this study, silica gel modified with various organic compound containing S and N functional groups was proposed as adsorbent material for preconcentration of REEs in environmental waters before ICP-MS determination. These organic compounds are (3-aminopropyl)trimethoxysilane (APTMS), (3-mercaptopropyl)trimethoxysilane (MPTMS), 2–aminophenol, 2-aminothiophenol, 2-aminobenzothiazole and L-glutamic acid dimethyl ester. It was shown that REEs can be sorbed by only APTMS and MPTMS modified silica gel quantitatively in a broad pH range (pH>3). At high REEs concentration APTMS modified silica gel (silica-amino) worked better than silica gel. Up to 10.0 mg/L, silica-amino have sorbed higher than 80% of the REEs while silica gel could sorb only 30% of them. Among the sorbents investigated silica-amino was chosen for subsequent experiments. Desorption from APTMS modified silica and silica gel was realised with 1.0 M HNO_3. Spike recovery tests were performed in various water types including ultra pure water, sea water, tap water and geothermal water and were found to change between 81-110%.

ÖZET

NADİR TOPRAK ELEMENTLERİNİN ÇEŞİTLİ FONKSİYONEL GRUPLARLA MODİFİYE EDİLMİŞ SİLİKA JEL İLE ÖN-DERİŞTİRİLMESİ

Çevre örneklerindeki nadir toprak element tayinleri genellikle spektrometrik ve kromatografik tekniklerinin yanı sıra plazma teknikleri (endüktif eşleşmiş plazma optik emisyon spektrometri, ICP-OES, ve endüktif eşleşmiş plazma kütle spektrometri, ICP-MS) ile gerçekleştirilmektedir. Plazmaya dayalı bu teknikler nadir toprak elementlerinin tayini için etkili yöntemler olarak bilinse de; bu elementlerin derişimlerinin çok düşük olması ve numunelerin içerdiği ağır matriksten dolayı, doğru ve güvenilir sonuçlar elde etmek için enstrümantal ölçümlerden önce etkili bir matriks ayırma/ön-deriştirme işlemi gerekmektedir.

Bu çalışmada, silika jele N ve S fonksiyonel grup içeren çeşitli organik gruplar takılmaya çalışılmıştır. Modifiye silika jelin, çevre örneklerindeki nadir toprak elementlerinin ICP-MS veya ICP-OES ile tayininden önce ön-deriştirilmesinde kullanılması önerilmektedir. Bu organik gruplar (3-aminopropil)trimetoksisilan, (3-merkaptopropil)trimetoksisilan, 2-aminofenol, 2-aminotiyofenol, 2-aminobenzotiazol ve L-glutamik asit dimetil esterdir. Çalışmalar nadir toprak elementlerinin sadece (3-aminopropil)trimetoksisilan, (3-merkaptopropil)trimetoksisilan modifiye edilmiş silika jel tarafından geniş bir pH aralığında tutunduklarını (pH>3) göstermiştir. Yüksek derişimlerde yapılan sorpsiyon çalışmalarında, silika-aminonun, 10.0 mg/L'ye kadar olan derişimlerdeki nadir toprak elementlerini %80'den daha fazla bir oranda tuttuğu bulunurken, silika jel sadece %30'unu tutabilmiştir. Sorbentten geri alma çalışmalarında, 1.0 M HNO_3 kullanılmıştır. Takip eden çalışmalar silika-amino ile gerçekleştirilmiştir. Deiyonize su, çeşme suyu, deniz suyu ve jeotermal sulara dışardan yapılan katımların geri kazanım testlerinde (spike recovery tests), %81-110 arasında değişen değerler elde edilmiştir.

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CHAPTER 1

RARE EARTH ELEMENTS (REEs)

1.1. Introduction to Rare Earth Elements (REEs)

In the last row of Mendeleev's periodic table there are two series of metals: the lanthanoids (the 14 elements that follow lanthanum in the periodic table) and actinoids (the 14 elements following actinium). Lanthanum and lanthanoids are called rare earth elements (REEs).

The term rare earths was propound by Johann Gadolin in 1794 (Evans 1997). In fact they are neither rare nor earths. Rare earth elements were called "rare" because just after their discovery they thought to be present in the earth's crust only in a small amounts, and "earths" because their oxides have an earthy appearance (Evans 1997).

Rare earth elements include lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. Scandium and yttrium members of Group IIIB transition metals although not a lanthanoid are generally included with the REEs since they occur with them in natural minerals and have similar chemical properties. These are shown in Figure 1.1. The REEs are usually classified into three groups:

i. The light REEs: from lanthanum to promethium
ii. The medium REEs: from samarium to holmium
iii. The heavy REEs: from erbium to lutetium

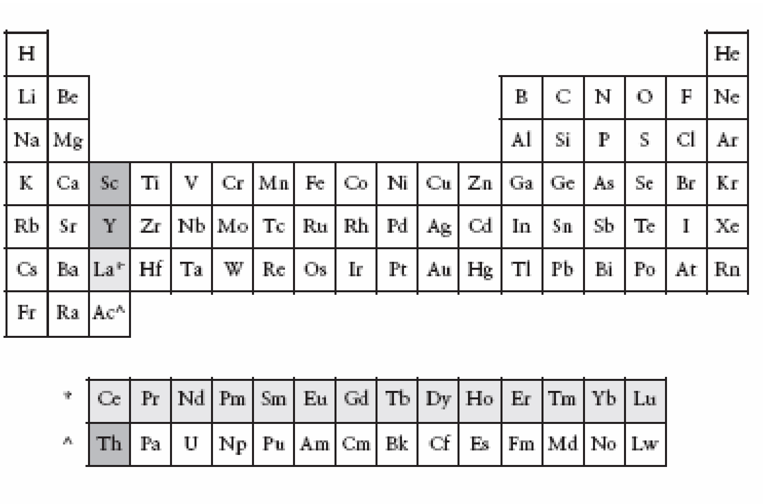


Figure 1.1. Periodic table with rare earth elements and scandium, yttrium and thorium. (Source: Pasinli 2004)

Despite their names, rare earth elements are not rare in nature except promethium which is a radioactive element. Cerium (60 mg/kg), lanthanum (34 mg/kg) and neodymium (33 mg/kg) are the most common and they are all more abundant than lead (10mg/kg) (Cotton 1988). Lutetium and thulium are the least abundant (about 0.5 mg/kg) while the concentration of the remainder ranges from 1 to 9 mg/kg. Thus even the scarcest, thulium is as common as Bi and more common than arsenic, cadmium, mercury or selenium **(**Cotton 1994).

REEs have similar chemical and physical properties. They look like silver, silvery-white or grey in colour. REEs are strong reducing agents and their compounds are generally ionic. Most of the REEs are trivalent. Europium, samarium and ytterbium also have a valence of +2 and cerium, terbium and praseodymium have a valence of +4. Europium, followed by cerium, are the most reactive elements of the REEs. They never exist as pure elements in nature. Bastnaesite [$(Ce,La)(CO_3)F$], monazite [$(Ce,La,Nd,Th)(PO_4)$] [$(REE)PO_4$] and xenotime [YPO_4] are the main ores for lanthanoids (Evans 1997).

1.2. Uses of REEs

The REEs find various applications in many different fields. At present, metallurgy utilizes 30% of lanthanides and their compounds which is used to remove oxygen and to enrich steel. They are used as catalysts/chemicals (39%), in glass/ceramic industry (25%) and in electronics (6%). High purity indivudial REEs are increasingly used as major components in lasers (e.g. halogenes of neodymium, holmium and erbium), phosphors, magnetic bubble memory films, permanent magnets (alloys of samarium and neodymium) refractive index lenses, fibre optics cathode ray tubes and superconductors. They are also used as magnetic resonance imaging (MRI) contrast reagents in medicine. $LaCl_3$ is added to chemical fertilizers in China (Qui et al. 2000a, Liang et al. 2005a and Prasada et al. 2004). Their industrial uses are summarised in Table 1.1.

1.3. Biological Effects of REEs

Since lanthanides and their compounds have a broad application in industry, there is an increased risk of their penetration into humans and animals, which may affect their metabolic processes (Nakamura et al. 1997). Although so far there is no reported incidence of intoxication because of the intake of REEs through to food chain, several deleterious effects due to occupational and environmental exposure to REEs have been reported (Sabbioni et al. 1982 and Sax 1984). As indicated in the report, REEs have both positive and negative effects on human healths. For instance, REEs show benefit in the liver where gadolinium selectively inhibits secretion by Kupffer cells and it decreases cytochrome P450 activity in hepatocytes, thus protecting liver cells against toxic products of xenobiotic biotransformation. Praseodymium ion (Pr^{3+}) produces the same protective effect in liver tissue cultures. Cytophysiological effects of lanthanides appear to result from the similarity of their cationic radii to the size of Ca^{2+} ions. Trivalent lanthanide ions, especially $La^{3+}$and Gd^{3+}, block different calcium channels in human and animal cells. Lanthanides can affect numerous enzymes: $Dy^{3+}$and La^{3+} block Ca^{2+} -ATPase and Mg^{2+} -ATPase, while Eu^{3+} and Tb^{3+} inhibit calcineurin. In neurons, lanthanide ions regulate the transport and release of synaptic transmitters and block some membrane receptors, e.g. GABA and glutamate receptors (Palazs et al. 2000).

Table 1.1. Industrial uses of REEs
(Source: WEB_1)

Element	**Application**
Lanthanum	Ceramic glazes, high quality optical glass, camera lenses, microwave crystals, ceramic capacitors, glass polishing, petroleum cracking.
Cerium	Glass polishing, petroleum cracking catalysts, alloys with iron for sparking flints for lighters, with aluminium, magnesium and steel for improving heat and strength properties, radiation shielding, many others.
Praseodymium	Yellow ceramic pigments, tiles, ceramic capacitors.with neodymium in combination for goggles to shield glass makers against sodium glare, permanent magnets, cryogenic refrigerant.
Neodymium	Ceramic capacitors, glazes and coloured glass, lasers, high strength permanent magnets as neodymium-iron-boron alloy, petroleum cracking catalysts.
Promethium	Radioactive promethium in batteries to power watches, guided missile instruments, in harsh environments.
Samarium	In highly magnetic alloys for permanent magnet as samarium-cobalt alloy, probably will be superseded by neodymium.glass lasers, reactor control and neutron shielding.
Gadolinium	Solid state lasers, constituent of computer memory chips, high temperature refractories, cryogenic refrigerants.
Terbium	Cathode ray tubes, magnets, optical computer memories; future hard disk components, magnetostrictive alloys.
Dysprosium	Controls nuclear reactors, alloyed with neodymium for permanent magnets, catalysts.
Holmium	Controls nuclear reactors, catalysts, refractories.
Erbium	In ceramics to produce a pink glaze, infrared absorbing glasses.
Thulium	X-ray source in portable x-ray machines.
Lutetium	Deoxidiser in stainless steel production, rechargeable batteries, medical uses, red phosphors for colour television, superconductors.
Yttrium	Deoxidiser in stainless steel production, rechargeable batteries, medical uses, red phosphors for colour television, superconductors.
Scandium	X-ray tubes, catalysts for polymerisation, hardened Ni-Cr superalloys, dental porcelain.
Thorium	Gas mantles, as nuclear fuel in place of uranium.

1.4 Determination of REEs

Since the use of REEs in industrial applications has been increased, the possibility of their release into the environment has also increased. Accurate and precise analytical methods are thus needed for their determination in various samples.

Neutron activation analysis (NAA) (Figueiredo et al. 2002 and Minowa et al. 2003), isotope dilution mass spectrometry (IDMS) (Shaw et al. 2003 and Greaves et al. 1989), inductively coupled plasma optic emission spectrometry (ICP-OES) (Pasinli et al. 2005, Djingova et al. 2002, Rucandio et al. 1997 and Liang et al. 2005a) and inductively coupled plasma mass spectrometry (ICP-MS) (Hirata et al. 2002, Inagaki et al. 2000 and Vicente et al. 1998) are the most frequently employed analytical techniques for the determination of REEs. Among these, neutron activation analysis (NAA) and isotope dilution mass spectrometry (IDMS) are time consuming and require very sophisticated equipment, thus, are unaccessible to most laboratories. Inductively coupled plasma optic emission spectrometry (ICP-OES) is one of the most effective multi-element techniques for determination of many trace elements including REEs. Instrumental detection limits are stated to be in the order of 50 μg/L. (Djingova et al. 2002). A more recent technique for determination of REEs is ICP-MS with detection limits in the order of sub μg/L. It also provides multielement detection capability, high sensitivity and wide linear dynamic range which allows direct determination of trace metals at ppt (ng/L) levels (Pedriera et al. 2002).

ICP-MS has been widely used in the determination of trace REEs. For example Zhang et al. developed a method based on 2-ethylhexyl hydrogenethylhexyl phosphonate (EHEHP) extraction chromatographic separation for trace of REEs impurities and Sm matrix prior to ICP-MS detection (Zhang et al. 2007). Zhu et al. developed a chelating resin-packed Chelex 100 minicolumn for preconcentration of REEs in seawater before ICP-MS determination (Zhu et al. 2006). They preconcentrated the seawater 20 fold by loading the mini column with 50 mL of seawater eluting with 2.25 mL of 2 M HNO_3 and adding 0.25 mL of internal standard. They showed that detection limits for REEs ranged from 0.06 ng/L for Lu to 0.5 ng/L for Sm can be obtained. Ming et al. used ICP-MS for the determination of REEs in human hair and and wheat flour (Ming et al. 1998). They compare three sample digestion methods, dry ashing, microwave digestion and open vessel acid digestion for biological samples and showed there is no statistical difference in these methods with respect to accuracy.

Pedreira et al. separated and determined several REEs in a highly pure neodymium oxide, by HPLC and ICP-MS (Pedreira et al. 2003). Murakami et al. extracted REEs from seawater by using bis(2-ethyl-hexyl)hydrogen phosphate (HDEHP) impregnated porous PTFE filter tube then the sorbed REEs were quantitatively eluted by 5 M HCl and determined with ICP-MS (Murakami et al. 2005).

1.5. Preconcentration and Separation of REEs

Athough ICP-MS is one of the most suitable techniques for determination of REEs and has the abilitiy to detect trace elements at sub-μg/L levels, it suffers from problems of ionization suppression by matrix elements, isobaric polyatomic interferences and clogging of sample introduction system when a sample containing high dissolved salts like seawater. To overcome these difficulties efficient preconcentration of REEs and their separation from matrix is required.

Co-precipitation has been one of the most widely used techniques for separation and preconcentration of REEs. For example Roychowdhury et al. precipitated REEs and Y as oxalates using calcium as carrier (Roychowdhury et al. 1989). The oxalate and precipitate is ignited to the oxide, which is then dissolved in dilute nitric acid and the solution is used for ICP-OES measurements. Greaves et al. extracted rare earth elements by co-precipitation with hydrated iron (III) oxide and purified them on a single cation-exchange column by using hydrochloric and nitric acids as eluents (Greaves et al. 1989).

Liquid-liquid extraction is another type of separation technique used for REEs. Wang et al. performed selective extraction of yttrium from heavy lanthanides by liquid–liquid extraction using a novel organic carboxylic acid extractant *s*-Nonylphenoxy acetic acid (CA-100) in the presence of the complexing agent, such as EDTA, DTPA, and HEDTA (Wang et al. 2004). Tsurubo et al. improved the extraction of REEs with bis(2-ethylhexy1)-phosphoric acid (DEHPA), one of the most important acidic organophosphorus extractants for lanthanides, by using 18-crown-6 ether, an ion size selective masking reagent (Tsurubo et al. 1995). Nakashima et al. used ctyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethyl phosphine oxide (CMPO) for extraction of rare earth metals into ionic liquids from aqueous solutions (Nakashima et al. 2005). Ion exchange techniques have also been employed for preconcentration and separation of REEs.

Djingova et al. used Dowex 50WX8 cation exchange resin for the determination of the rare earth elements in soils and sediments (Djingova et al. 2002). Rucandio used the same cation exchange resin for the determination of 14 rare earth elements (REEs) and Y in geological materials (Rucandio 1997). In this study separation of REEs from barium (Ba) was also achieved. Dowex 50WX8 was also utilized by Rimskaya in another study for determination of REEs in sulfide minerals (Rimskaya 2003). Inakagi and Haraguchi preconcentrated REEs by heating the perchloric acid digested human blood serum sample solution with Chelex-100 resin (Inakagi and Haraguchi 2000). Cao et al. developed an effective procedure to avoid spectral interference from ligtht REEs and barium polyatomic ions on heavy REEs in ICP-MS with AG50W-X8 cation exhange chromatography (Cao et al. 2001). Qin et al. used a 2-ethylhexyl hydrogen 2-ethylhexylphosphonate resin as the stationary phase and dilute nitric acid as the mobile phase (Qin et al. 2000b). Möller et al. used Chelex-100 chelating resin for preconcentration of REEs in seawater (Möller et al. 1992).

In addition to other preconcentration and separation techniques, solid phase extraction (SPE) technique has been increasingly popular in recent years (Shabani et al. 1992, Esser et al. 1994, Lorena et al. 1998, Bahramifar et al. 2005, Liang et al. 2005b, Wang et al. 2006, Jain et al. 2007, Vicente et al. 1998 and Hirata et al. 1992). Solid phase extraction relies on partitioning between a liquid (sample matrix) and a solid (sorbent) phase. This sample treatment technique enables the concentration and purification of analytes from solution by sorption on a solid sorbent. The basic approach involves passing the liquid sample through a column, a cartridge, a tube or a disk containing an adsorbent that retains the analytes. After all of the sample has been passed through the sorbent, retained analytes are subsequently recovered upon elution with an appropriate solvent. SPE has several advantages (i) it is simple to implement, (ii) it offers high preconcentration factor to be attained, (iii) it enables rapid phase seperation, and (iv) it is easily incorporated into automated analytical techniques.

This method is widely used in chromatographic preconcentration and it can be applied in two different forms. These are batch and column method. In our study we used batch method. In the batch method, a quantity of the chromatographic stationary phase or sorbent is added to the sample and the mixture is shaken for a specified time. Then the sorbent was separated from sample solution by filtration. Finally the resultant solution is analysed by an appropriate method.

Column preconcentration can be applied either off-line or on-line. In off-line method the solution sample is passed through a suitable column and the resultant solution is analysed by a suitable procedure. In the on-line method, the column containing the sorbent is coupled directly to the analytical instrument. Thus, the sample enrichment, desorption and analysis steps can be performed at the same run automatically.

1.5.1. Preconcentration Using Silica Gel Modified with Various Functional Groups

New types of SPE sorbents, such as naphthalene, silica and silica gel, glass beads, cellulose, polyurethane foam, molecular imprinted polymers (MIPs) and other supports, are currently being developed to allow more effective extractions.

Silica gel can be used as a very successful adsorbing agent as it does not swell or strain, has good mechanical strength and can undergo heat treatment. In addition, chelating agents can be easily loaded on silica gel with high stability, or be bound chemically to the support, affording a higher stability. The surface of silica gel is characterized by the presence of silanol groups, which are known to be weak ion-exchangers, causing low interaction, binding and extraction of ionic species (Kvitek et al. 1982). In particular, silica gel presents high sorption capacity for metal ions, such as Cu, Ni, Co, Zn or Fe (Sarkar et al. 1996). Retention is highly dependent on sample pH with quantitative retention requiring pH values over 7.5–8, as under acidic conditions silanol groups are neutral and the ion-exchange capacity of the silica gel is greatly reduced or even decreased to zero at low pHs. In addition, this sorbent has a very low selectivity, and is prone to hydrolysis at basic pH. Consequently, modification of the silica gel surface has been performed to obtain solid sorbents with greater selectivity.

In most of the methods for preparation of immobilized silica gel, a two-step procedure has been used for loading the surface with specific organic compounds, physical adsorption and chemical immobilization. In the first method, the organic compound is directly adsorbed on the silanol group of silica gel surface (impregnated or loaded sorbent), either by passing the reagent solution through a column packed with the adsorbent (Liang et al. 2005b), or by shaking the adsorbent in the reagent solution (Lorena et al. 1998). In the second approach, a covalent bond is formed between the silica gel surface groups and those of the organic compound (functionalized sorbent). Chemisorption of chelating molecules on silica surface provides immobility, mechanical stability and water insolubility, thereby increasing the efficiency, sensitivity and selectivity of the analytical applications (Jal et al. 2004). Chemical modification of silica surface by organic chelating group acts as ion-exchanger, which provides greater selectivity for the analyte than that offered by traditional ion-exchanger. The most convenient way to develop a chemically modified surface is by simple immobilization (or fixing) of the group on the surface by adsorption or electrostatic interaction or hydrogen bond formation of other type of interaction. Simple impregnation of the solution of modifiers or covalent binding, the so called covalent grafting of the chelating molecule to silica matrix via silanization, is the common practice of developing a functionalized silica surface.

Several organic functional groups have been immobilized to the silica gel surface in preconcentration studies. For example Mahmoud et al. used silica gel phase-impregnated with dithizone for selective extraction and solid phase pre-concentration of mercury(II) from aqueous and natural water samples (Mahmoud et al. 2000). P´erez-Quintanilla et al. modified mesoporous silicas (SBA-15 and MCM-41) with 2-mercaptothiazoline for mercury removal from aqueous media (P´erez-Quintanilla et al. 2006). Pu et al. studied 2-mercaptobenzothiazole-modified silica gel for the flow injection on-line preconcentration–separation and determination of silver by flame atomic absorption spectrometry (Pu et al. 1998). Ekinci and Köklü prepared (3-aminopropyl)triethoxysilane modified silica-gel for the separation and preconcentration of vanadium, silver, manganese and lead prior to their determination by graphite furnace atomic absorption spectrometry (Ekinci and Köklü 2000). The same sorbent was used for solid-phase extraction of bismuth, lead and nickel from seawater by Tokman et al. (Tokman et al. 2003). Hassanien et al. functionalized silica gel with (3-aminopropyl)trimethoxysilane (Hassanien et al. 2006). Then obtaining aminopropylsilica gel (APSG) was reacted with morin yielding morin-bonded silica gel. The prepared sorbent was then used for separation and preconcentration of Ag(I), Au(III), Pd(II), Pt(II) and Rh(III) from aqueous medium. Roldan et al. determined copper, iron, nickel and zinc in gasoline by FAAS after sorption and preconcentration on silica modified with 2-aminothiazole groups (Roldan et al. 2005). Göktürk et al. preconcentrated germanium using silica having mercapto functional groups, determined it by hydride generation flame atomic absorption spectrometry HGAAS (Göktürk et al.

2000). Garg et al. synthesised *o*-vanillin-immobilized silica gel for the adsorption and estimation of copper, cobalt, iron and zinc by both batch and column techniques (Garg et al. 1999). Safavi et al. synthesised glycerol-bonded silica gel as a new sorbent for effective preconcentration of traces of Co(II) in aqueous solutions (Safavi et al. 2006). Evangelista et al. used hexagonal mesoporous silica modified with 2-mercaptothiazoline for removing mercury from water solution (Evangelista et al. 2007). Mahmoud prepared Eriochrome black-T indicator immobilized silica gel. Then this sorbent was used as phase extractor for zinc (II) and magnesium (II) from calcium (II) (Mahmoud 1997).

1.6. Aim of this Work

The purpose of this study is to develop a sensitive enrichment/matrix separation procedure for the determination of REEs in environmental water samples. For this purpose for modification of silica gel different strategies were followed. In the first strategy silica gel was synthesised by sol-gel method (Eroğlu 1996) and after synthesis its surface was modified with (3-mercaptopropyl)trimethoxysilane (MPTMS). In the second approach (3-aminopropyl)trimethoxysilane (APTMS) was modified during sol-gel process. In another approach commercial silica gel was modified with MPTMS, APTMS, L-glutamic acid dimethyl ester, 2-aminophenol, 2-aminothiophenol and 2-aminobenzothiaozole. Sorption capability of these synthesised sorbents towards REEs were investigated and APTMS-modified silicagel (silica-amino) was suggested as a proper sorbent for subsequent studies. The efficiency of silica-amino was evaluated through preconcentration and recovery studies. Determination of REEs concentrations were obtained by ICP-MS or ICP-OES.

CHAPTER 2

EXPERIMENTAL

2.1. Chemicals and Reagents

All chemicals were of analytical reagent grade. Ultra pure water (18MΩ) was used throughout the study. Glassware and plasticware were cleaned by soaking in 10% v/v nitric acid and rinsed with distilled water prior to use.

i) Standard multi-element REEs stock solution (1000 mg/L) was prepared by dissolving 0.3117 g of lanthanum nitrate haxahydrate ($La(NO_3)_3.6H_2O$), 0.3100 g of cerium nitrate hexahydrate ($Ce(NO_3)_3.6H_2O$), 0.2397 g of praseodymium oxide (Pr_2O_3), 0.1166 g of neodymium oxide (Nd_2O_3), 0.1156 g of samarium oxide (Sm_2O_3), 0.1158 g of europium oxide (Eu_2O_3), 0.1153 g of gadolinium oxide (Gd_2O_3), 0.1148 g of dysprosium oxide (Dy_2O_3), 0.1146 g of holmium oxide (Ho_2O_3), 0.1147 g of erbium oxide (Er_2O_3), 0.1139 of ytterbium oxide (Yb_2O_3) in 60 mL of ultrapure water, 5 mL of conc. HNO_3 and 3 mL of conc. HCl was added and heating and stirring with magnetic stirrer until completely dissolution was obtained. Then the solution was transferred to 100 mL volumetric flask and diluted to mark with ultra pure water.

iii) Calibration standards were prepared daily from multi-element REEs stock solution.

iii) Tetraethylortosilicate (TEOS) (Merck), (3-mercaptopropyl)trimethoxysilane (MPTMS) (Fluka), (3-aminopropyl)trimethoxysilane (APTMS) (Fluka), 2-aminophenol (Fluka), 2-aminothiophenol (Fluka), 2-aminobenzothiazole (Merck), (3-chloropropyl) triethoxysilane (CPTS) (Alfa Aesar) and L-glutamic acid dimethyl ester hydrochloride (Alfa Aesar) were used as received.

iv) pH adjustments were prepared with HNO_3 (Merck) (1.0 M, 0.1 M and 0.01 M) and NH_3 (Merck) (1.0 M, 0.1 M and 0.01 M) solutions.

2. 2. Instrumentation and Apparatus

2.2.1. Apparatus

In batch sorption studies, Yellowline RS 10 (Staufen, Germany) lateral shaker was used to provide efficient mixing. pH measurements were performed using InoLab pH720 pH meter .

2.2.2. Instrumentation

The REEs concentrations were determined by an Agilent 7500 ICP-MS instrument or a Varian Liberty Series II ICP Axial view optical emission spectrometer. The operating conditions were listed in Table 2.1and Table 2.2 for ICP-MS and ICP-OES, respectively.

Table 2.1. Operating parameters for Agilent 7500 ICP-MS.

Forward power	1500 W
Reflected power	1W
Coolant gas flow rate	15 L min^{-1}
Auxilary flow rate	0.90 L min^{-1}
Sample uptake time	25 sec
Integration time	100 msec
Mass of elements	^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{157}Gd, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{172}Yb
Internal Standard	^{209}Bi and ^{115}In

Table 2.2. Operating parameters for Varian Liberty Series II Axial view ICP-OES.

Monochromator	
Czerny-Turner	0.75 meters
Grating	90x100 mm holographic
Grating density	1800 grooves/mm
Detection	
R199UH UV enhanced solar blind 175-300 nm with Cs-Te photocathode for UV region R446 300-940 nm wide range with multi-alkali photocathode for visible region	
Plasma conditions	
40 MHz, axial view	
Incident power (kW)	1.2
Argon flow rates (L min^{-1})	
Plasma	15
Auxiliary	1.5
Nebulizer	0.75
Nebulizers	
Concentric Glass Nebulizer	
Concentric (Sturman-Masters double pass type) with cyclonic chamber	
Sample injection modes	
Continuous nebulization	
Signal processing	
Line measurement	Peak height
Background correction	Polynomial plotted background correction

Spectral Lines (nm)

Ce	413.380	Dy	353.170
Er	337.276	Eu	420.505
Gd	342.247	Ho	345.600
La	379.478	Nd	401.225
Pr	440.884	Sm	359.262
Yb	369.419		

2.3. Synthesis and Characterization of the Sorbents for REEs Sorption

2.3.1. Synthesis of Sorbents

2.3.1.1. Synthesis of Silica Gel by Sol-gel Method

Synthesis of silica gel by sol-gel method was carried out as described by Eroğlu (1996). In this method silica gel was synthesised using tetraethylortosilicate as starting material. 25 mL of tetraethylortosilicate, 8 mL of water and 27 mL of ethanol was mixed immediately in a beaker. The pH of the mixture was adjusted to 4.5 with $2x10^{-4}$ M HCl and stirred for 30 min. After that it was allowed to gel at room temperature for 3 days in a closed container and dried for one week at 60 °C. Finally the obtained silica gel (sol-gel) was crushed in a porcelain cup.

2.3.1.2. Synthesis of (3-Mercaptopropyl)trimethoxysilane (MPTMS)-Modified Silica Gel

MPTMS-modified silica gel (silica-mercapto) was prepared by the method reported by Göktürk et al. (2000). 5 grams of silica gel was washed with 100 mL of 0.01 M acetic acid solution under vacuum for 10 min. Then it was filtered using a vacuum pump and transferred to a round bottomed flask containing 25 mL of toluene. After that 3.0 mL of (3-mercaptopropyl)trimethoxysilane (MPTMS) was added drop by drop in order to prevent self polymerization with vigorous magnetic stirring. Later 0.15 mL of acetic acid was added dropwise and the mixture was stirred overnight. Before refluxing the solution at 60 °C for 2 h by magnetic stirring, a second volume of 0.15 mL acetic acid was added. Finally the samples were filtered using a vacuum pump and washed well with toluene before being left overnight in an oven at 80 °C. The proposed functionalization reaction is illustrated in Figure 2.1.

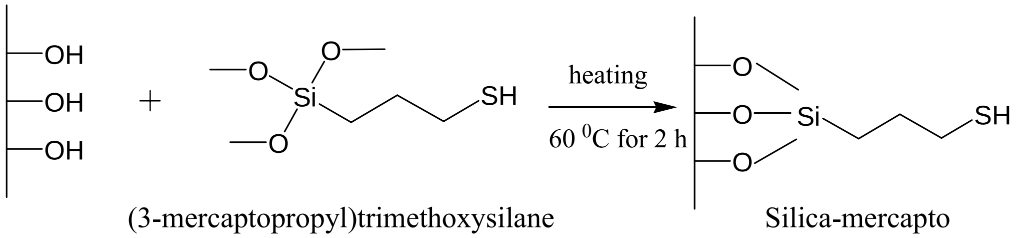


Figure 2.1. Schematic illustration of modification of silica gel with (3-mercaptopropyl) trimethoxysilane (MPTMS).

2.3.1.3. Synthesis of (3-Mercaptopropyl)trimethoxysilane (MPTMS)-Modified Silica Gel Prepared by Sol-gel Method (sol-gel mercapto)

Synthesis of MPTMS-modified silica gel (prepaired bysol-gel method) was performed as described in Part 2.3.1.2. The only difference was that sol-gel was used instead of commercial silica gel.

2.3.1.4. Synthesis of (3-Aminopropyl)trimethoxysilane (APTMS)-Modified Silica Gel (Silica-amino)

APTMS-modified silica gel was prepared using the same procedure as described in Part 2.3.1.2 but instead of MPTMS, APTMS was added to the silica gel which was suspended in 25 mL of toluene. Schematic illustration of APTMS modified silica gel with proposed functionilazion reaction is given in Figure 2.2.

2.3.1.5. Synthesis of Amino Sol-Gel Resin

In this procedure silica gel was modified with APTMS during sol-gel synthesis as reported by Eroğlu (1996). Tetraethylortosilicate (TEOS, 25 mL), water (8 mL) and ethanol (27 mL) was mixed immediately. The pH of the mixture was adjusted to 4.5 with $2x10^{-4}$ M HCl. Then 2.75 mL of APTMS was added drop by drop with cocnstant stirring After being stirred for an additional 30 min., the mixture was allowed to gel at room temperature for 3 days in a closed container and dried for one a week at 60 °C. After drying the glass were crushed in a porcelain cup.

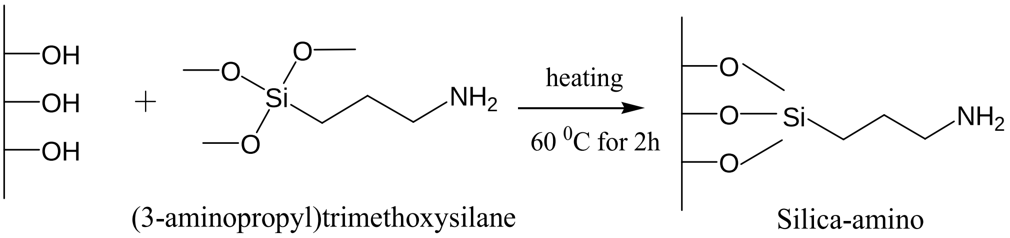


Figure 2.2. Schematic illustration of modification of silica gel with (3-aminopropyl) trimethoxysilane (APTMS).

2.3.1.6. Synthesis of L-glutamic acid dimethyl ester-Modified Silica Gel (Silica-aminoacid)

L-glutamic acid dimethyl ester hydrochloride-modified silica gel was prepared by modifying of the method reported by P′erez-Quintanilla et al. (2006). 5 g of silica gel was activated at 160 °C under vacuum for 5 h. Next activated silica gel was suspended in 50 mL of dry toluene and 5 mL (20.76 mmol) of (3-chloropropyl)triethoxysilane (CPTS) was added to this mixture. After the mixture was stirred for 48 h under reflux conditions at 110 °C under N_2 atmosphere. The resulting product was filtered off and washed with ethanol (2×30 mL), diethyl ether (2×30 mL) and dry toluene (2×30 mL). After removal of the traces of solvent at 70 °C, 150 mbar for 4 h, it was immersed in 50 mL of dry toluene and then previously prepared L-glutamic acid dimethyl ester solution was added. The mixture was stirred for 11 h at room temperature under N_2 atmosphere. Then the temparature was increased to 80 °C and heated for an additional 18 h. The resulting modified silica (silica-aminoacid) with a white color was filtered off and washed with toluene (2×30 mL), ethanol (2×30 mL) and diethyl ether (2×30 mL). Eventually, the resulting product was further dried at 70 °C at 150 mbar for 4 h. The proposed functionalization reaction is illustrated in Figure 2.3.

L-glutamic acid dimethyl ester solution was prepared by treatment of 4.8331 g (22.836 mmol) of L-glutamic acid dimethyl ester hydrochloride with 4.2502 g of Na_2CO_3 in 40 mL of water. The solution was extracted three times with 30 mL of ethyl acetate and organic phases were combined. Then organic phase was washed with 40 ml of brine solution and it was dried with $MgSO_4$. Finally the solvent was concentrated under vacuum (at 200 mbar) Thus L-glutamic acid dimethyl ester solution was obtained.

2.3.1.7. Synthesis of 2-Aminothiophenol, 2-Aminophenol and 2-Aminobenzothiazole-Modified Silica Gel

Firstly silica gel was chlorinated as described in part 2.3.1.6 using 10 g of silica gel and 10 mL of CPTS. 3.5 g of the obtained silica chloride was taken and immersed in 35 mL of dry toluene. 1.71 mL (15.98 mmol) of 2-aminothiophenol was added and the mixture was refluxed at 110 °C for 39 h under N_2 atmosphere. The resulting product (silica 2-aminothiophenol) with a yellow color was filtered off and washed well with toluene, ethanol and diethyl ether until the product did not contain unreacted reagent,. (a colorless solution was obtained after washihg steps). Finally, the resulting product was dried at 70 °C at 150 mbar for 4 h.

In each case 3.5 g of silica chloride was taken and treated with 1.7439 g (15.98 mmol) of 2-aminophenol to produce silica 2-aminophenol or 2.4010 g (15.98 mmol) of 2-aminobenzothiazole to produce silica 2-aminobenzothiazole as described above.

2-aminophenol-modified silica gel (silica 2-aminophenol) has red vine color and 2-aminobenzothiazole-modified silica gel (silica 2-aminobenzothiazole) has white color. The proposed functionalization reaction of silica gel modified with 2-aminothiophenol, 2-aminophenol and 2-aminobenzothiazole are illustrated in Figures 2.4, 2.5 and 2.6, respectively.

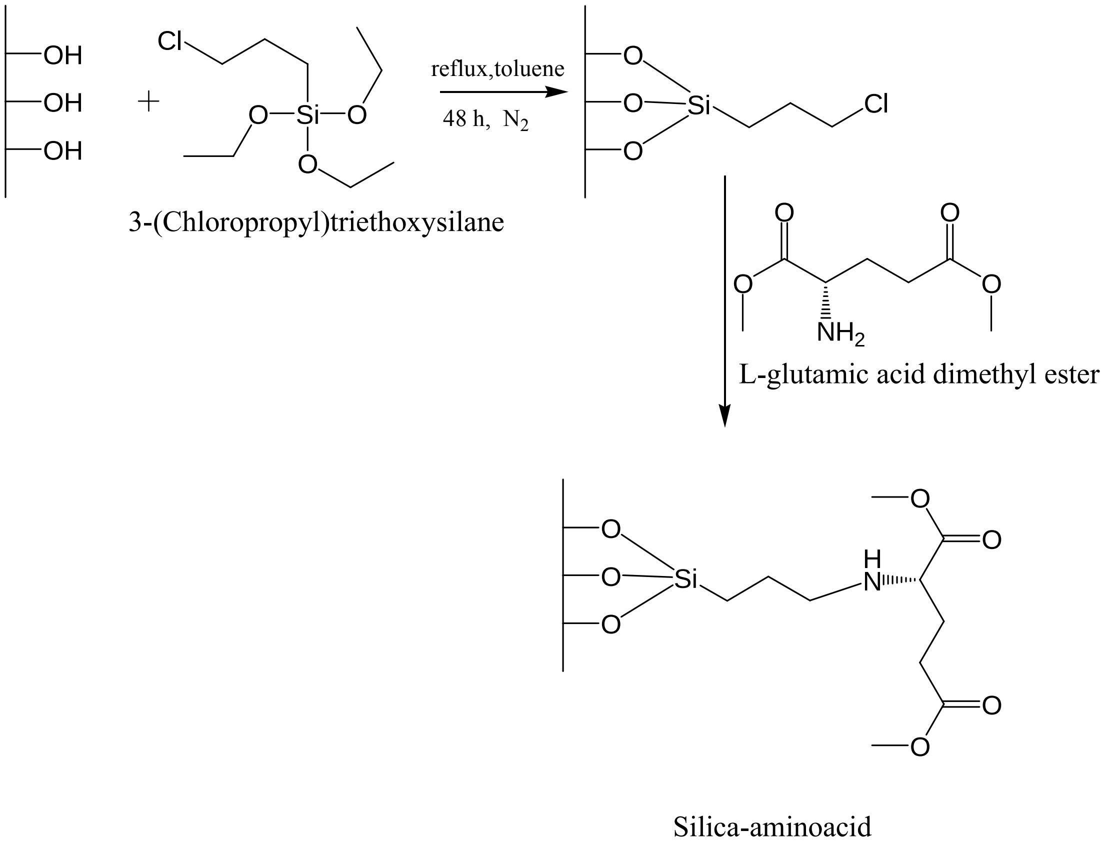


Figure 2.3. Schematic illustration of modification of silica gel with L-glutamic acid dimethyl ester.

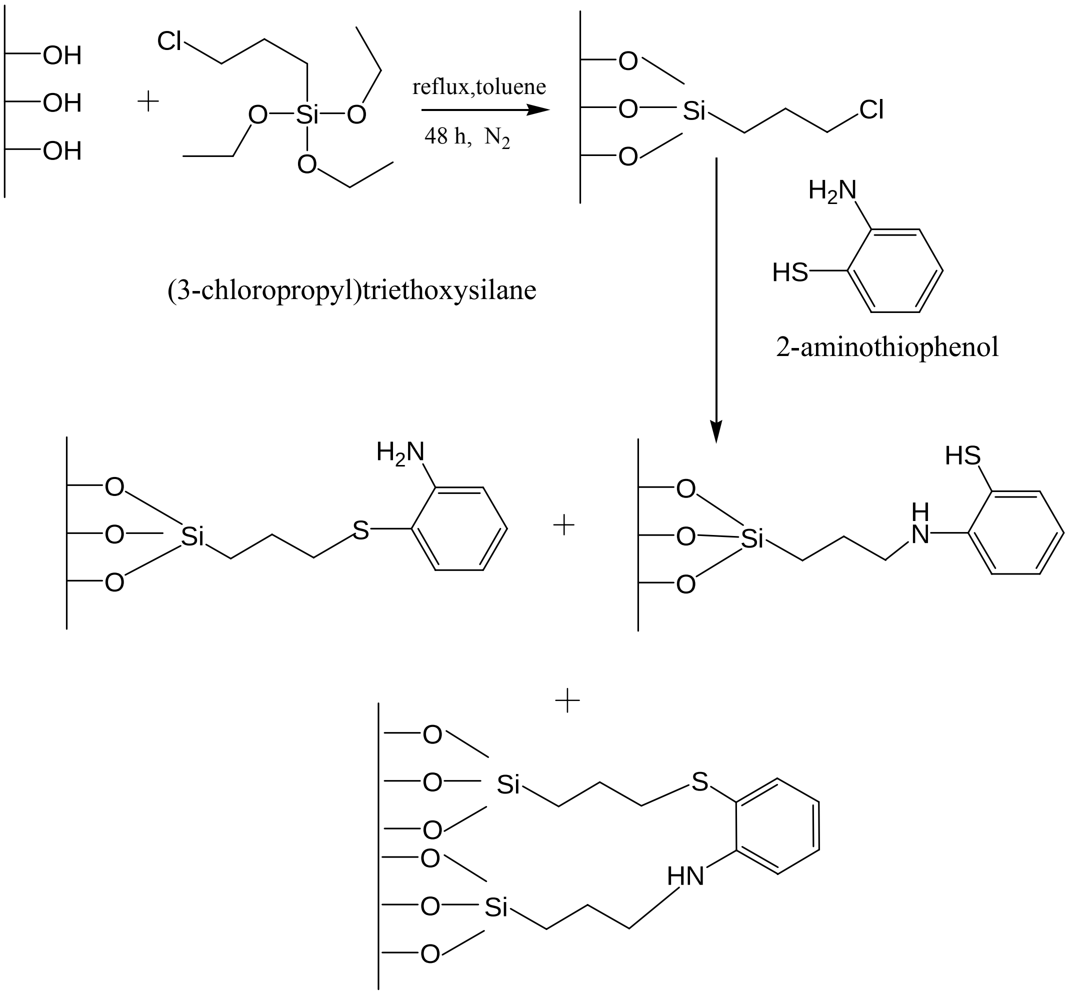


Figure 2.4. Schematic illustration of modification of silica gel with 2-aminothiophenol.

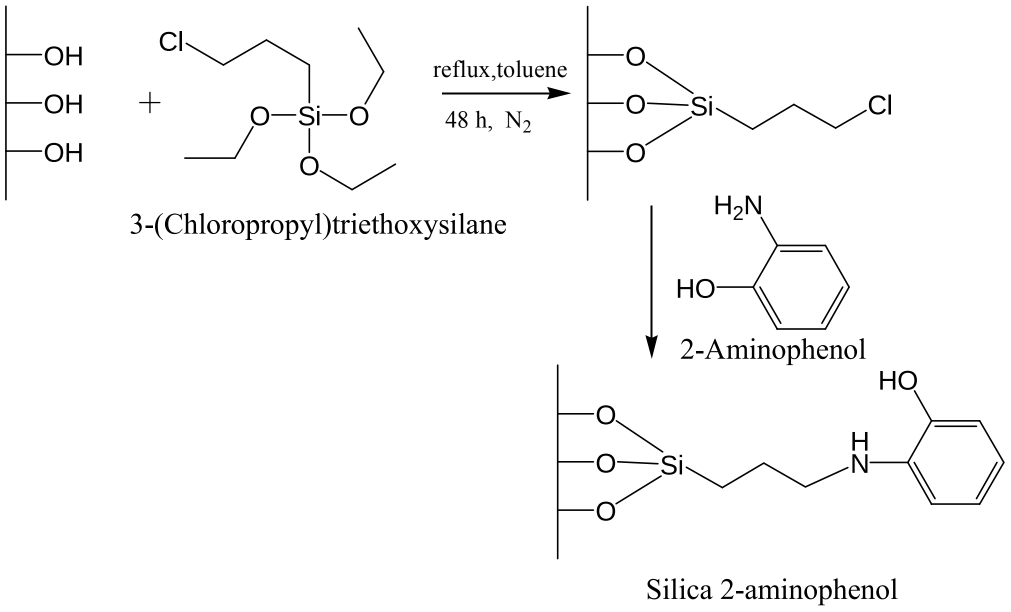


Figure 2.5. Schematic illustration of modification of silica gel with 2-aminophenol.

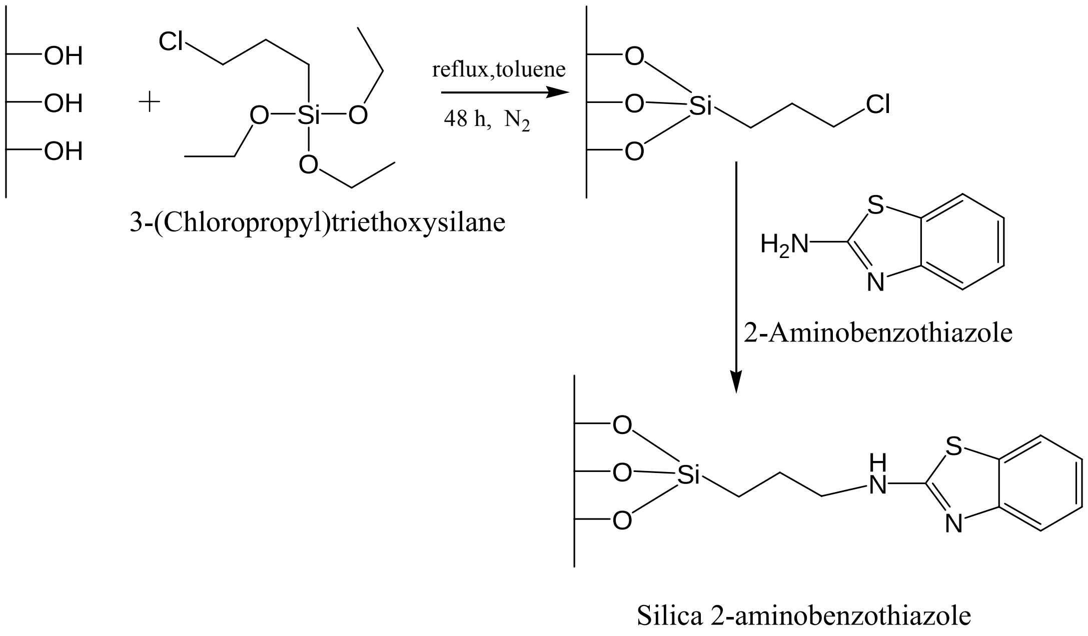


Figure 2.6. Schematic illustration of modification of silica gel with 2-aminobenzothiazole.

2.4. Characterization of the Synthesised Sorbents

Characterization of the sorbents was carried out using scanning electron microscope (SEM), elemental analysis and thermo gravimetric analysis (TGA).

2.4.1. Characterization of Sorbents Using SEM/EDX

SEM/EDX characterization was performed using a Philips XL-30S FEG type instrument. Prior to analysis, solid samples were sprinkled onto adhesive carbon tapes which were supported on metallic disks. An Energy-Dispersive X-ray Spectroscopy (EDX) analysis was carried out on randomly selected points on the solid surfaces and back-scatter electron (BSE) detector was utilized during SEM analysis. The backscatter electron detector allows materials with different compositions to be imaged as different (greyscale/atomic) contrast and it is used for the elements having a large atomic number difference between each other.

2.4.2. Elemental Analysis

Carbon, nitrogen, sulfur and hydrogen contents were determined using a Leco 932 CHNS analyser**.**

2.4.3. Thermo Gravimetric Analysis

TGA was performed using a Perkin Elmer Diamond TG/DTA instrument. The solid samples were heated from 50 °C to 800 °C by a heating rate of 10 °C/min in the presence of N_2 atmosphere.

2.5. Determination of REEs

2.5.1. Calibration Curves for REEs

Determination of REEs was performed using ICP-MS and ICP-OES with the condition given in Tables 2.1 and 2.2.

2.5.1.1. Aqueous Calibration Plot

Standard solutions from 10.0 µg/L to 1000 µg/L were prepared from 1000 mg/L multi-element REEs standard with simple dilution. All standards contained 1% (v/v) HNO_3 corresponding to a molarity of 0.144 M.

In ICP-MS studies ^{209}Bi or ^{115}In were used as internal standard. For comparison, quantitation was made by both including these internal standards and not taking them into consideration. In both cases same results were obtained. Therefore, internal standardization was only applied randomly to check any change in the response of the instrument.

2.5.1.2. Matrix-matched Calibration Plot

The matrix-matched calibration standards were prepared by applying the proposed sorption/desorption procedure using silica-amino. Among the various synthesised sorbents silica-amino exhibited better results. Therefore, for subsequent experiments silica-amino was decided to be used. In order to plot matrix-matched calibration plots of REEs, standard solutions from 0.2 mg/L to 2.0 mg/L were mixed with 0.05 g of silica-amino. The solutions were shaken manually for 1 min. and then placed on the shaker for 30 min. at room temperature. The contents were collected on filter papers and then were eluted using 1.0 M HNO_3 solution. In later experiments it was obtained that 1.0 M HNO_3 was sufficient to elute REEs from silica-amino completely. Since 1.0 M HNO_3 can damage the sampling and interface cones of ICP-MS instrument, the eluent solutions were diluted 5 times before being introduced to ICP-MS. So the diluted matrix matched standards concentration corresponded to from

0.04 mg/L to 0.4 mg/L. Graphs of counts per second versus concentration were constructed using these standards.

2.5.2. Sorption Studies

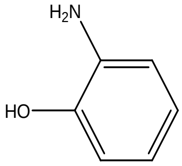
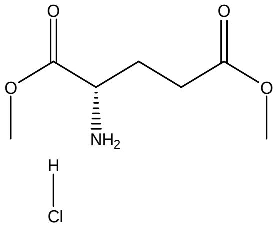
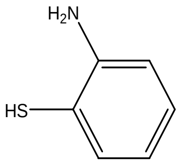
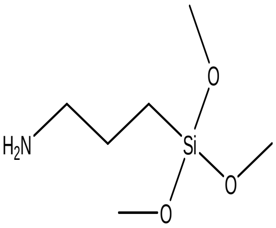
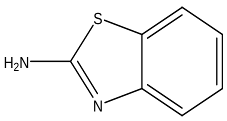
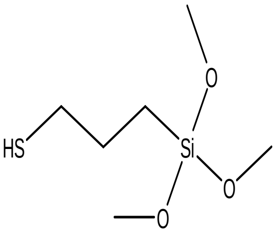
2.5.2.1. Types of Sorbents

In order to find the suitable sorbent for the sorption of REEs, silica gel was tried to be modified with several organic compunds containing S and N functional groups which are thought to react with REEs in order to remove them from solution. The modified organic compouds are given in Table 2.3. The sorption experiments were performed with the batch method. As an initial experiment, 1.0 mg/L multi-element REEs standard solution was prepared at a pH of 7 and 50 mg of the tested sorbent was added to 20.0 mL of this solution. The resulting mixture was shaken manually for 1-2 min. and then for a further 30 min. on a shaker at room temperature. At the end of the shaking period, the mixture was filtered and filtrate was analysed by ICP-MS.

2.5.2.2. Effect of pH

In order to investigate the effect of pH on the sorption of REEs, 1.0 mg/L multi-element REEs standard solutions were prepared at different pHs from pH 1 to 10. From each of these solutions 20.0 mL were taken and 50 mg of sorbent was added. The mixture was shaken for 1-2 min. manually then 30 min on a shaker. After the solid and the liquid phases were separated by filtration, the liquid parts were analysed for REEs with ICP-MS.

Table 2.3. Organic compounds used in the modification of silica gel.

2–aminophenol		L-glutamic acid dimetyl ester hydrochloride	
2–aminothiophenol		(3-aminopropyl) trimethoxysilane APTMS	
2-aminobenzothiazole		(3-mercaptopropyl) trimethoxysilane MPTMS	

2.5.2.3. Effect of Initial Metal Concentration

Sorption ability of silica gel, silica-amino and silica-aminoacid at high concentration of REEs was investigated. For an initial study, REEs solution at three different concentrations (1.0 mg/L, 50.0 mg/L and 100.0 mg/L) were prepared. 20.0 mL of these solutions (at pH 5) were taken and 50 mg of sorbent was added to each of them. Then the mixture was shaken for 1 min. manually and 30 min. on a shaker. After filtration, the filtrates were analysed with ICP-MS. More detailed experimental plan was decided to be carried out for only silica and silica-amino since silica-aminoacid did not exhibit sorption capacity higher than silica gel. So, sorption capacity of silica gel and silica amino was investigated at concentrations varying from 1.0 mg/L to 100.0 mg/L prepared at pH 5.

2.5.2.4. Effect of Shaking Time

In order to obtain efficient sorption, the optimum contact time was investigated. For this purpose, 20.0 mL of 50.0 mg/L multi-element REEs solutions at pH 5 containing 50 mg of silica gel and silica-amino were shaken from 1 min. to 4h. After filtration, the resulting solutions were analysed by ICP-OES and percent sorption was calculated.

2.5.2.5. Effect of Sorbent Amount

Determination of sorbent amount is an important factor for quantitative sorption of the analyte from the solution. So the effect of sorbent amount on sorption was examined. An amount of sorbents (silica gel and silica-amino) varying from 25 mg to 100 mg were added to 20.0 mL of 50.0 mg/L multi-element REEs solutions at pH 5 and shaken 1 min. manually then for 30 min. on a shaker. After filtration the content of REEs in solution was determined with ICP-OES.

2.5.3. Desorption from the Sorbent

After collection of REEs by silica gel and silica-amino, their release was investigated using HNO_3 at different concentrations. 20.0 mL of 1.0 mg/L multielement REEs solutions were prepared at pH 5 and 0.05 g of sorbent was added. After shaking for 30 minutes, the mixtures were filtered and the sorbent with filter paper were put into the 20.0 mL of desorbing solution. The new mixtures were shaken once again for 30 minutes. At the end of this period, the mixtures were filtered and the filtrates were analysed for their REEs content with ICP-MS.

2.5.4. Method Validation

Method validation was realised through spike recovery test with ultra pure water (UPW), tap water (TW), sea water (SW) and geothermal water (GW) samples. 20.0 mL of aliquots of sample were spiked with 1.0 mg/L multi-element REEs and mixed with silica-amino. After usual sorption procedure, the mixtures were filtered and the sorbents with filter paper were placed into 20.0 mL of 1.0 M HNO_3 for desorption. The blank solution and the calibration standards were prepared using the same procedure. For quantitation matrix-matched calibration standars were used. The concentration of REEs in the eluates was determined by ICP-MS and the percent recoveries were calculated.

CHAPTER 3

RESULTS AND DISCUSSION

3.1. Characterization of the Synthesised Sorbents

3.1.1. Characterization of Sorbents Using SEM/EDX Mapping

In order to follow the success of the modification procedures, firstly EDX mapping was applied.

EDX spectra of silica gel and silica-amino is provided in Figure 3.1. It indicates the presence of N on the sorbent surface and mapping figures (Figure 3.2 on page 31) indicates the homogenous distribution of O and N functional groups on the sorbent surface.The N atoms were observed to be representing the amine functional group.

EDX characterization and mapping microimage of silica-mercapto are given in Figures 3.3 (on page 29) and 3.4 (on page 31), respectively. From these figures the presence and homogeneous disribution of S functional group, as the matrix elements Si and O, on the surface can be seen. The S atoms were observed to be representing the mercapto functional group.

In Figure 3.5 EDX spectra of sol-gel mercapto and sol-gel are presented. The presence of S are depicted in Figure 3.5. b. The distrubiton of O, S and Si on the sorbent surface are presented in Figure 3.6. (on page 32).

EDX spectra of amino-sol-gel with N and O functional groups is shown in Figure 3.7 and the homogenous pattern of O and N functional groups bound to amino sol-gel surface can be seen in Figure 3.8 (on page 32).

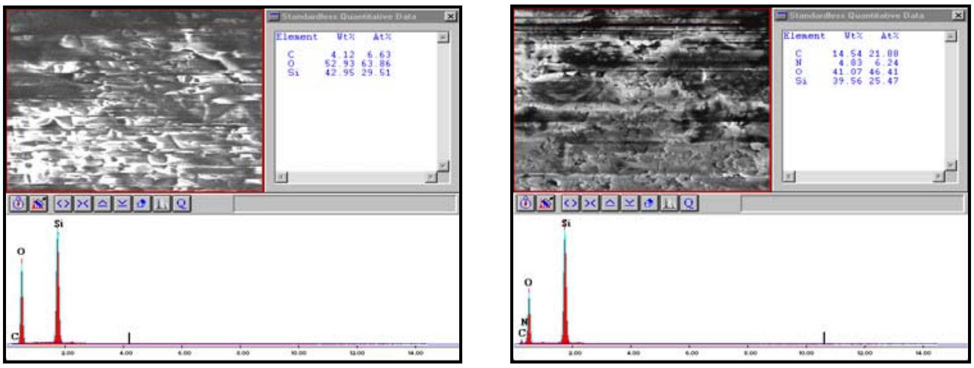
EDX results of silica 2-aminophenol, silica 2-aminothiophenol, silica 2-aminobenzothiazole and silica-aminoacid are provided in Figure 3.9. In figure 3.10 (on page 33) mapping microimage of silica 2-aminophenol are given showing N, O and S groups bounded to the silica surface. Beside these groups the presence of Cl which comes from silica chloride was also observed.

These results demonstrated that the immobilization procedures provided homogenous distribution of the functional groups on the surface of matrix for all chemical compounds investigated.

3.1.2. Elemental Analysis

Modified silica gel with different functional groups was investigated in terms of functionalization capacity. The molar contents of the attached N or S functional groups were calculated from N or S content of samples. Elemental analysis results of synthesised sorbent materials having both S and N functional groups are shown in Table 3.1. Synthesised sorbents having only N functional group are depicted in Table 3.2. Sorbents having only S functional group are presented in Table 3.3. The detailed calculations are given in Appendix A.

As it can be seen from the Tables 3.1, 3.2 and 3.3, among the sorbent materials having N functional group silica-amino gave better functionalization yield with a value of 2.29 mmol of attached N/g sample. It also can be said that commercial silica gel gave better functionalization than the synthesised with a value of 2.29 and 1.97 mmol of attached N/g sample, respectively (Table 3.2). Different functionalization capacity between purchased silica and synthesised silica can be resulted from the differences in accessible silanol groups of silica materials. When sorbent materials having S functional groups are compared it can be said that sol-gel mercapto has greater functionalization capacity with a value of 1.67 mmol of attached S/g sample

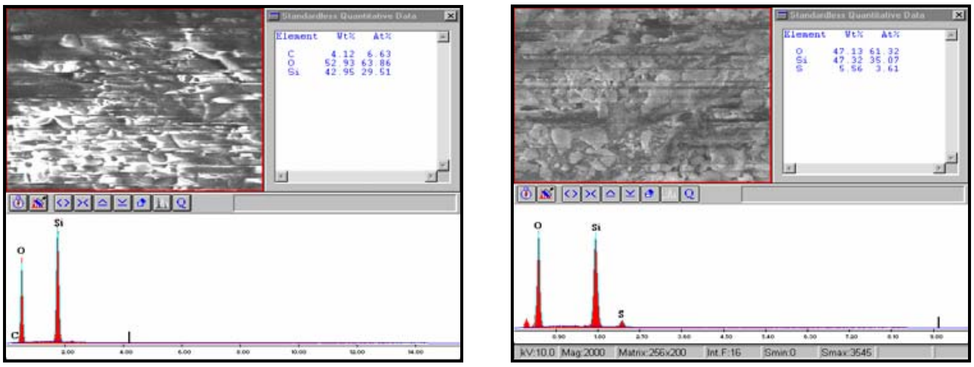


Element	Wt%	At%
C	4.12	6.63
O	52.93	63.86
Si	42.95	29.51

Element	Wt%	At%
C	14.54	21.88
N	4.83	6.24
O	41.07	46.41
Si	39.56	25.47

(a) **(b)**

Figure 3.1. EDX spectra of (a) silica gel (1000x) and (b) silica-amino (1000x).



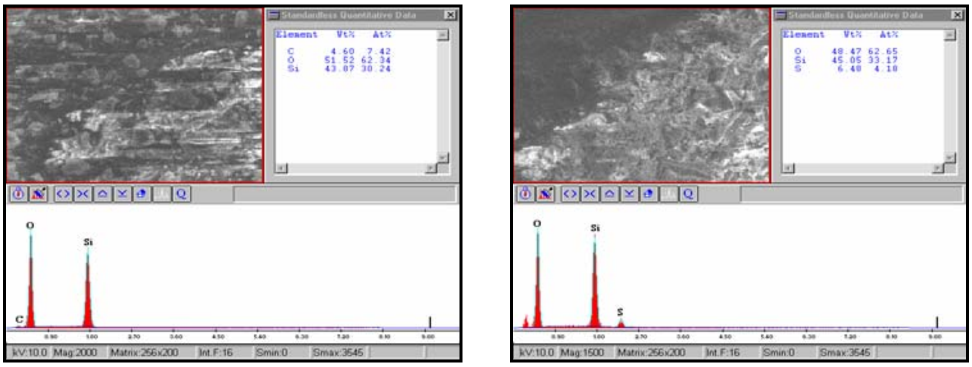
Element	Wt%	At%
C	4.12	6.63
O	52.93	63.86
Si	42.95	29.51

Element	Wt%	At%
O	47.13	61.32
Si	47.32	35.07
S	5.56	3.61

kV:10.0 Mag:2000 Matrix:256x200 Int.F:16 Smin:0 Smax:3545

(a) **(b)**

Figure 3.3. EDX spectra of (a) silica gel (1000x) and (b) silica-mercapto (2000x).



Element	Wt%	At%
C	4.60	7.42
O	51.52	62.34
Si	43.07	30.24

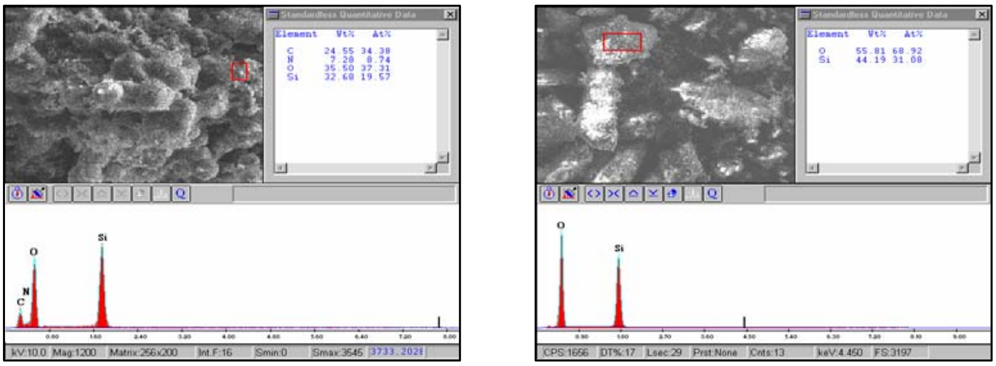
Element	Wt%	At%
O	48.47	62.65
Si	45.05	33.17
S	6.40	4.10

kV:10.0 Mag:2000 Matrix:256x200 Int.F:16 Smin:0 Smax:3545

kV:10.0 Mag:1500 Matrix:256x200 Int.F:16 Smin:0 Smax:3545

(a) **(b)**

Figure 3.5. EDX spectra of (a) sol-gel (2000x) and (b) sol-gel mercapto (1500x).

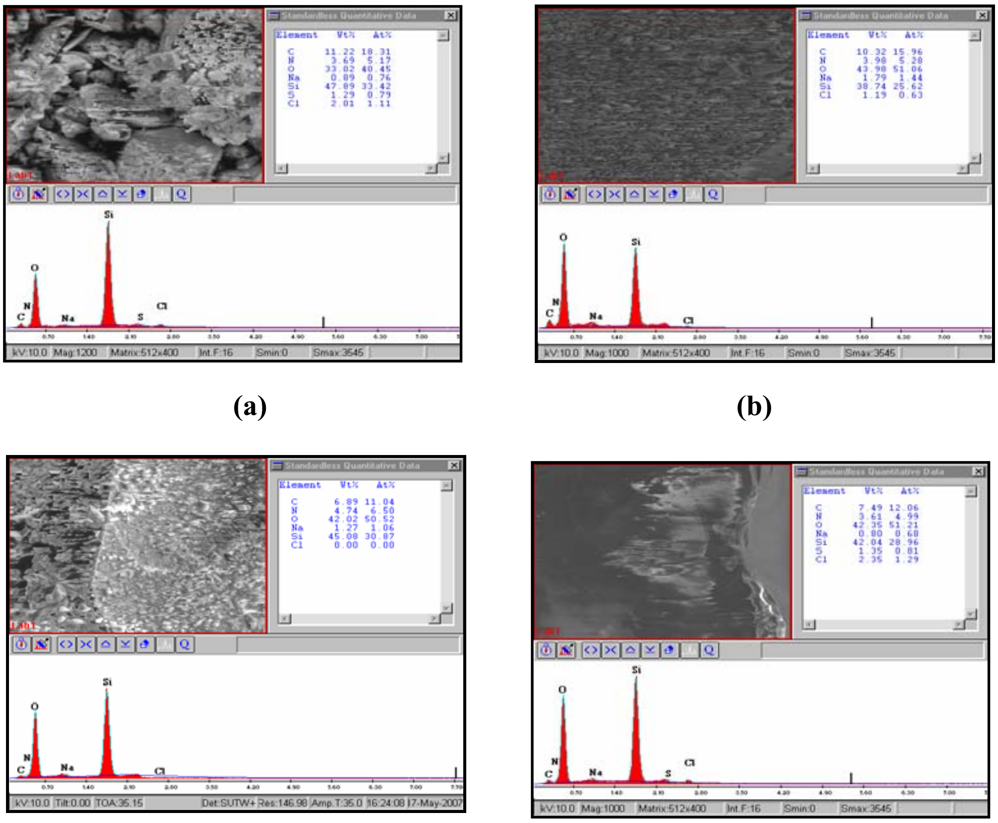


```
Element    Wt%    At%

  C       24.55  34.38
  N        7.28   8.74
  O       35.50  37.31
  Si      32.60  19.57
```

```
Element    Wt%    At%

  O       55.81  68.92
  Si      44.19  31.08
```

(a) **(b)**

Figure 3.7. EDX spectra of (a) amino sol-gel (1200x) and (b) sol-gel (2000x).



```
Element    Wt%    At%

  C       11.22  18.31
  N        3.69   5.17
  O       33.02  40.45
  Na       0.89   0.76
  Si      47.89  33.42
  S        1.29   0.79
  Cl       2.01   1.11
```

```
Element    Wt%    At%

  C       10.32  15.96
  N        3.98   5.28
  O       43.98  51.06
  Na       1.79   1.44
  Si      38.74  25.62
  Cl       1.19   0.63
```

```
Element    Wt%    At%

  C        6.89  11.04
  N        4.74   6.50
  O       42.02  50.52
  Na       1.27   1.06
  Si      45.08  30.87
  Cl       0.00   0.00
```

```
Element    Wt%    At%

  C        7.49  12.06
  N        3.61   4.99
  O       42.35  51.21
  Na       0.80   0.68
  Si      42.04  28.96
  S        1.35   0.81
  Cl       2.35   1.29
```

(a) **(b)**

(c) **(d)**

Figure 3.9 EDX spectra of (a) silica 2-aminobenzothiazole (1200x) (b) silica 2-aminophenol (1000x) (c) silica-aminoacid (1200x) and (d) silica 2-aminothiophenol (1000x).

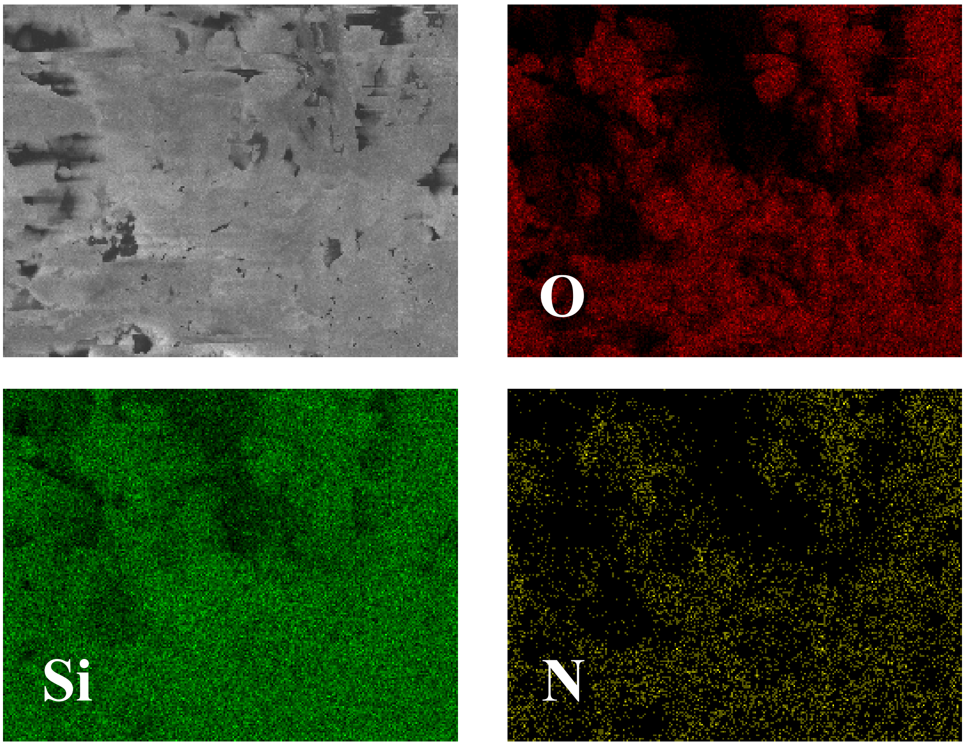


Figure 3.2. Mapping microimage of silica-amino with O and N functional groups (2500x).

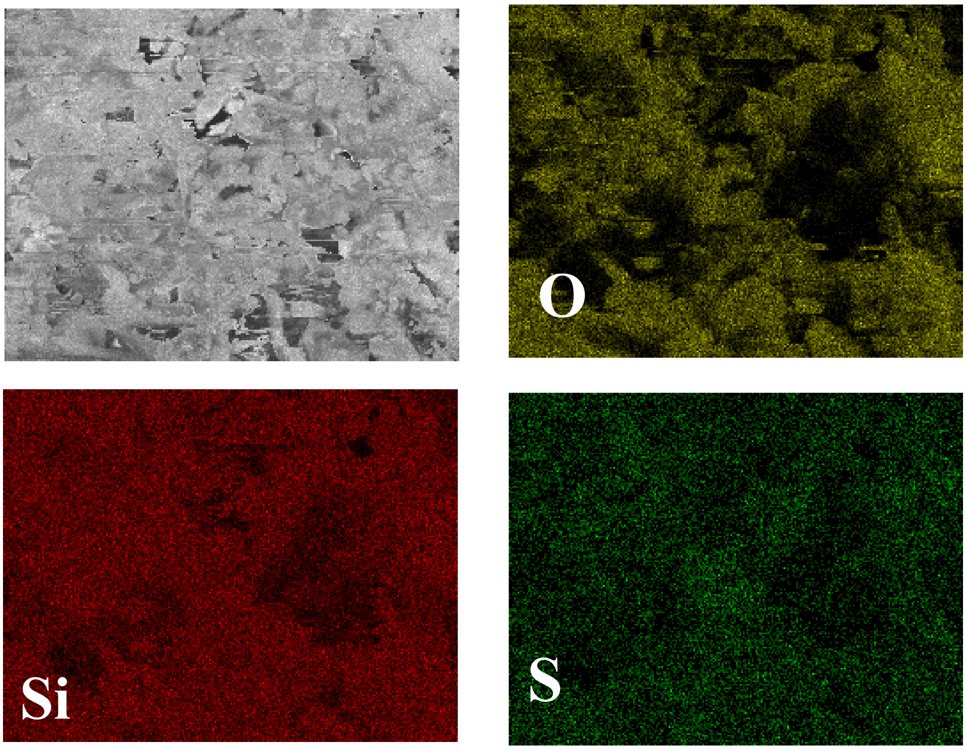


Figure 3.4. Mapping microimage of silica-mercapto with O and S functional groups (2500x).

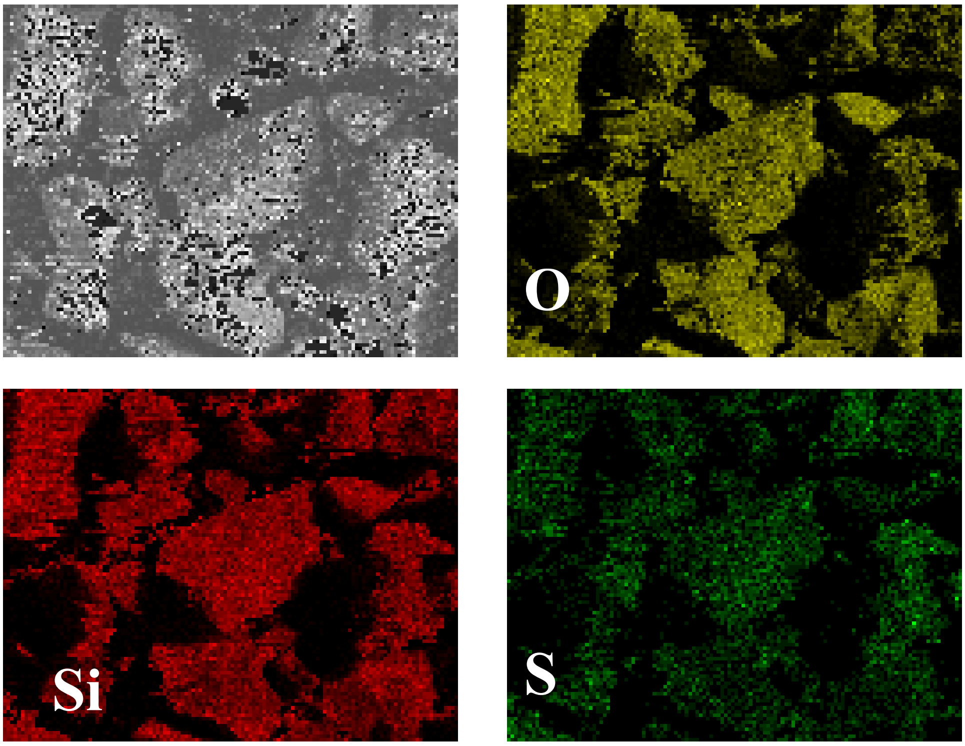


Figure 3.6. Mapping microimage of sol-gel mercapto with O and S functional groups (8000x).

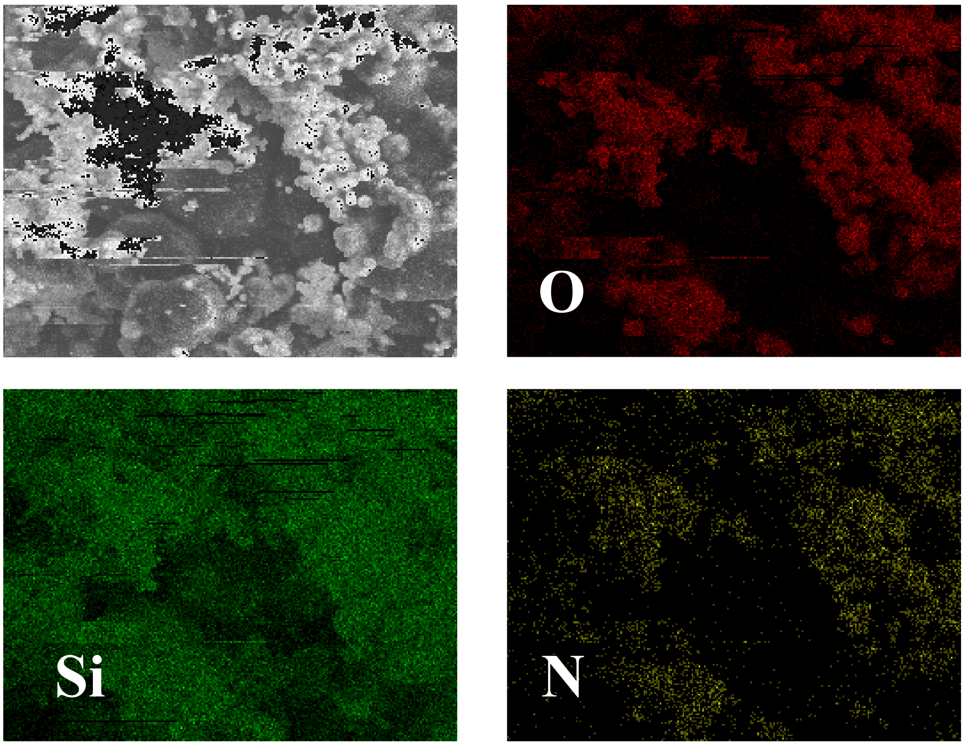


Figure 3.8. Mapping microimage of amino sol-gel with O and N functional groups (8000x).

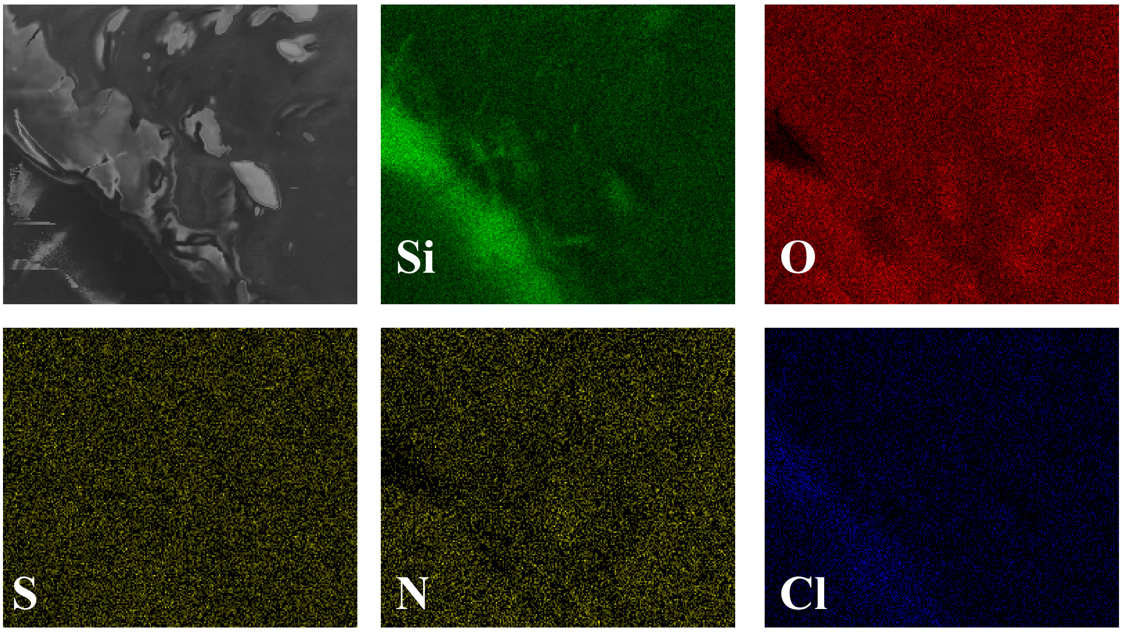


Figure 3.10. Mapping microimage of silica 2-aminothiphenol with O, S, N, and Cl functional groups (2500x).

Table 3.1. Elemental analysis results of synthesised sorbent materials having both S and N functional groups.

Materials	% C (w/w)	% S (w/w)	% N (w/w)	Calculated mmol of attached S /g sample	Calculated mmol of attached N /g sample
Silica 2-aminobenzothizole	7.08	0.65	0.56	0.20	0.20
Silica 2-aminothiophenol	7.55	0.56	0.28	0.18	0.20

Table 3.2. Elemental analysis results of synthesised sorbents materials having N functional group.

Materials	% C (w/w)	% N (w/w)	Calculated mmol of attached N /g sample
Silica-amino	10.07	3.20	2.29
Amino sol-gel	7.44	2.76	1.97
Silica-aminoacid	9.98	2.19	1.56
Silica 2-aminophenol	10.56	1.15	0.82

Table 3.3. Elemental analysis results of synthesised sorbent materials having S functional group.

Materials	% C (w/w)	% S (w/w)	Calculated mmol of attached S /g sample
Silica-mercapto	4.33	3.56	1.11
Sol-gel mercapto	5.84	5.35	1.67

3.1.3. Thermo Gravimetric Analysis (TGA)

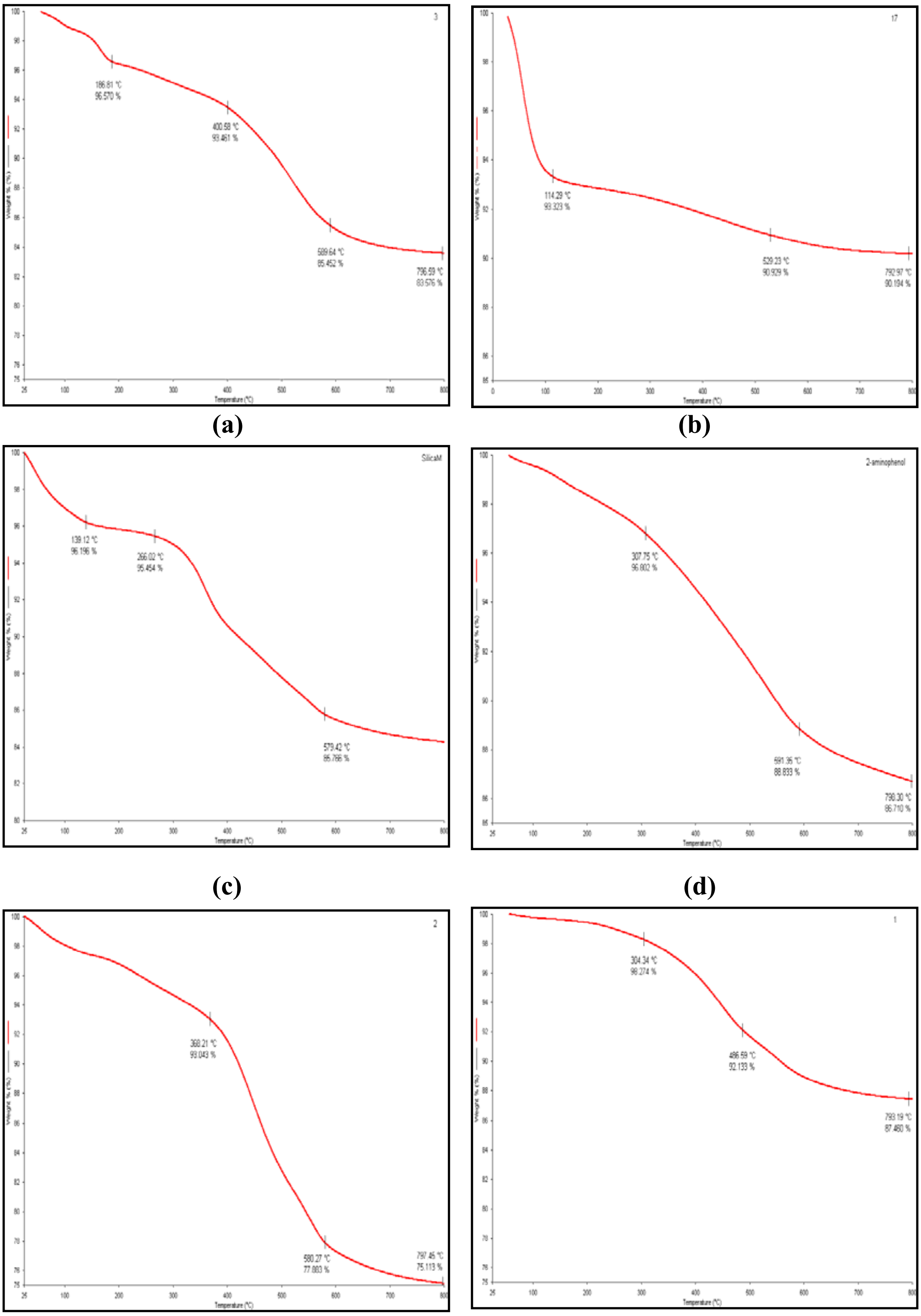
TGA analysis was performed in order to see the effect of heat on the structure of synthesised sorbents. The results are provided in Figure 3.11 for purchased silica gel modified with different functional groups and Figure 3.12 for sythesised silica gel modified with APTMS. When the TGA curve of silica gel is considered (Figure 3.11 b) 7% w/w weight loss at ~110 ^{0}C can be seen which is caused by water removed from silica structure. After 500 ^{0}C weight loss remains constant up to 800 ^{0}C and only 10% w/w weight loss is observed. When silica gel modified with different organic compounds was heated to 800 ^{0}C the total loss from the sample was about 25-15% w/w. Although presence of functional groups were proven with elemental analysis and mapping results, by considering TGA results, without making much speculation, we can say that additional weight loss of silica gel can also give information about presence of functional groups on the silica surface. TGA curves of sol-gel (Figure 3.12 a) and purchased silica gel (Figure 3.11 b) is similar so it can be concluded that silica gel was synthesised succesfully by sol-gel method.

3.2. Determination of REEs

Determination of REEs was performed by ICP-MS or ICP-OES. Experiments related to optimization of shaking time and sorbent amount were performed with ICP-OES since initial the REEs concentration was high (50.0 mg/L). In these experiments, concentrations of REEs were also determined by ICP-MS after dilution; giving similar results. ICP-MS was used only for lower concentrations.

3.2.1. Calibration Curves for REEs

Two calibration graphs, aqeuous calibration plot and matrix-matched calibration plot, were employed throughout the study. The matrix-matched standard graph was obtained by employing the proposed sorption/desorption steps with silica-amino as described in experimental part. Graphs of counts per second versus concentration were constructed for all REEs. In this part, three selected graphs are given; Figure 3.13 for La(III) (as a representative of the light REEs; La, Ce, Pr, Nd), Figure 3.14 for Eu(III) (as a representative of the medium REEs; Sm, Eu, Gd, Tb, Dy, Ho), and Figure 3.15 for Yb(III) (as a representative of the heavy REEs, Er, Tm, Yb, Lu). In these figures aqueous standard graphs are provided. Calibration graphs for the remaining REEs are given in Appendix B. The matrix-matched calibration standards are given in part 3.2.4.

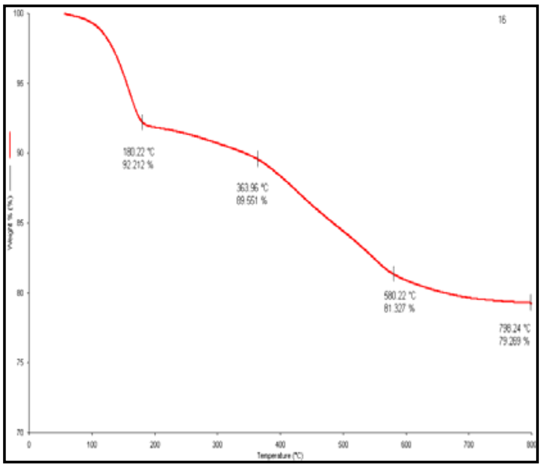


(a) **(b)**

(c) **(d)**

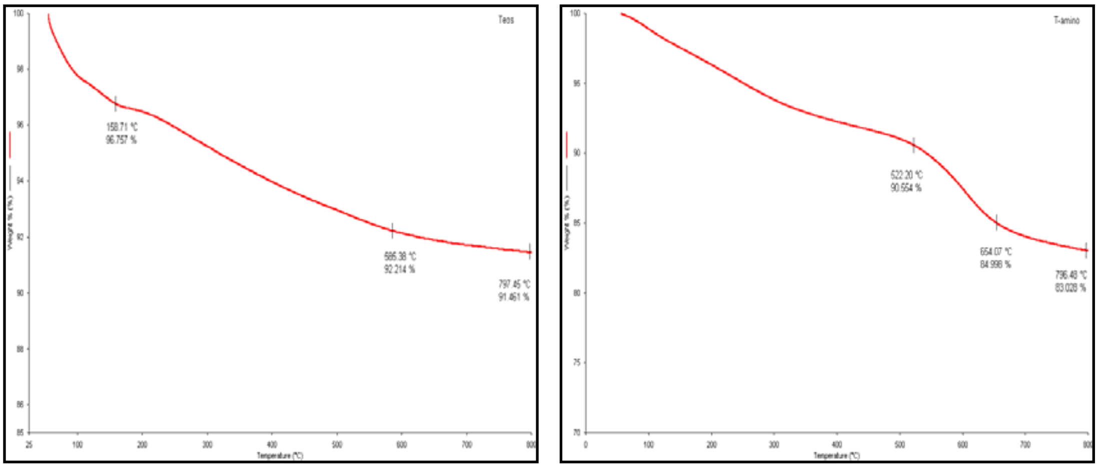
(e) **(f)**

Figure 3.11. TGA curves of (a) silica-amino (b) silica gel (c) silica-mercapto (d) silica 2-aminophenol (e) silica 2-aminobenzothiazole (f) silica 2-aminothiophenol and (g) silica-aminoacid.



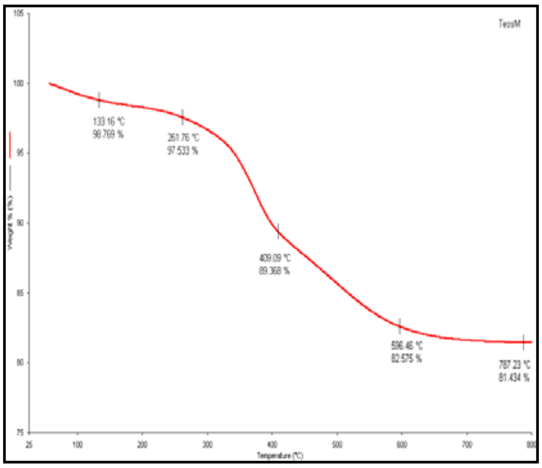
(g)

Figure 3.11. TGA curves of (a) silica-amino (b) silica gel (c) silica-mercapto (d) silica 2-aminophenol (e) silica 2-aminobenzothiazole (f) silica 2-aminothiophenol and (g) silica-aminoacid.(cont.)



(a) **(b)**

Figure 3.12. TGA curves of (a) sol-gel (b) amino sol-gel and (c) sol-gel mercapto.



(c)

Figure 3.12. TGA curves of (a) sol-gel (b) amino sol-gel and (c) sol-gel mercapto.(cont.)

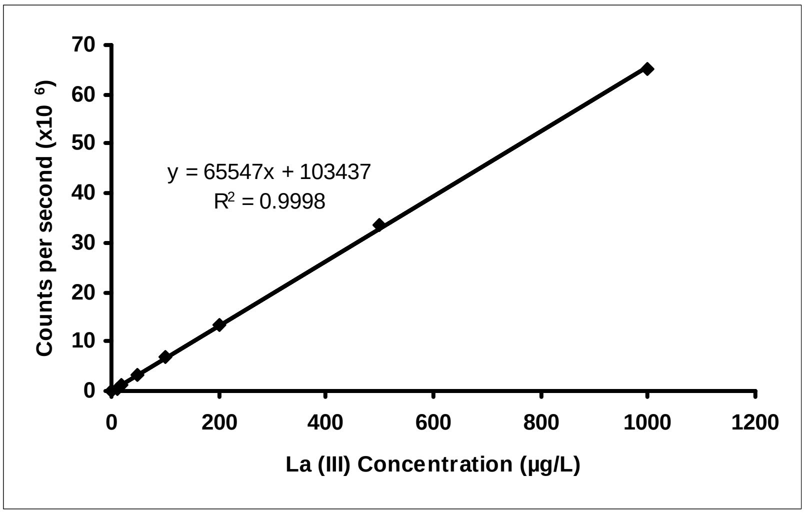


Figure 3.13. Calibration graph for La(III).

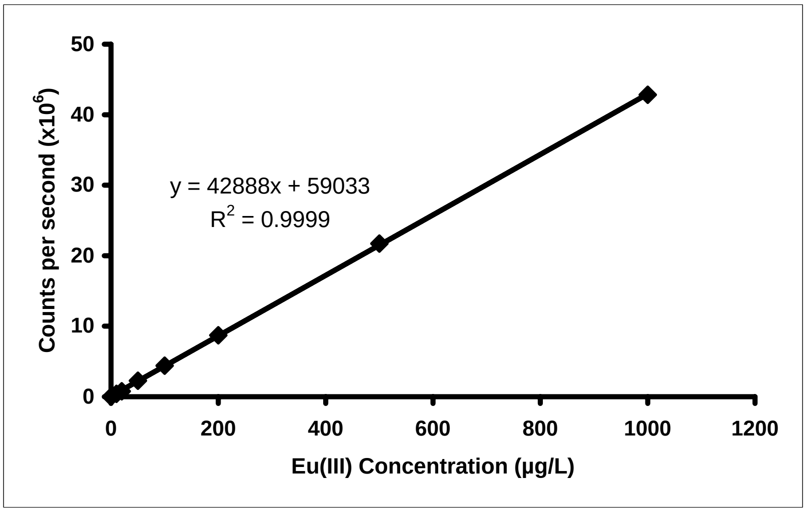


Figure 3.14. Calibration graph for Eu(III).

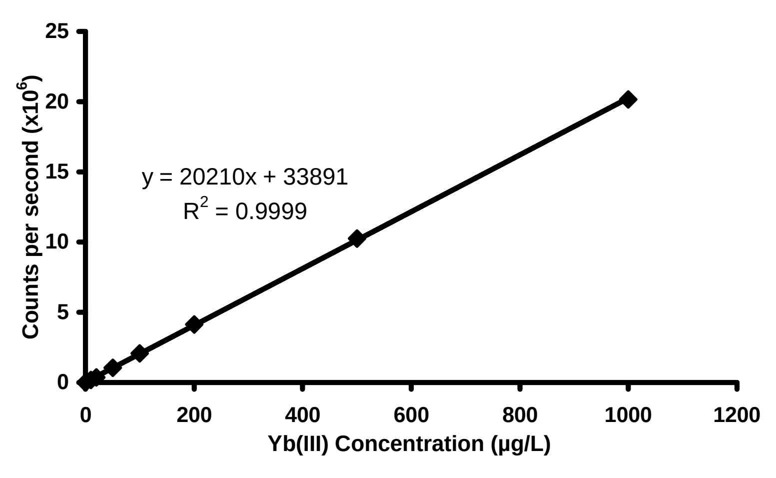


Figure 3.15. Calibration graph for Yb(III).

3.2.2. Sorption Studies with Various Sorbents

As an initial study, a 1.0 mg/L REEs multi-element standard solution was prepared at a pH of 7 and 20.0 mL aliquots of this solution were mixed with 0.05 g of sorbents as explained in 2.5.2.1. Since all of the sorbents investigated offered significant results a detailed study was carried out to understand the effect of pH .

3.2.2.1. Effect of pH

Effect of pH on sorption was studied as described in part 2.5.2.2. The percent sorption versus pH graphs are provided in Figures 3.16 and 3.17 for La(III), in Figures 3.18 and 3.19 for Eu(III) and in Figures 3.20 and 3.21 for Yb(III).

As can be seen from the figures, all of the sorbents offer significant results for sorption of REEs at wide pH range. Although silica modified with 2-aminophenol, 2-aminothiophenol, 2-aminobenzothiazole and L-glutamic acid dimethyl ester show significant sorption capacity, sorption of REEs on them is lower than the unmodified silica gel. Thus they were not used for subsequent experiments. MPTMS and APTMS-modified silica gel exhibit high sorption capacity at pHs higher than 3 for all REEs. For subsequent experiments pH of 5 was used because at high pH REEs become hydrolysed.

The low sorption capacity of the sorbents at pH of 1 and 2 indicates that HNO_3 can be used as desorbing reagent. This was proven by later experiments and 1.0 M HNO_3 was used as a desorbing solution.

3.2.2.2. Effect of Initial Metal Concentration

Investigation of sorption capacity of silica gel and silica-amino at high concentration of REEs was performed as mentioned in part 2.5.2.3. As an initial study three different concentrations were studied using silica gel, silica-amino and silica-aminoacid. Percent sorption of REEs versus initial metal concentration plots are provided in Figures 3.22, 3.23 and 3.24 for La(III) Eu(III) and Yb(III), respectively. As can be inferred from these figures, silica-aminoacid shows the lowest sorption capacity; silica-amino offers higher sorption capability than silica gel. So detailed study was decided to be performed for silica-amino and silica gel in order to see the effect of initial metal concentration on sorption of REEs. The results obtained were given in Figures 3.25, 3.26 and 3.27 for La(III), Eu(III) and Yb(III), respectively. As expected % sorption decreases with increase in initial metal concentration.

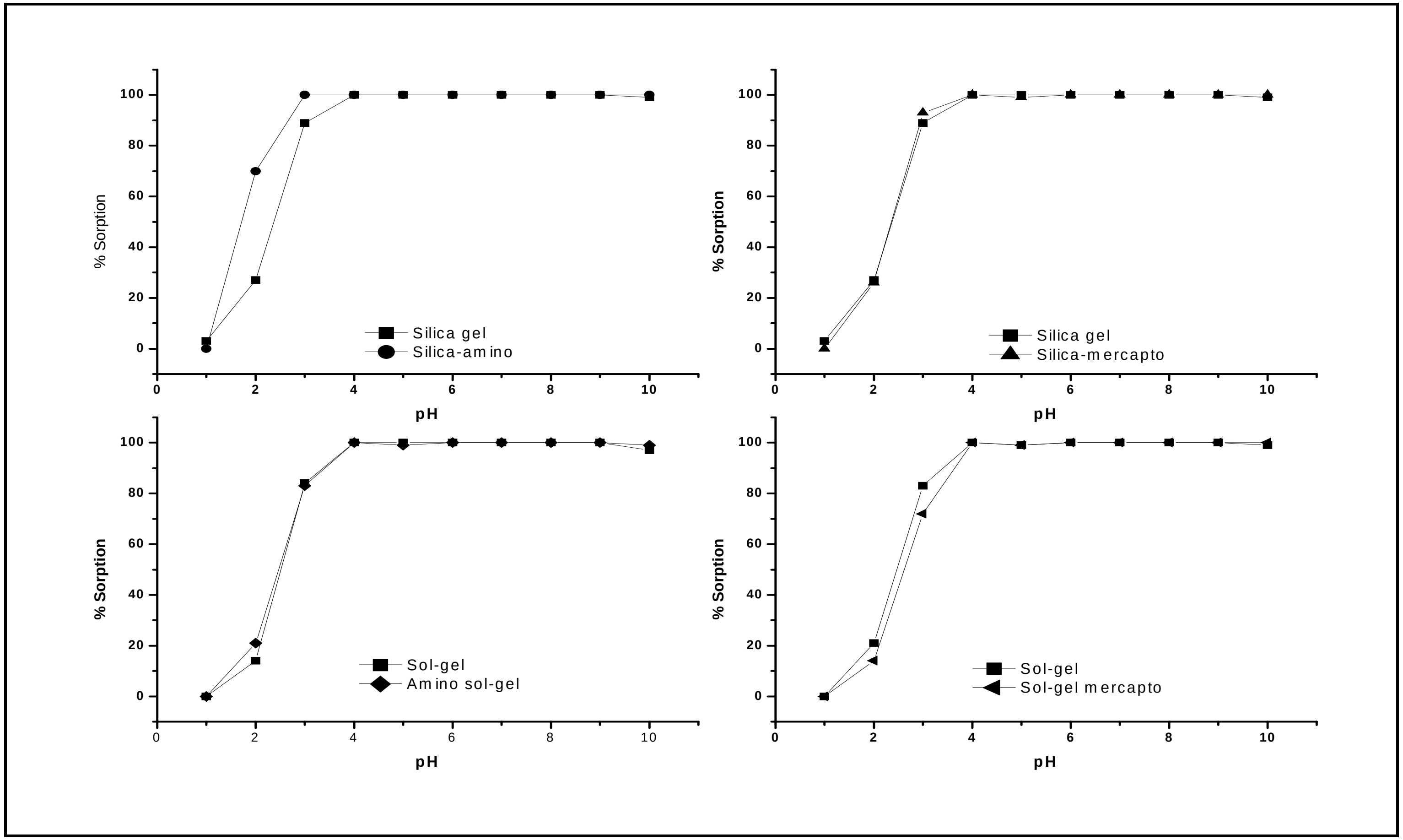


Figure 3.16. La(III) sorption as a function of pH on different sorbents (20.0 mL of 1.0 mg/L solution, sorbent amount: 50 mg, shaking time: 30 min.)

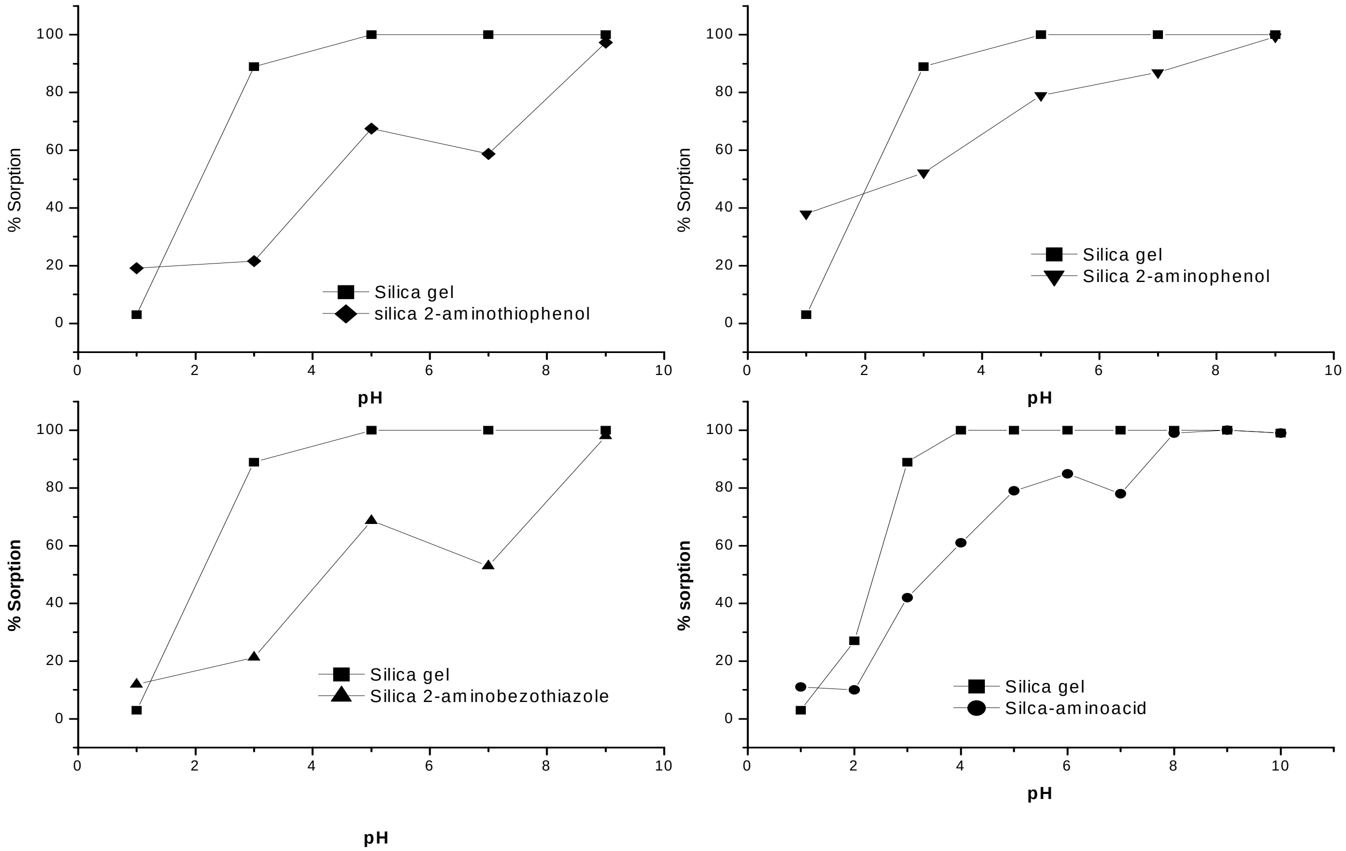


Figure 3.17. La(III) sorption as a function of pH on different sorbents. (20.0 mL of 1.0 mg/L solution, sorbent amount: 50 mg, shaking time: 30 min.)

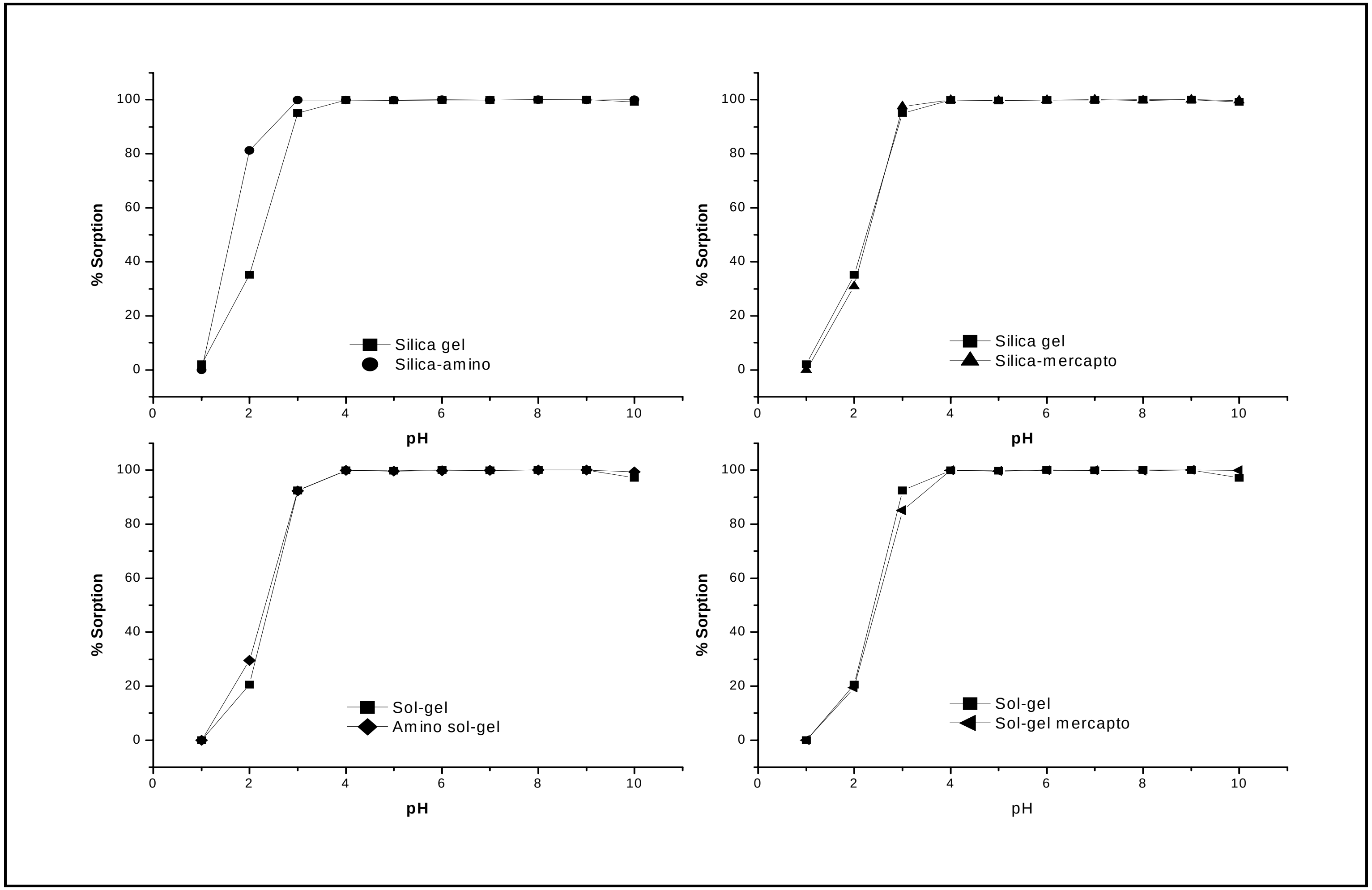


Figure 3.18. Eu(III) sorption as a function of pH on different sorbents. (20.0 mL of 1.0 mg/L solution, sorbent amount: 50 mg, shaking time: 30 min.)

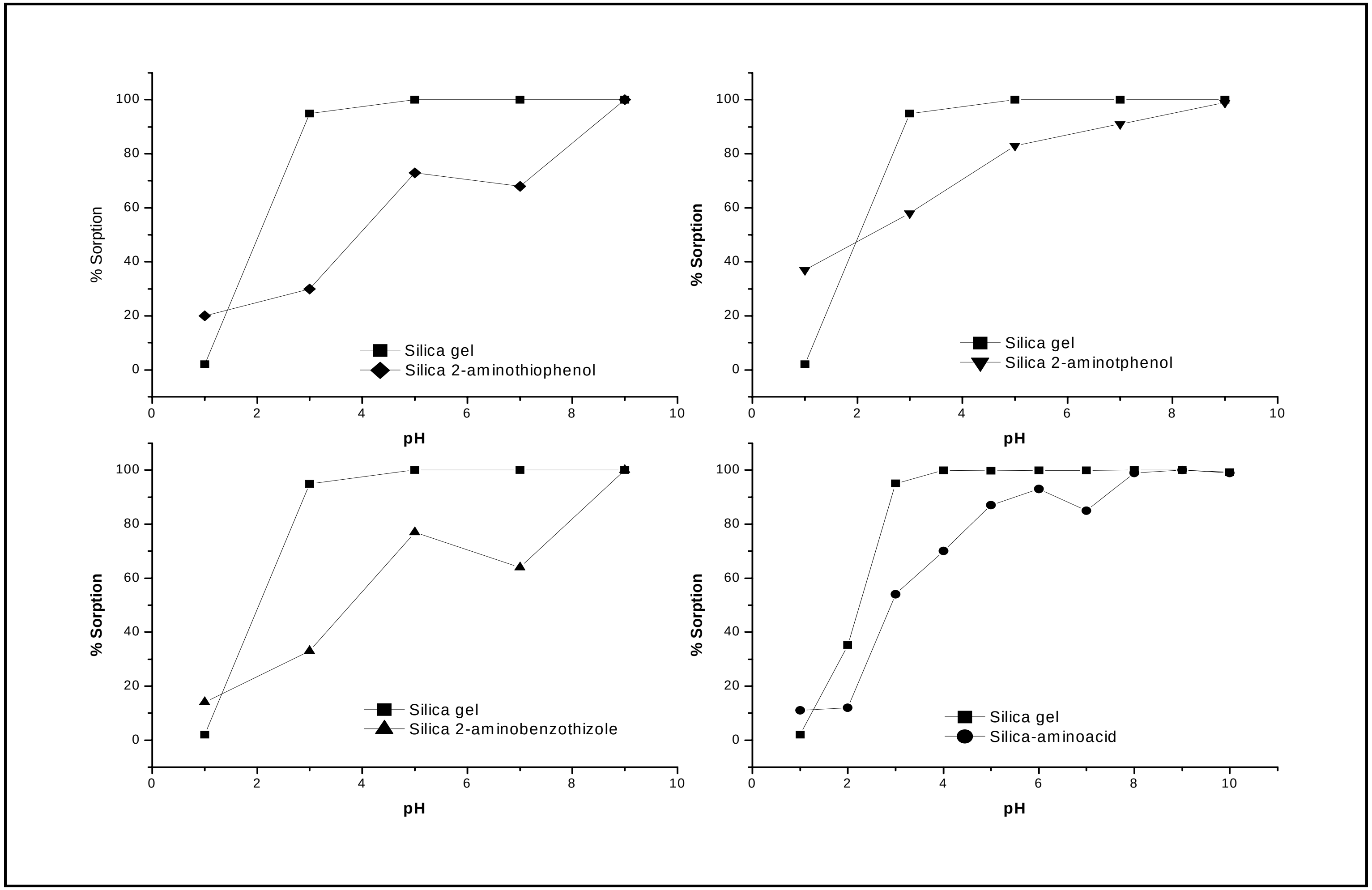


Figure 3.19. Eu(III) sorption as a function of pH on different sorbents. (20.0 mL of 1.0 mg/L solution, sorbent amount: 50 mg, shaking time: 30 min.)

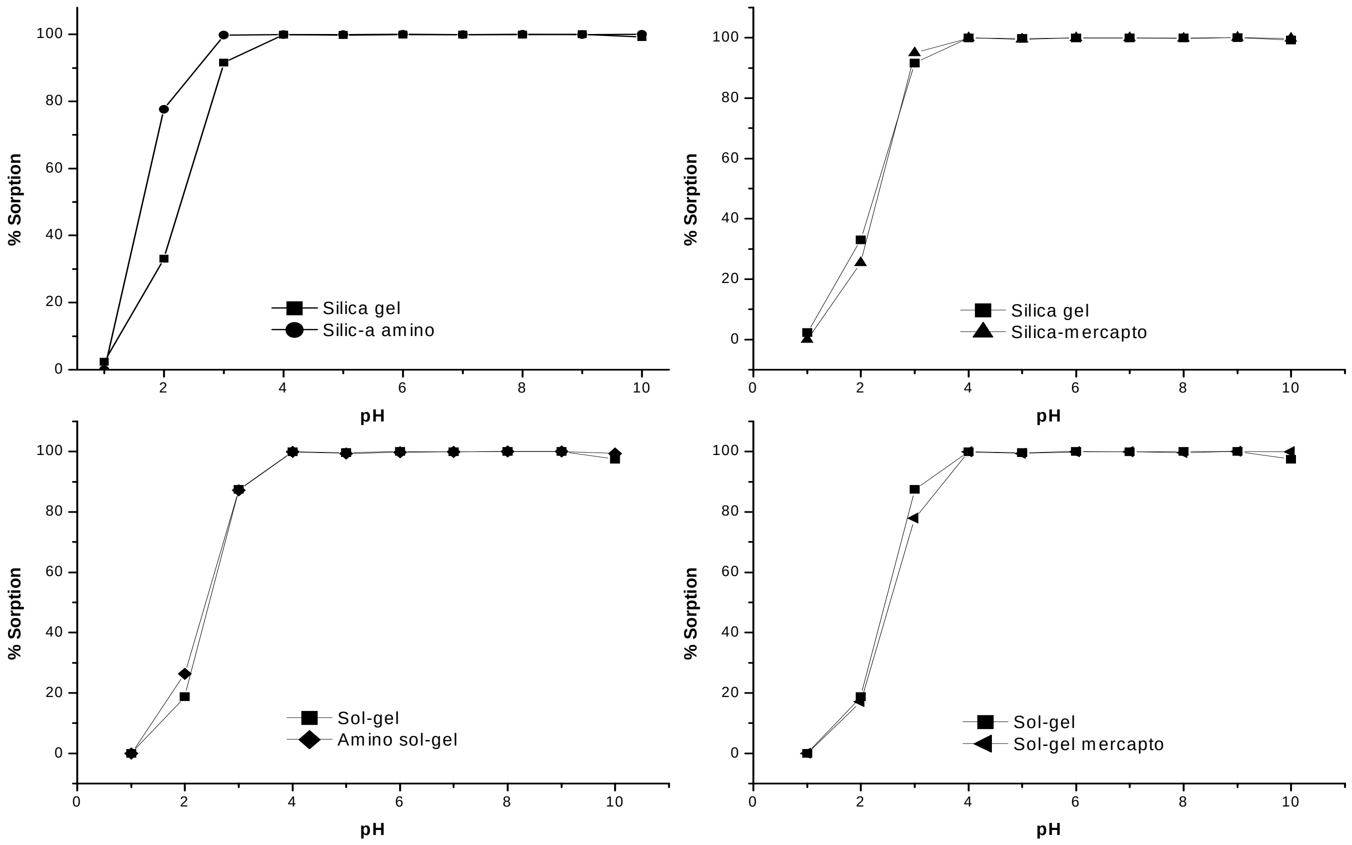


Figure 3.20. Yb(III) sorption as a function of pH on different sorbents. (20.0 mL of 1.0 mg/L solution, sorbent amount: 50 mg g, shaking time: 30 min.)

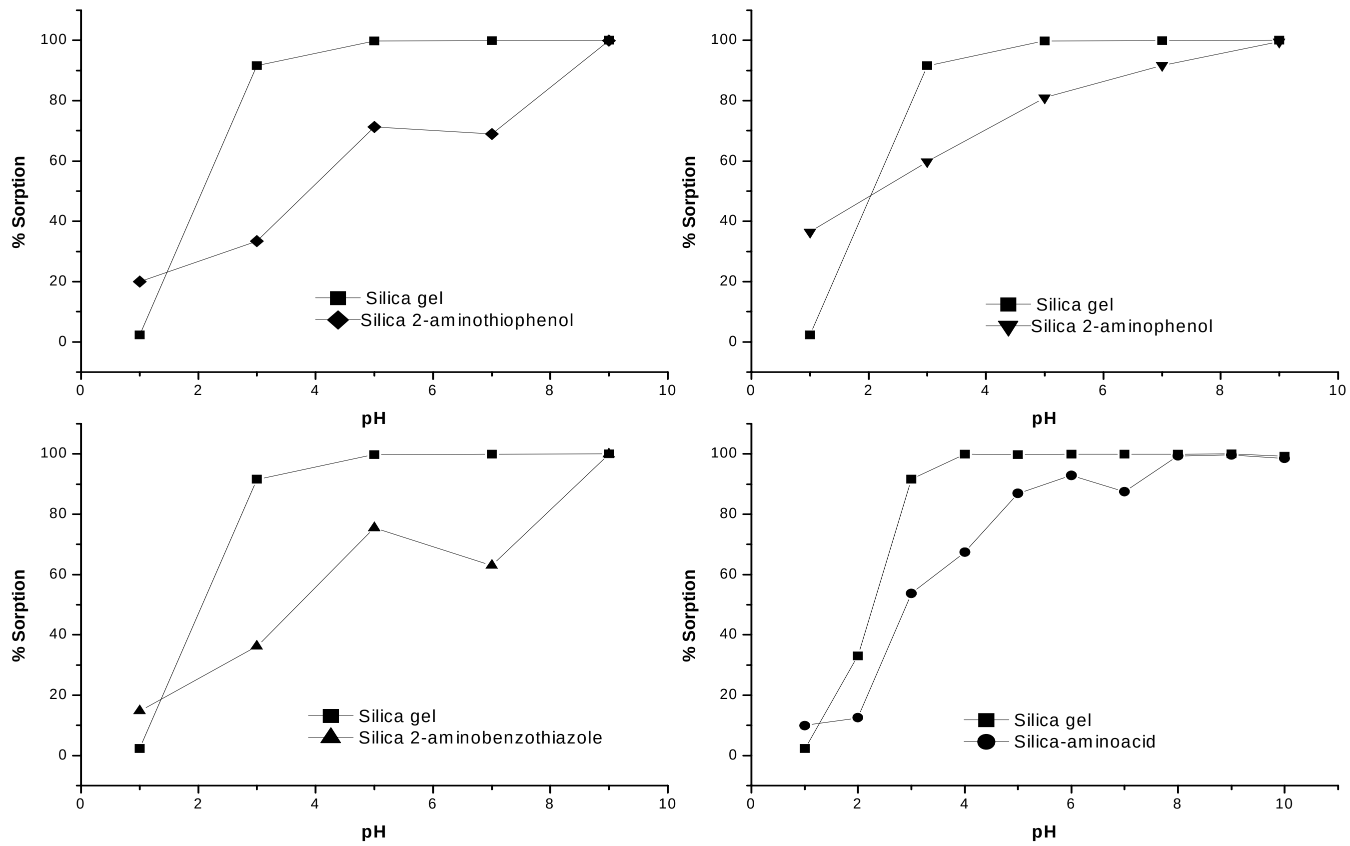


Figure 3.21. Yb(III) sorption as a function of pH on different sorbents. (20.0 mL of 1.0 mg/L solution, sorbent amount: 50 mg, shaking time: 30 min.)

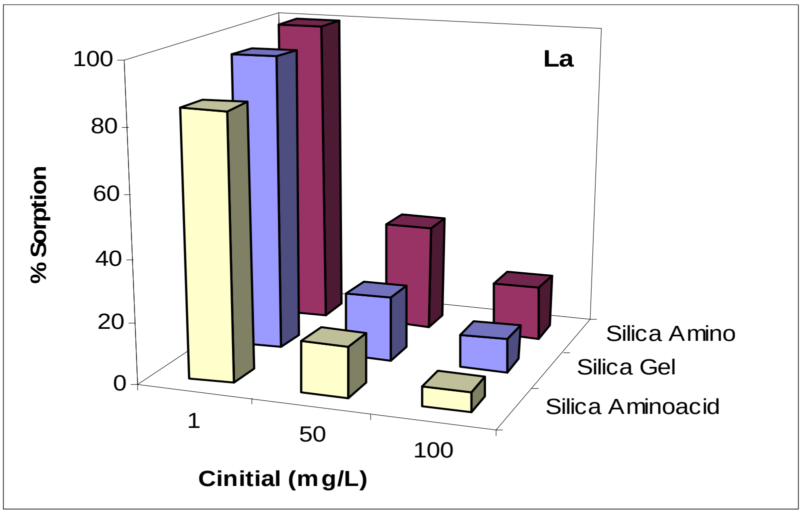


Figure 3.22. La(III) sorption as a function of initial metal concentration on different sorbents (20.0 mL solution, pH: 5, sorbent amount: 50 mg, shaking time: 30 min.).

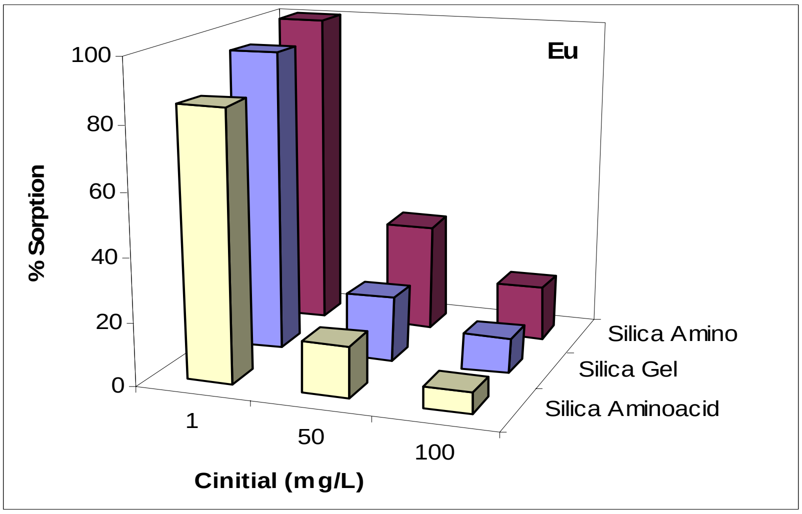


Figure 3.23. Eu(III) sorption as a function of initial metal concentration on different sorbents (20.0 mL solution, pH: 5, sorbent amount: 50 mg, shaking time: 30 min.).

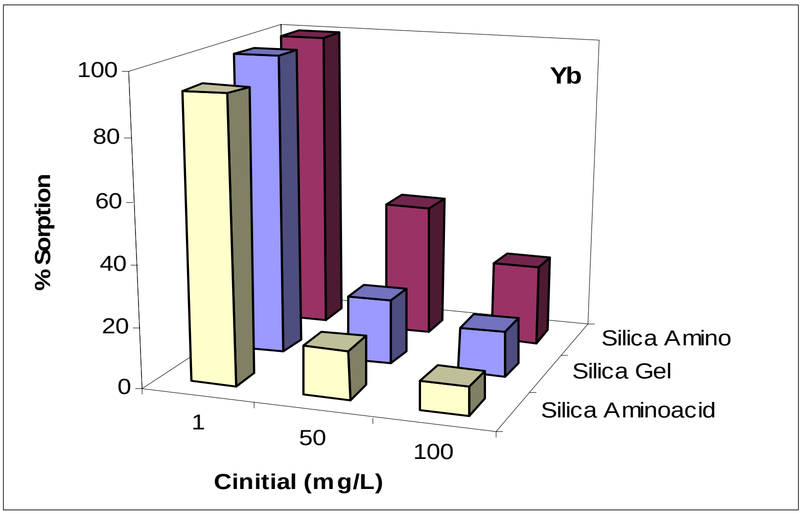


Figure 3.24. Yb(III) sorption as a function of initial metal concentration on different sorbents. (20.0 mL solution, pH: 5, sorbent amount: 50 mg, shaking time: 30 min.)

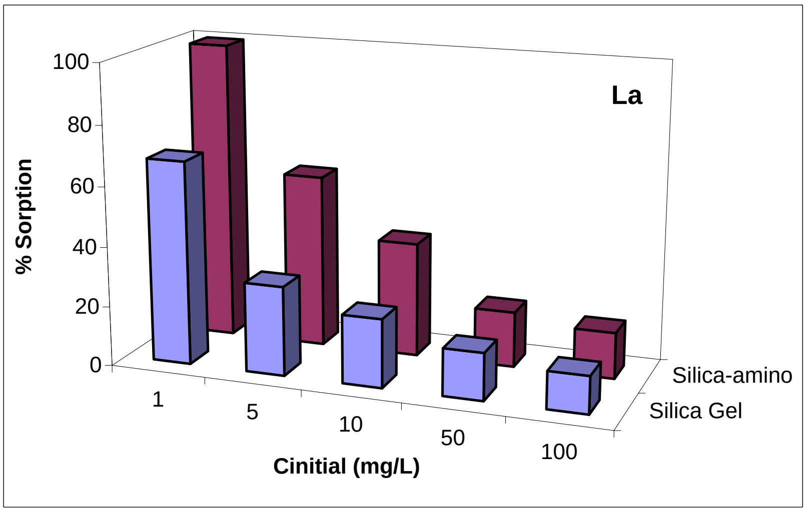


Figure 3.25. Effect of initial metal concentration on sorption of La(III) on silica gel and silica-amino (20.0 mL solution, pH: 5, sorbent amount: 50 mg, shaking time: 30 min.).

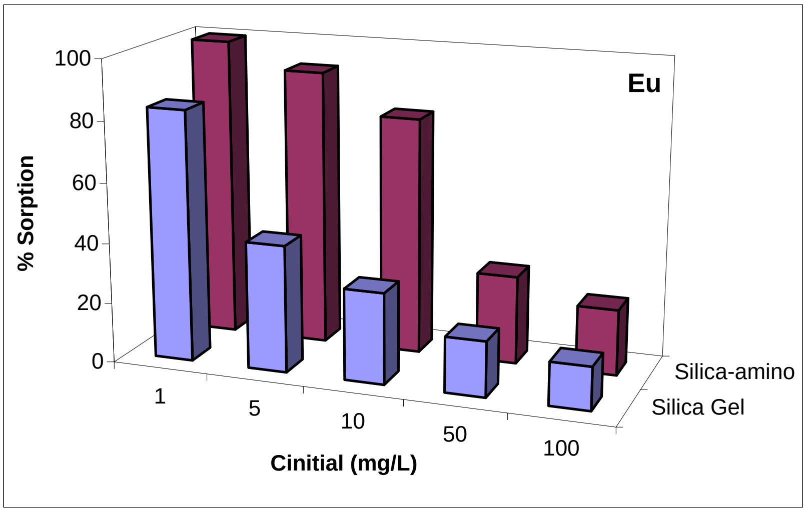


Figure 3.26. Effect of initial metal concentration on sorption of Eu(III) on silica gel and silica-amino (20.0 mL solution, pH: 5, sorbent amount: 50 mg, shaking time: 30 min.).

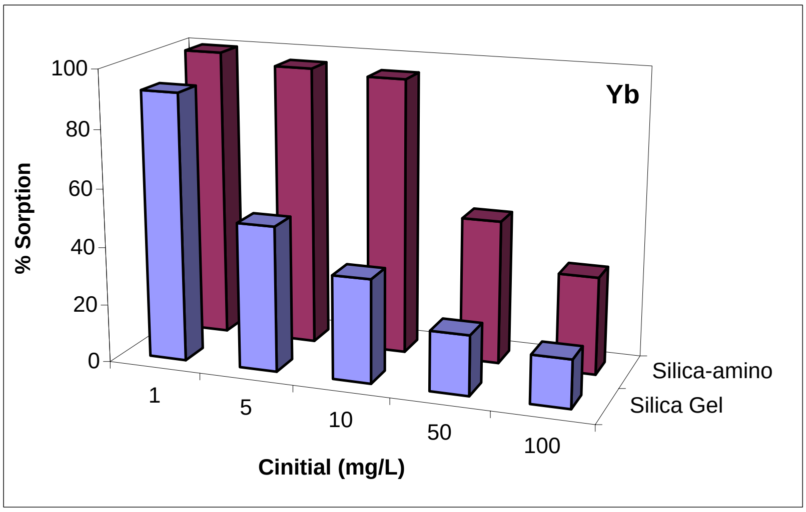


Figure 3.27. Effect of initial metal concentration on sorption of Yb(III) on silica gel and silica-amino (20.0 mL solution, pH: 5, sorbent amount: 50 mg, shaking time: 30 min.).

3.2.2.3. Effect of Shaking Time

Effect of shaking time on sorption of REEs by silica gel and silica-amino was investigated as explained in section 2.5.2.4. Twenty mililiters of 50.0 mg/L REEs solution was shaken with 50 mg sorbent for different time intervals. Effect of sorption time was studied at two different tempeatures. The results for La(III), Eu(III) and Yb(III) are exhibited in Table 3.4 for 25 °C and in Table 3.5 for 50 °C.

The results indicated that there is no significant change in sorption with increasing temperature. The percent sorption of REEs on silica gel and silica-amino remained between 2-42% at all sorption times tried. Also there is no linear change in sorption capacity of the adsorbent with increasing sorption time.

3.2.2.4. Effect of Sorbent Amount

As explained in part 2.5.2.5, the optimum amount of the sorbent for maximum take up was determined by increasing the amount of silica gel and silica-amino added into 20.0 mL of 50.0 mg/L REEs. Results are given in Table 3.6. As can be seen from the table when sorbent amount is increased, percent sorption of REEs on silica gel does not change significantly whereas sorption on silica-amino is increased with increasing sorbent amount.

In addition, from light REEs to heavy REEs, sorption capability of silica-amino is increased for a studied sorbent amount. It can be concluded that silica-amino exhibits higher selectivity for heavy REEs.

3.2.3. Desorption from Silica Gel and Silica-amino

Possible candidate for desorption was HNO_3 since silica gel and silica-amino have very low sorption capacity at a pH of 1. For this purpose, silica gel or silica-amino was shaken with 1% (0.143 M), 2% (0.286 M), 5% (0.717 M) and 10% (1.434 M) (v/v) HNO_3 solutions and the previously sorbed REEs were eluted and resultant solutions were analysed by ICP-MS. Elution efficiencies (percent recoveries) calculated for various concentrations of HNO_3 are given in Table 3.7. These values were between 36-83% with 10% HNO_3. Another important point is that 1.0 mg/L of solution at pH 5 was sorbed in equal amounts by two sorbents (silica gel and silica-amino), however, REEs can be more easily recovered from silica-amino than silica gel, with HNO_3. Therefore, 1.0 M HNO_3 eluent and silica-amino sorbent were choosen for the desorption studies.

Table 3.4. Effect of shaking time on sorption of REEs at 25 °C (20.0 mL of 50.0 mg/L, solution pH: 5, sorbent amount 50 mg).

25 °C	**La(III)**				**Eu(III)**			
	Silica-amino		**Silica Gel**		**Silica-amino**		**Silica Gel**	
Time (min.)	**% Sorption**	**Cs (mg/g)**	**% Sorption**	**Cs (mg/g)**	**% Sorption**	**Cs (mg/g)**	**% Sorption**	**Cs (mg/g)**
1	12	2.4	17	3.5	13	2.6	16	3.3
10	14	2.8	5	1.1	15	3.1	3	0.6
30	15	3.0	11	2.2	15	2.9	10	2.0
60	13	2.6	8	1.7	16	3.3	6	1.2
120	12	2.5	2	0.5	14	2.8	1	0.2
240	11	2.3	5	1.0	17	3.4	4	0.7

25 °C	**Yb(III)**			
	Silica-amino		**Silica Gel**	
Time (min.)	**% Sorption**	**Cs (mg/g)**	**% Sorption**	**Cs (mg/g)**
1	18	3.6	17	3.4
10	21	4.2	6	1.3
30	20	4.0	11	2.2
60	24	4.8	8	1.6
120	24	4.9	3	0.7
240	35	6.9	7	1.5

Table 3.5. Effect of shaking time on sorption of REEs at 50 °C (20.0 mL of 50.0 mg/L solution pH: 5, sorbent amount: 50 mg).

50 °C	**La(III)**				**Eu(III)**			
	Silica-amino		**Silica Gel**		**Silica-amino**		**Silica Gel**	
Time (min.)	**% Sorption**	**Cs (mg/g)**	**% Sorption**	**Cs (mg/g)**	**% Sorption**	**Cs (mg/g)**	**% Sorption**	**Cs (mg/g)**
1	9	1.9	13	2.5	10	1.9	12	2.5
10	10	1.9	11	2.2	12	2.3	12	2.4
30	15	2.9	11	2.2	15	3.0	13	2.6
60	24	4.7	8	1.7	26	5.2	9	1.8
120	10	2.0	3	0.6	14	2.9	3	0.6
240	13	2.6	8	1.6	17	3.3	8	1.7

50 °C	**Yb(III)**			
	Silica-amino		**Silica Gel**	
Time (min.)	**% Sorption**	**Cs (mg/g)**	**% Sorption**	**Cs (mg/g)**
1	16	3.3	12	2.4
10	21	4.3	12	2.4
30	22	4.4	22	4.3
60	38	7.5	11	2.1
120	34	6.9	7	1.3
240	42	8.4	11	2.2

Table 3.6. Effect of sorbent amount on sorption of REEs. (20.0 mL of 50.0 mg/L solution pH: 5, shaking time: 30 min.)

Sorbent amount (mg)	% Sorption					
	La(III)		Ce(III)		Pr(III)	
	Silica gel	Silica-amino	Silica gel	Silica-amino	Silica gel	Silica-amino
25	22	9	23	11	23	12
50	23	24	23	26	24	28
75	22	26	23	29	24	31
100	23	26	23	29	24	32

Sorbent amount (mg)	% Sorption					
	Nd(III)		Sm(III)		Eu(III)	
	Silica gel	Silica-amino	Silica gel	Silica-amino	Silica gel	Silica-amino
25	23	13	24	17	24	17
50	24	28	25	33	25	33
75	24	31	24	39	25	39
100	23	32	25	41	24	42

Sorbent amount (mg)	% Sorption					
	Gd(III)		Dy(III)		Ho(III)	
	Silica gel	Silica-amino	Silica gel	Silica-amino	Silica gel	Silica-amino
25	23	15	23	19	23	18
50	24	30	25	33	25	32
75	24	36	24	43	24	42
100	24	39	24	48	24	48

Sorbent amount (mg)	% Sorption			
	Er(III)		Yb(III)	
	Silica gel	Silica-amino	Silica gel	Silica-amino
25	21	17	21	26
50	21	31	23	39
75	21	42	23	55
100	21	49	24	64

Table 3.7. Desorption of REEs from silica gel and silica-amino.

% Recovery						
Eluent	**La(III)**		**Eu(III)**		**Yb(III)**	
	Silica Gel	**Silica-amino**	**Silica Gel**	**Silica-amino**	**Silica Gel**	**Silica-amino**
1% HNO_3	36	65	50	65	59	65
2% HNO_3	32	69	44	69	51	70
5% HNO_3	33	79	51	82	61	81
10% HNO_3	43	81	64	82	75	83

3.2.4. Method Validation

Spike recovery test was performed in order to investigate the applicability of desorption from silica-amino by using real samples. For this purpose ultra pure water (UPW), tap water (TW), sea water (SW) and geothermal water (GW) were spiked with 1.0 mg/L multi-element REEs solution. Then usual sorption procedure was applied (20.0 ml of REEs solution, pH 5 and 30 min. shaking time). Desorption was realised with 1.0 M of HNO_3. At the end of sorption and desorption steps, the solutions were filtered, the filtrates were analysed for REEs with ICP-MS and the percent recovery of REEs was calculated in each sample.

Calibration standards were prepared with the same procedure. Each standard was added to the water types and sorption/desorption was applied. Detailed procedure can be found in experimental part (section 2.5.1.2). These calibration standards were named as matrix-matched calibration standards since the resultant solutions were expected to contain very similar matrices as the samples. For quantitation these calibration standards were used. The matrix-matched calibration standards were provided in Figures 3.28, 3.29 and 3.30 for La(III), Eu(III) and Yb(III), respectively. Other calibration curves can be found in Appendix C. As can be seen from the plots, all elements show similar responses. Calibration sensitivity (slope) is affected from sorption/desorption steps. Spike recovery results are summarised in Table 3.8. As can be seen from the table all REEs can be recovered significantly from UPW, GW, SW and TW with a percent recovery value of higher than 81%.

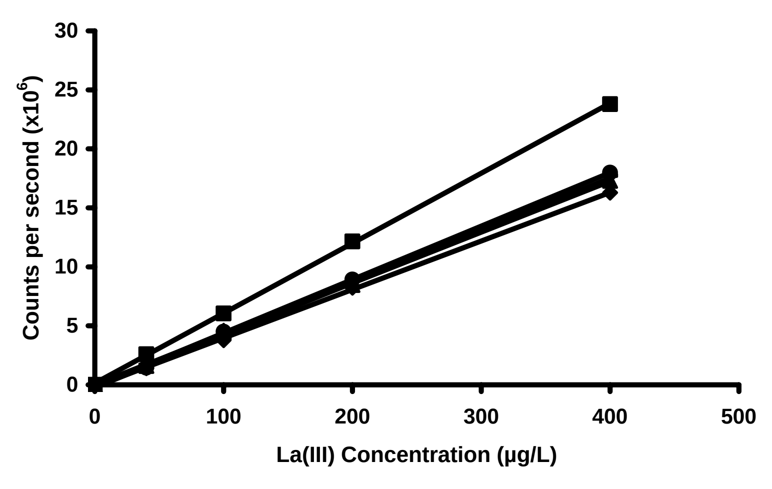


Figure 3.28. Matrix-matched calibration graphs for La(III). -■- La(III) aqueous standard calibration graph (y = 59331x + 132020, R^2=0.9999), -♦- La(III) SW matrix-matched calibration graph (y = 41126x – 146567, R^2 = 0.9995), -▲- La(III) UPW matrix-matched calibration graph (y = 43142x + 1149.1 R^2 = 0.9994) -●- La(III) GW matrix-matched calibration graph (y = 45300x – 131484, R^2 = 0.9996), -▬- La(III) TW matrix-matched calibration graph (y = 44379x – 232898, R^2 = 0.9986)

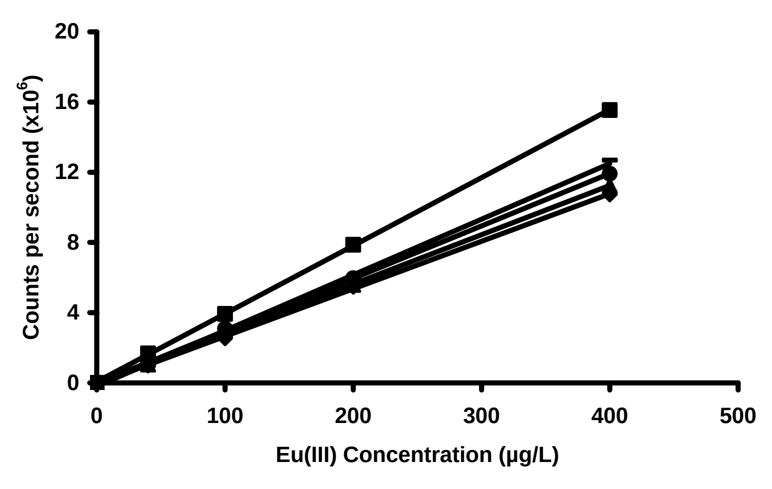


Figure 3.29. Matrix-matched calibration graphs for Eu(III). -■- Eu(III) aqueous standard calibration graph (y = 38766x + 65884, R^2 = 0.9999), -♦- Eu(III) SW matrix-matched calibration graph (y = 27062x – 54184, R^2 = 0.9996), -▲- Eu(III) UPW matrix-matched calibration graph (y = 28066x + 22558, R^2 = 0.9994), -●- Eu(III) GW matrix-matched calibration graph (y = 29901x – 28532, R^2 = 0.9996), -▬- Eu(III) TW matrix-matched calibration graph (y = 31728x – 193307, R^2 = 0.9979)

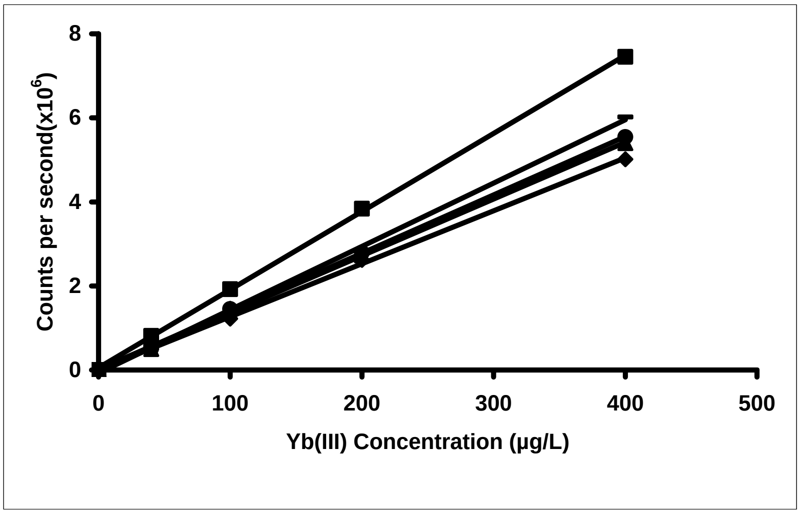


Figure 3.30. Matrix-matched calibration graphs for Yb(III). -■- Yb(III) aqueous standard calibration graph (y = 18588x + 53587, R^2 = 0.9997), -♦- Yb(III) SW matrix-matched calibration graph (y = 12606x + 5909.9, R^2 = 0.9993), -▲- Yb(III) UPW matrix-matched calibration graph (y = 13506x + 17654, R^2 = 0.9993), -●- Yb(III) GW matrix-matched calibration graph (y = 13881x + 4545.6, R^2 = 0.9997), -▬- Yb(III) TW matrix-matched calibration graph (y = 15074x – 73901, R^2 = 0.9988)

Table 3.8. REEs recovery results for ultrapure water, geothermal water, tap water and sea water.

	% Recovery					
Water types	**La(III)**	**Ce(III)**	**Pr(III)**	**Nd(III)**	**Sm(III)**	**Eu(III)**
UPW	107 ± 5	107 ± 5	107 ± 5	108 ± 5	107 ± 5	107 ± 4
SW	109 ± 3	108 ± 4	107 ± 3	109 ± 3	108 ± 4	108 ± 4
TW	89 ± 7	84 ± 7	82 ± 7	82 ± 6	81 ± 6	81 ± 6
GW	89 ± 5	88 ± 4	89 ± 4	90 ± 4	88 ± 4	89 ± 4

	% Recovery				
Water types	**Gd(III)**	**Dy(III)**	**Ho(III)**	**Er(III)**	**Yb(III)**
UPW	107 ± 5	108 ± 6	108 ± 6	107 ± 5	109 ± 5
SW	110 ± 3	110 ± 3	110 ± 4	110 ± 3	109 ± 3
TW	82 ± 6	83 ± 7	82 ± 6	83 ± 6	82 ± 6
GW	91 ± 5	91 ± 5	91 ± 4	92 ± 5	91 ± 4

CHAPTER 4

CONCLUSION

ICP-OES and ICP-MS are the most widely used techniques in determination of rare earth elements in environmental samples. Although these techniques enable very sensitive determinations for REEs, it may still be necessary to apply a preconcentration step due to their presence of low concentrations in environmental water samples. In addition, the presence of heavy matrix in some matrices gives rise to apply an efficient separation/matrix removal step prior to instrumental measurements.

In this thesis, a new method was proposed for the separation and/or preconcentration of REEs in environmental samples prior to their determination by ICP-based techniques. For this purpose, silica gel immobilized with (3-aminopropyl) trimethoxysilane (APTMS), (3-mercaptopropyl) trimethoxysilane (MPTMS), 2–aminophenol, 2-aminothiophenol, 2-aminobenzothiazole and L-glutamic acid dimetyl ester were tested as adsorbent materials. The characterization of the new sorbents was performed with SEM/EDX, TGA and elemental analyses Initial studies were concentrated on the investigation of a proper adsorbent for the sorption of REEs. Among the tested adsorbents APTMS-and MPTMS-modified silica gel demonstrated efficient sorption capabilities in a broad pH range (pH>3). However, silica gel modified with 2-aminothiophenol, 2-aminobenzothiazole and L-glutamic acid dimethyl ester exhibited lower sorption capability than the unmodified silica gel. Although silica gel and silica gel modified with APTMS (silica-amino) show high sorption capacity for 1.0 mg/L (>99%) after pH 3, silica gel was shown to give a lower sorption capacity than silica-amino at higher concentrations.

The applicability of the method to real samples was examined by spike recovery tests. The percent recovery tests were performed in various water types including ultra pure water, sea water, tap water and geothermal water. For all water types percent recovery values were found to range between 81-110%.

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APPENDICES

APPENDIX A. Calculation of the Amount (mmol) of Functional Groups Attached to Silica Gel from Elemental Analysis Results

Some of modified organic compound has only N or S some has both N and S functional groups. (3-aminopropyl)trimethoxysilane (APTMS), 2-aminophenol, L-glutamic acid dimethyl ester consist of a primary amine. They contain 1 mol of N for 1 mol APTMS, 2-aminophenol or L-glutamic acid dimethyl ester. For this reason the N content of sorbent material (immobilized silica) can be used to calculate the amount of functional groups attached on the surface of silica.

The calculations are as follows:

$$\frac{\text{g of N}}{\text{100 g Sample}} \times \frac{\text{1000 mg N}}{\text{1 g N}} \times \frac{\text{1 mmolN}}{\text{14 mg N}} \times \frac{\text{1 mmol functional group}}{\text{1 mmol N}} = \frac{\text{mmol APTMS}}{\text{1 g silica-amino}}$$

(3-mercaptopropyl)trimethoxysilane (MPTMS) has only S functional groups. It consists of 1 mol of S for 1 mol MPTMS. Thus, the S content of the sorbent material, MPTMS/silica, can be used to calculate the amount of functional groups attached on the surface of silica as follows:

$$\frac{\text{g of S}}{\text{100 g Sample}} \times \frac{\text{1000 mg S}}{\text{1 g S}} \times \frac{\text{1 mmol S}}{\text{32 mg S}} \times \frac{\text{1 mmol functional group}}{\text{1 mmol S}} = \frac{\text{mmol MPTMS}}{\text{1 g silica-mercapto}}$$

2-aminothiophenol and 2-aminobenzothiazole have both S and N functional groups. 2-aminothiophenol consists of 1 mol of S and 1 mol of N for 1 mol of 2-aminothiophenol. For this reason, the N and S content of sorbent material were calculated by using both formulas given above. In the case of 2-aminobenzothiazole, it should be noted that 1 mol of 2-aminobenzothiazole contains 2 moles of N and 1 mol of S.

APPENDIX B. Aqueous Calibration Graphs for REEs

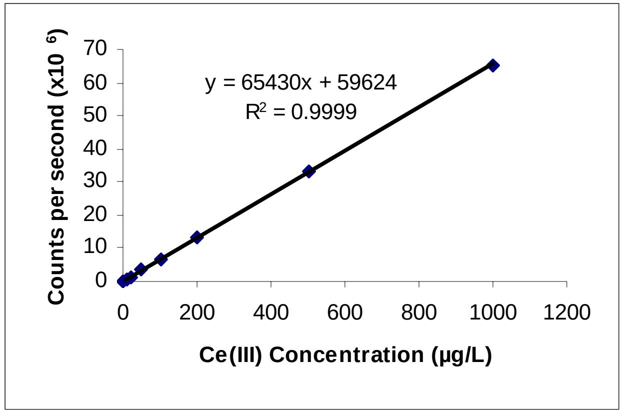

Figure B. 1. Calibration graph for Ce(III).

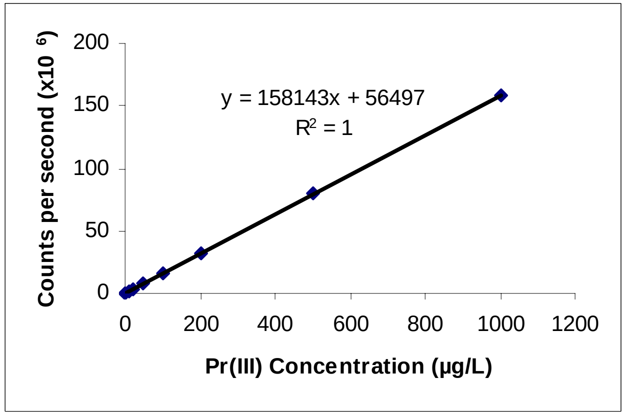

Figure B.2. Calibration graph for Pr(III).

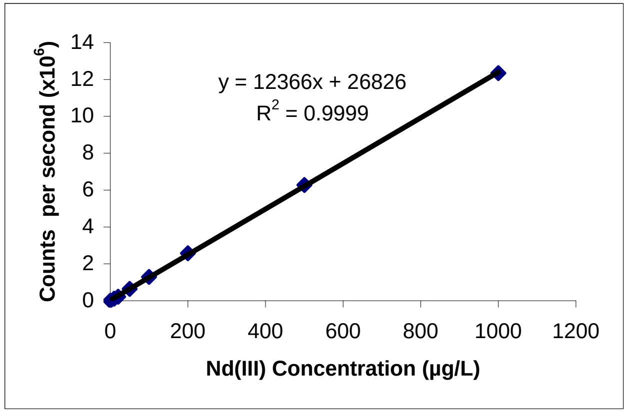

Figure B.3. Calibration graph for Nd(III).

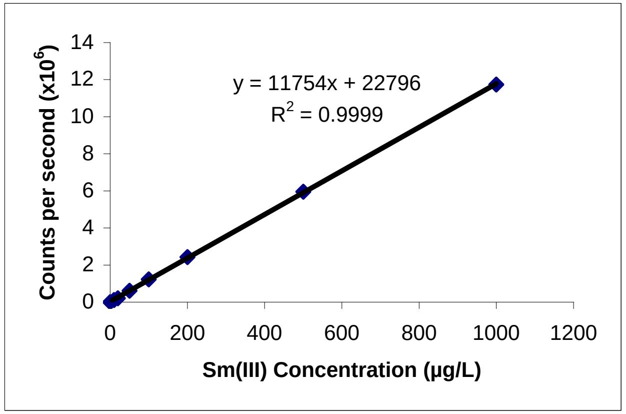

Figure B.4. Calibration graph for Sm(III).

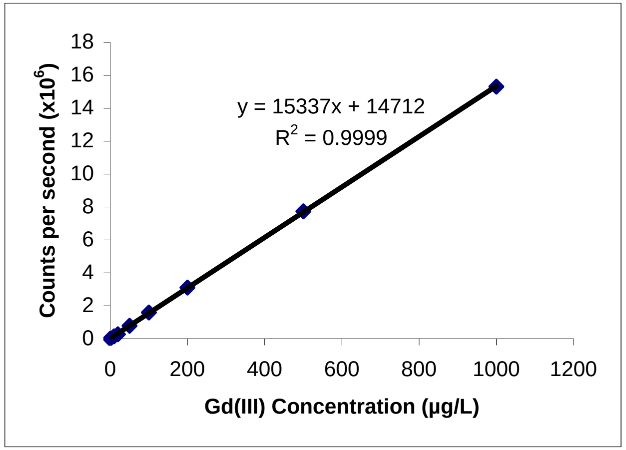

Figure B.5. Calibration graph for Gd(III).

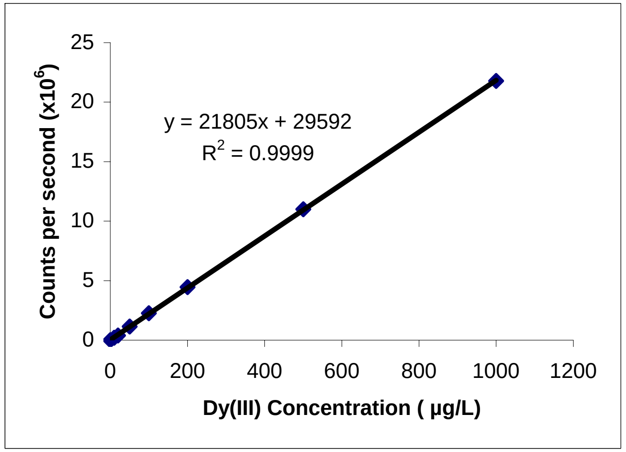

Figure B.6. Calibration graph for Dy(III).

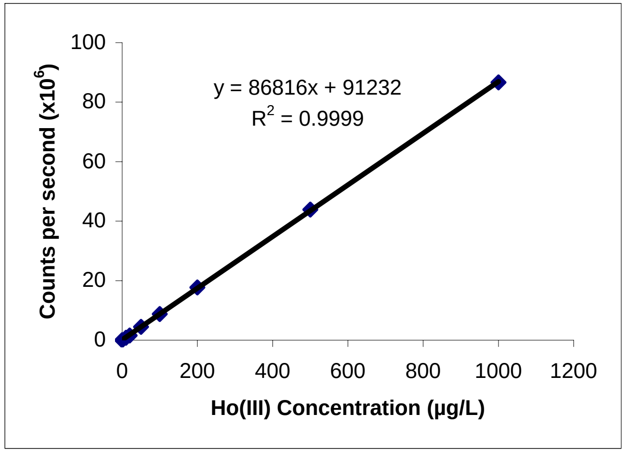

Figure B.7. Calibration graph for Ho(III).

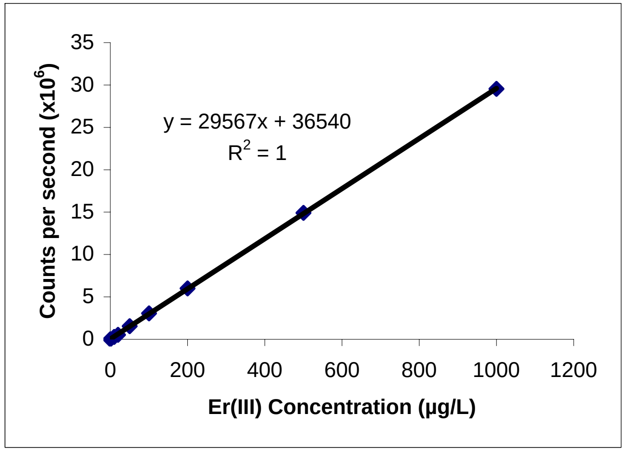

Figure B.8. Calibration graph for Er(III).

APPENDIX C. Matrix-matched Calibration Graphs for REEs

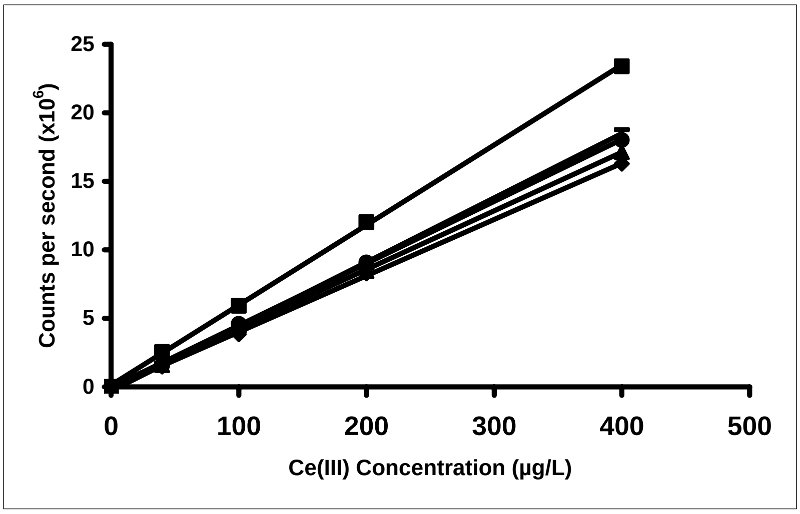

Figure C.1. Matrix-matched calibration graphs for Ce(III). -■- Ce(III) aqueous standard calibration graph ($y = 58400x + 130039$, $R^2 = 0.9998$), -♦- Ce(III) SW matrix-matched calibration graph ($y = 41062x – 100458$, $R^2 = 0.9996$), -▲- Ce(III) UPW matrix-matched calibration graph ($y = 42790x + 8224.2$, $R^2 = 0.9995$), -●- Ce(III) GW matrix-matched calibration graph ($y = 45280x – 52043$, $R^2 = 0.9997$), -▬- Ce(III) TW matrix-matched calibration graph ($y = 46996x – 305004$, $R^2 = 0.9979$)

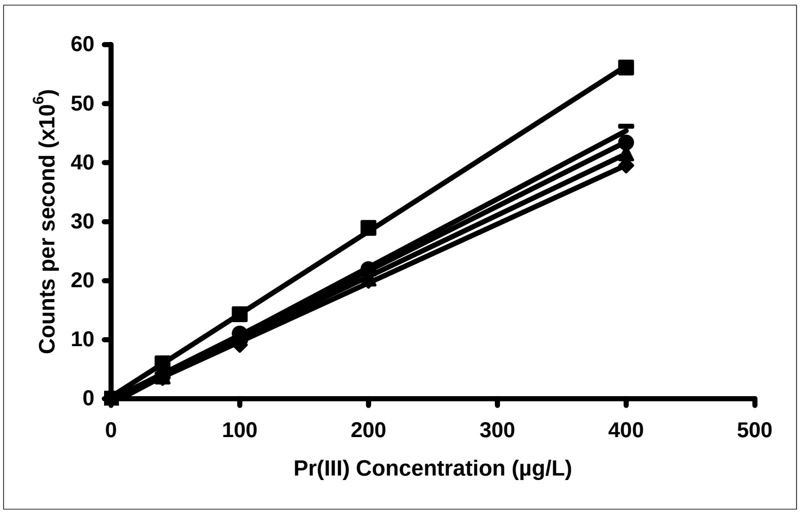

Figure C.2. Matrix-matched calibration graphs for Pr(III). -■- Pr(III) aqueous standard calibration graph ($y = 140175x + 324578$, $R^2 = 0.9997$), -♦- Pr(III) SW matrix-matched calibration graph ($y = 99749x – 332265$, $R^2 = 0.9995$), -▲- Pr(III) UPW matrix-matched calibration graph ($y = 103957x – 82210$, $R^2 = 0.9996$), -●- Pr(III) GW matrix-matched calibration graph ($y = 109151x – 140504$, $R^2 = 0.9997$), -▬- Pr(III) TW matrix-matched calibration graph ($y = 115726x – 878160$, $R^2 = 0.9974$)

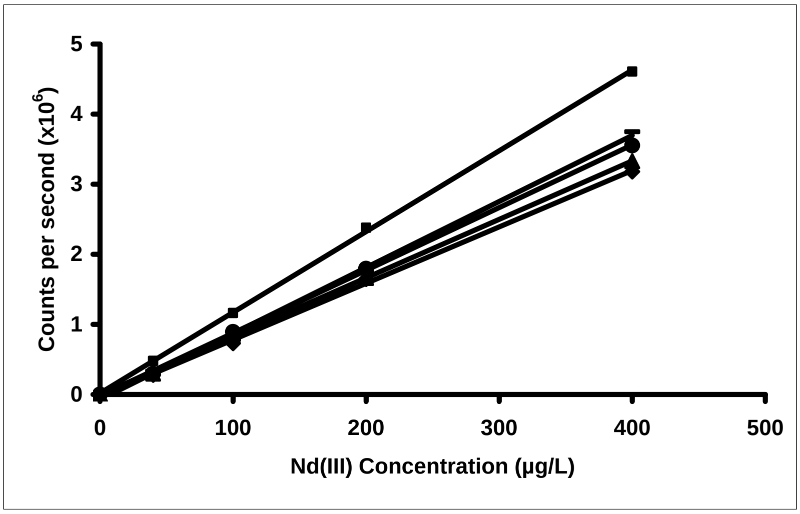

Figure C.3. Matrix-Matched calibration graphs for Nd(III). -■- Nd(III) aqueous standard calibration graph ($y = 11530x + 19070$, $R^2 = 0.9997$), -♦- Nd(III) SW matrix-matched calibration graph ($y = 8053x – 24694$, $R^2 = 0.9989$), -▲- Nd(III) UPW matrix-matched calibration graph ($y = 8346x - 4840.4$, $R^2 = 0.9997$), -●- Nd(III) GW matrix-matched calibration graph ($y = 8949.7x – 17178$, $R^2 = 0.9996$), -▬- Nd(III) TW matrix-matched calibration graph ($y = 9422.3x – 73076$, $R^2 = 0.9977$)

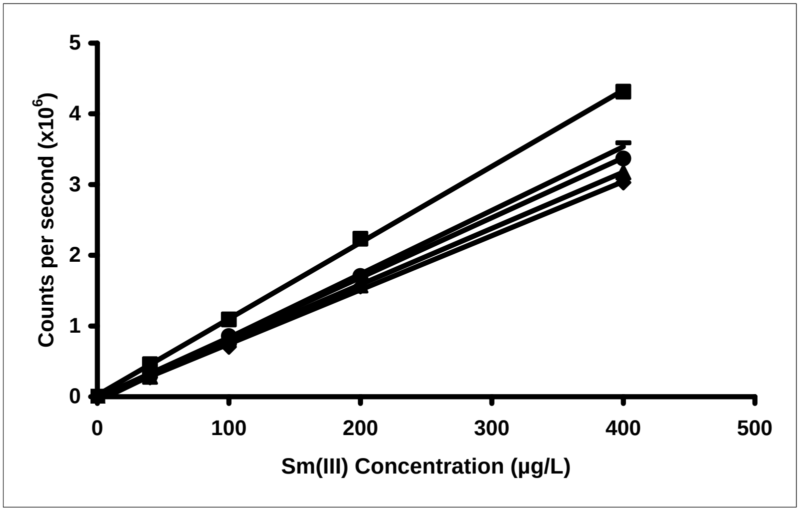

Figure C.4. Matrix-matched Calibration graphs for Sm(III). -■- Sm(III) aqueous standard calibration graph ($y = 10782x + 23166$, $R^2 = 0.9997$), -♦- Sm(III) SW matrix-matched calibration graph ($y = 7652.7x – 19303$, $R^2 = 0.9992$), -▲- Sm(III) UPW matrix-matched calibration graph ($y = 7948.1x - 4329.1$, $R^2 = 0.9996$), -●- Sm(III) GW matrix-matched calibration graph ($y = 8475.4x – 10816$, $R^2 = 0.9996$), -▬- Sm(III) TW matrix-matched calibration graph ($y = 9003.6x – 65878$, $R^2 = 0.9977$)

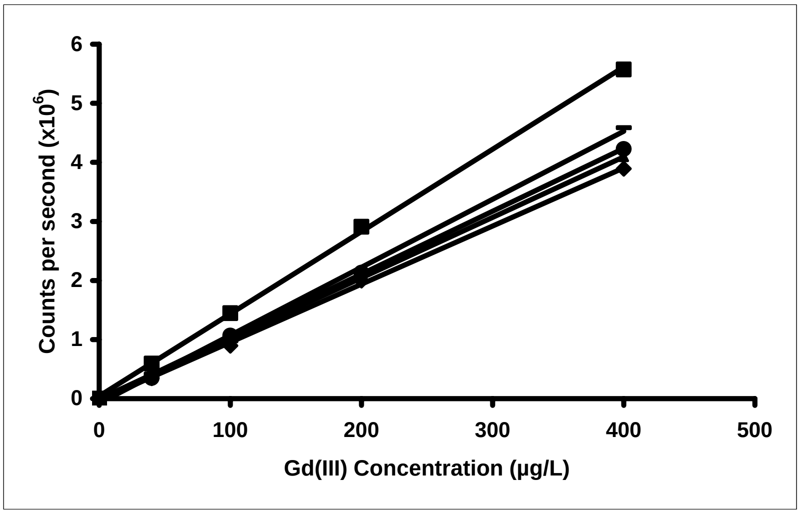

Figure C.5. Matrix-matched calibration graphs for Gd(III). -■- Gd(III) aqueous standard calibration graph ($y = 13930x + 42544$, $R^2 = 0.9995$), -◆- Gd(III) SW matrix-matched calibration graph ($y = 9836.8x – 28622$, $R^2 = 0.9991$), -▲- Gd(III) UPW matrix-matched calibration graph ($y = 10249x - 6370.9$, $R^2 = 0.9996$), -●- Gd(III) GW matrix-matched calibration graph ($y = 10645x – 20298$, $R^2 = 0.9996$), -▬- Gd(III) TW matrix-matched calibration graph ($y = 11516x – 79876$, $R^2 = 0.9981$)

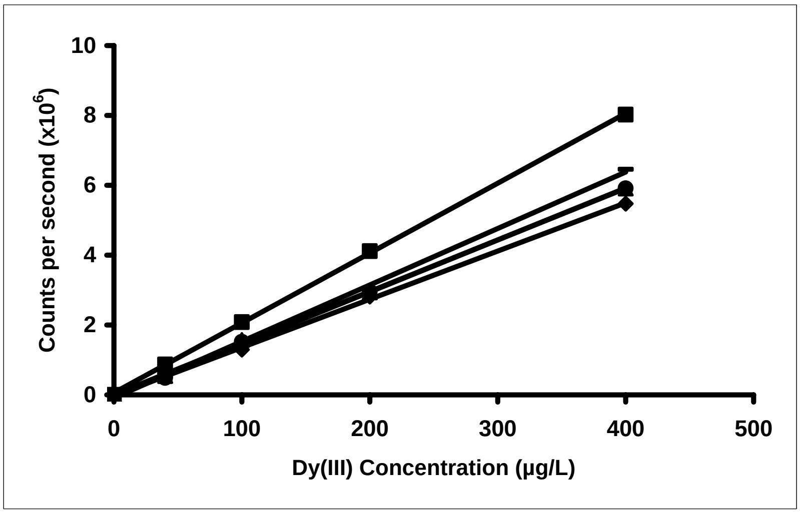

Figure C.6. Matrix-matched calibration graphs for Dy(III). -■- Dy(III) aqueous standard calibration graph ($y = 20006x + 57288$, $R^2 = 0.9998$), -◆- Dy(III) SW matrix-matched calibration graph ($y = 13791x – 21479$, $R^2 = 0.9994$), -▲- Dy(III) UPW matrix-matched calibration graph ($y = 14773x + 4605.9$, $R^2 = 0.9995$), -●- Dy(III) GW matrix-matched calibration graph ($y = 14874x – 26009$, $R^2 = 0.9995$), -▬- Dy(III) TW matrix-matched calibration graph ($y = 16172x – 87959$, $R^2 = 0.9985$)

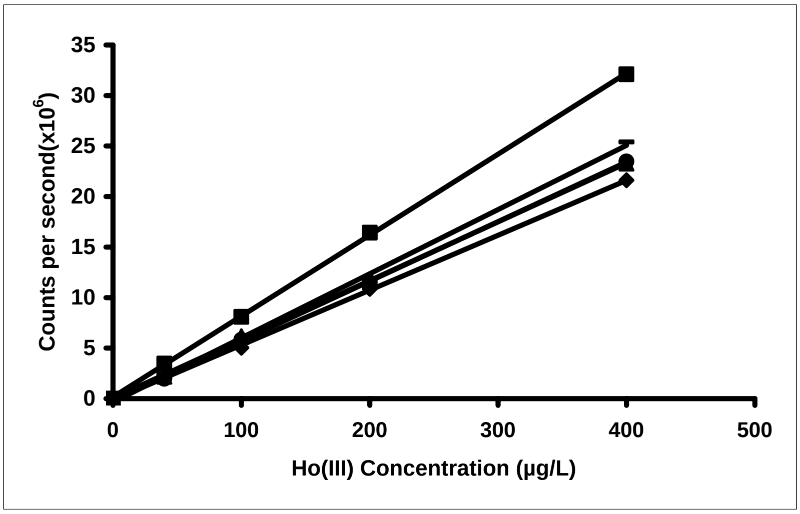

Figure C.7. Matrix-matched calibration graphs for Ho(III). -■- Ho(III) aqueous standard calibration graph (y = 80162x + 154858, R^2 = 0.9998,), -♦- Ho(III) SW matrix-matched calibration graph (y = 54352x – 132428, R^2 = 0.9997), -▲- Ho(III) UPW matrix-matched calibration graph (y = 58166x + 40469, R^2 = 0.9996), -●- Ho(III) GW matrix-matched calibration graph (y = 58993x – 176521, R^2 = 0.9997), -▬- Ho(III) TW matrix-matched calibration graph (y = 63559x – 355464, R^2 = 0.9982)

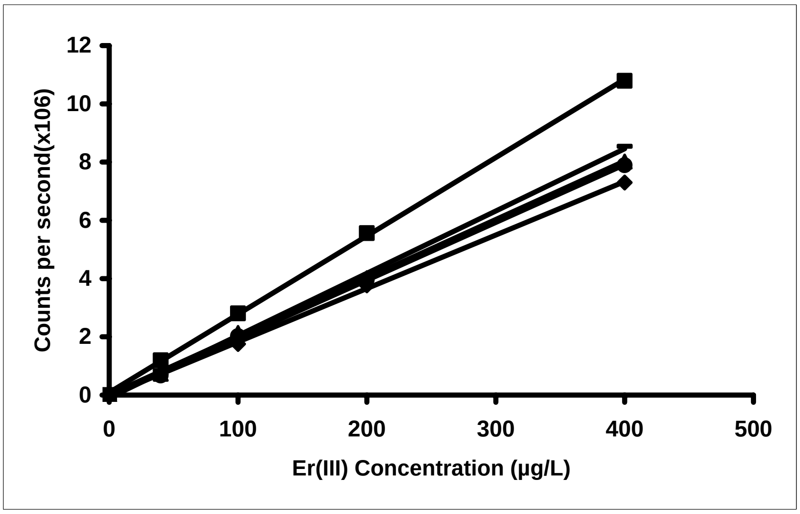

Figure C.8. Matrix-matched calibration graphs for Er(III). -■- Er(III) aqueous standard calibration graph (y = 26888x + 89033, R^2 = 0.9997), -♦- Er(III) SW matrix-matched calibration graph (y = 18353x – 11444, R^2 = 0.9995), -▲- Er(III) UPW matrix-matched calibration graph (y = 20056x + 11731, R^2 = 0.9995), -●- Er(III) GW matrix-matched calibration graph (y = 19843x – 25396, R^2 = 0.9996), -▬- Er(III) TW matrix-matched calibration graph (y = 21377x – 91748, R^2 = 0.9989)