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ON-LINE PRECONCENTRATION OF LEAD FOR THE DETERMINATION WITH FLAME ATOMIC ABSORPTION SPECTROMETRY

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การดัดแปรซิลิกาเจลด้วย 3-เมอแคปโทโพรพิลไตรเมทอกซีไซเลนได้เป็น Si-MPTS เพื่อใช้เป็นตัวดูดซับ จากนั้นพิสูจน์เอกลักษณ์ของ Si-MPTS ด้วยเทคนิคฟูเรียร์ทรานส์ฟอร์มอินฟราเรดสเปกโทรสโกปีและเทคนิคเทอร์โมแกรวิเมตริก อะนาไลซิส จากนั้นทำการศึกษาสมบัติการเพิ่มความเข้มข้นของไอออนตะกั่วแบบออนไลน์ร่วมกับเทคนิคเฟลมอะทอมิกแอบซอร์ปชันสเปกโทรเมตรี โดยใช้สารละลายตะกั่วเข้มข้น 10 มิลลิลิตร ที่อัตราการไหล 9.0 มิลลิลิตรต่อนาที พบว่าไอออนตะกั่วที่ถูกดูดซับจะถูกชะด้วยสารละลายกรดไฮโดรคลอริกเข้มข้น 0.05 โมลต่อลิตร ปริมาตร 200 ไมโครลิตร ที่อัตราการไหล 1.4 มิลลิลิตรต่อนาทีและทำการตรวจสอบประสิทธิภาพของระบบภายใต้การศึกษาปัจจัยต่างๆ โดยใช้สารละลายที่มีการเติมไอออนตะกั่วเข้มข้น 20 และ 100 ไมโครกรัมต่อลิตร พบว่าให้ค่า preconcentration factor เท่ากับ 50 และ sample throughput เท่ากับ 37 ตัวอย่างต่อชั่วโมง ให้ค่าคืนกลับอยู่ในช่วง 102.2-106.8% และความแม่นในการวิเคราะห์ (%RSD) เท่ากับ 4.8 -10.2 % การศึกษาความถูกต้องของการวิเคราะห์ศึกษาโดยใช้ตัวอย่างอ้างอิงมาตรฐาน (SRM 1643e) ซึ่งพบว่าสามารถนำระบบนี้ไปประยุกต์ใช้ในการหาปริมาณของไอออนตะกั่วที่มีปริมาณน้อยในน้ำตัวอย่างได้

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NATTHAWAN MAMEECHAI: ON-LINE PRECONCENTRATION OF LEAD FOR THE DETERMINATION WITH FLAME ATOMIC ABSORPTION SPECTROMETER. THESIS ADVISOR: ASST.PROF. FUANGFA UNOB, Ph.D, 63 pp.

A method for on-line preconcentration and determination of Pb(II) by flame atomic absorption spectrometry was developed. The solid phase extraction was applied in the preconcentration and silica gel chemically modified with 3-mercaptopropyltrimethoxysilane (Si-MPTS) was used as column packing material. The Si-MPTS was synthesized and characterized by fourier transform infrared spectroscopy (FT-IR) and thermogravimetric analysis (TGA). In the determination of Pb(II), the sample solution (10 mL) was passed through the column with a flow rate of 9.0 mL min^{-1}. The sorbed Pb(II) ions were eluted with 200 µL of 0.05 mol L^{-1} HCl solution at a flow rate of 1.4 mL min^{-1}. The preconcentration factor of 50 and sample throughput of 37 samples h^{-1} were achieved. The performance of the system was investigated under the optimum conditions using the solution containing 20 and 100 µg L^{-1} of Pb(II). The percentage recovery and the precision (%RSD) of the method were 102.2-106.8% and 4.8 -10.2 %, respectively. The accuracy of the method was tested by using certified reference material (SRM 1643e). The proposed system was applied for the determination of trace levels of Pb(II) in water samples.

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LIST OF ABBREVIATIONS AND SIGNS

°C = degree Celsius
cm^{-1} = unit of wave number
FAAS = flame atomic absorption spectrometry
FI = flow injection
FIA = flow injection analysis
FT-IR = fourier transform infrared spectroscopy
g = gram
mg = milligram
μg = microgram
GFAAS = graphite furnace atomic absorption spectrometry
h = hour
HSAB = hard-soft-acid-base principle
ICP-AES = inductively coupled plasma atomic emission spectrometry
ICP-MS = inductively coupled plasma mass spectrometry
L = Liter
LLE = liquid liquid extraction
min = minute
mL = milliliter
mol = mole
RSD = relative standard deviation
Si-MPTS = silica gel functionalized with 3-mercaptopropyltrimethoxysilane
SD = standard deviation
SPE = solid phase extraction
w/v = weight per volume

CHAPTER I

INTRODUCTION

1.1 Statement of the problem

Nowadays many countries are encountering the environmental problems especially water pollution. The contamination of heavy metals in water is harmful to human, animals and plants. Among the widespread used heavy metals, lead is a common toxic substance used in storage batteries, gasoline anti-knock products and paint pigments [1] and it could also cause environmental and health problems. Lead poisoning causes health problems, such as brain dysfunction in children, neurobehavioral changes in adults, hypertension and chronic kidney disease [1,2]. Due to its high toxicity, the Ministry of Science Natural Resources and Environment and the Ministry of Public Health of Thailand set the guidelines and regulations for the maximum allowable lead concentration in wastewater discharged from industries and in drinking water as 0.2 mg L^{-1} and 0.05 mg L^{-1}, respectively [3,4]. Furthermore, the concentration of Pb in the environment should be regularly monitored.

The concentration of Pb in environmental samples is very low and the sensitive techniques are needed for the analysis. Flame atomic absorption spectrometry (FAAS) is a widely used technique for analysis of many elements in various samples and it offers many advantages, for example, rapid and low cost operation, good precision and accuracy. However, there are certain limitations in determination of trace metals in the environmental samples by FAAS due to matrix interferences and low sensitivity of FAAS. The preconcentration step is required prior to the determination of trace metals in order to improve the sensitivity of the method by increasing the analyte concentration as well as eliminating the interfering matrix. Among various methods used for preconcentration of metals, solid phase extraction (SPE) offers a number of important benefits, such as reducing the disposal costs, achievement of high preconcentration factor and the automated analysis is possible [5]. However, the conventional batch or off-line column preconcentration based SPE method is tedious and time-consuming. It requires large sample volume and reagents and may result in contamination and analyte losses. Thus, on-line flow injection (FI) SPE preconcentration coupled with FAAS is an interesting alternative. It has been utilized to improve the sensitivity and selectivity of the determination method of trace levels of metals. Moreover, on-line methods provide some advantages over the off-line column method or the batch method such as automated and rapid analysis with simple apparatus and easy operation, low reagents and samples consumptions, less risk of contamination and analyte losses. Furthermore, FI method offers high sample throughput, good reproducibility and accuracy [6].

Among many types of adsorbent used in SPE, silica gel chemically modified with organic molecules containing nitrogen, oxygen, sulfur have drawn a lot of interest and have been used in metal ions adsorption [7]. Silica gel sorbents show high thermal and chemical stability under various conditions. In addition, silica gel has large surface area and the surface consists of the siloxane group and several forms of silanol group which are easily modified. The silica gel chemically modified with chelating agents has been demonstrated as highly selective sorbents toward target metal ions [8-14]. Thus, they have been used as column packing materials in various FI systems for the preconcentration and determination of trace metals.

In this research, silica gel functionalized with 3-mercaptopropyltrimethoxysilane (Si-MPTS) was chosen as SPE sorbents for preconcentration of Pb(II) from aqueous solution due to the ease of preparation and the good selectivity in complexation with Pb(II). The on-line preconcentration system coupled to FAAS was designed for the determination of Pb(II) in solution. The conditions in preconcentration and determination of Pb(II) were optimized. The method was validated and applied to water samples.

1.2 Research objectives

The objective of this work is to develop an on-line method for preconcentration and determination of Pb in water samples by FAAS. The silica gel support easily functionalized with 3-mercaptopropyltrimethoxysilane (Si-MPTS) is used as solid phase in solid phase extraction preconcentration.

1.3 Scope of the research

The scope of this research includes the preparation and characterization of the silica gel functionalized with 3-mercaptopropyltrimethoxysilane (Si-MPTS). The extraction efficiency of the Si-MPTS was evaluated using Pb(II) aqueous solution with column method. Then the Si-MPTS was used as solid phase material in on-line SPE preconcentration system coupled to FAAS. The effects of solution pH, condition time, sample and eluent flow rate on the determination of Pb(II) were investigated. Afterwards, the proposed method was validated using standard Pb(II) solution and certified reference material. Finally, the proposed method was applied in the determination of trace level of Pb(II) in water samples.

1.4 The benefits of the research

To obtain a rapid and sensitive method for determination of trace level of Pb in water samples.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Heavy metals in the environment

Heavy metals are one group of pollutants in the environment that are harmful to human and animal due to their toxic effects [1]. This research focuses on the analysis of lead that is a very toxic metal and harmful to human even at a very low contamination level.

Lead has been used in many industrials and the contamination of lead in the environment brings to health problems. Lead can be absorbed very slowly in human body, but its rate of excretion is even slower. Lead can be emitted into the biosphere as a fuel additive, mainly as tetraethyl lead and tetramethyl lead and present in effluent from many industries [1,2]. It affects the central nervous system leading to brain damage. It also causes hematological damage, anemia, severe kidneys dysfunction and eventually causes death [1,8]. Due to its toxicity, there are regulations on the permitted concentration of lead in the discharged industrial effluent and also in drinking water [3]. The allowable concentration of lead in wastewater from the industries set by the Ministry of Natural Resources and Environment is 0.2 mg L^{-1} [4]. The drinking water quality standards are shown in Table 2.1. The determination of lead concentration in environmental samples and drinking water are required.

Table 2.1 Guidelines and maximum permitted levels of heavy metal in drinking water in Thailand [9]

Elements	Maximum acceptable concentration ($mg\ L^{-1}$)
Mercury (Hg)	0.002
Lead (Pb)	0.05
Arsenic (As)	0.05
Selenium (Se)	0.01
Cyanide (CN)	0.1
Cadmium (Cd)	0.005
Barium (Ba)	1.0

2.2 Determination of metal in water samples

The most commonly used techniques for metal determination are atomic spectrometric techniques, for example, flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS) [10]. The performance of atomic spectrometric techniques is summarized in Table 2.2. Moreover the detection limits achieved in single element analysis are very important in analytical techniques for determination of metals. The typical detection limits for FAAS, GFAAS, ICP-AES and ICP-MS are shown in Table 2.3.

Table 2.2 Comparison of performance of atomic spectrometric techniques [10]

Criterion	FAAS	GFAAS	ICP-AES	ICP-MS
Detection limit	high ppb	sub ppb	sub ppb-ppm	sub ppt
Analytical capability	single element	single element	multielement	multielement
Sample throughput	~3-10sec/ element/ sample	~2-3min/ element/ sample	~1-5 min/ sample	~1-4 min/ sample
Dynamic range	mid ppm range	low ppm range	high ppm range	mid ppm range
Elements applicable	>60	>50	>70	>80
Sample volume required	4-8 mL min^{-1}	~0.2-1 mL min^{-1}	~1-2 mL min^{-1}	~0.2-2 mL min^{-1}
Ease of use	very easy	more difficult	easy	more difficult
Operating cost	low	high	medium	high

Table 2.3 The detection limit (μg L^{-1}) for various elements by atomic spectrometric techniques [11]

Element	FAAS	GFAAS[a]	ICP-AES	ICP-MS
Ag	3	0.02	0.2	0.003
Cd	1	0.02	0.07	0.003
Cr	4	0.06	0.08	0.02
Cu	2	0.1	0.04	0.003
Ni	3	1	0.2	0.005
Pb	5	0.2	1	0.007
Zn	1	0.01	0.1	0.008

[a] Based on 10 μL of sample volume

From Tables 2.2 and 2.3, it shows that FAAS is the common technique for determination of trace metal determination in mg L^{-1} concentration level, which offers the specificity toward the analytes, rapid, low cost operation and high sample throughput. It is used in the routine analysis for most elements. In this research, FAAS is used to couple to the flow injection system for the determination of Pb.

In the analysis by FAAS, the following steps take place. The sample solution was drawn into the burner chamber in the nebulization process. Then, only a small fraction of sample droplets was mixed as an aerosol with the combustible gases mixture (e.g. acetylene gas and air) and transported to the flame. In the flame, the free metal atoms in gaseous phase were obtained. The absorption of monochromatic beam by the free metal atoms was measured.

2.3 Preconcentration of trace metal

The determination of heavy metals in the environmental samples can be done by using various techniques. The direct determination is very difficult due to the low concentration of heavy metals in samples. Moreover, some alkaline earth or alkali metal present in high concentration may interfere the determination of trace heavy metals by FAAS, GFAAS or ICP-MS. Hence the analytes must be separated from the matrix or preconcentrated prior to the measurement by instruments in order to improve the sensitivity of the analytical method. Several separation and preconcentration methods have been used such as solid phase extraction, co-precipitation and solvent extraction [12]. Among these methods, the solid phase extraction is widely used because this method is simple and easy to handle.

2.4 Solid phase extraction (SPE) [12]

Solid phase extraction is an efficient extraction method that can reduce the consumption of toxic organic solvent for the extraction. Moreover, it offers high preconcentration factor and the automated analysis is possible.

2.4.1 Theory of solid phase extraction (SPE)

SPE method consists of four steps: conditioning, loading, washing and elution, which are shown in Figure 2.1.

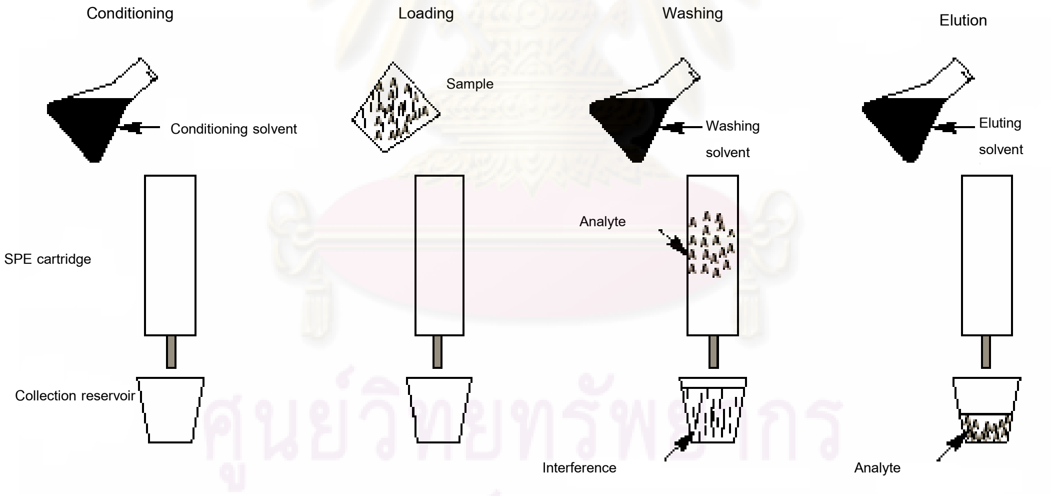


Figure 2.1 The four typical steps of SPE.

2.4.1.1) Conditioning

The first step is the conditioning step that is used to prepare the sorbent to be compatible with sample solution and to remove the impurities on the sorbent surface. The conditioning solvent should be the same solvent as the sample solvent.

2.4.1.2) Loading

In the second step, the sample solution is passed through the solid sorbent. The flow rate of sample should be low enough to enable efficient retention of the analytes and high enough to reduce analysis time.

2.4.1.3) Washing

Thirdly, the appropriate solvent is used to wash the solid sorbent to remove the matrix and interference. The solvent should has a low elution strength and eliminate only matrix components on the surface of sorbent.

2.4.1.4) Elution

The final step is the elution of the analyte by an appropriate solvent. The eluting solvent must elute only the analyte quantitatively.

2.4.2 Retention mechanism of elements on the sorbent

The mechanism of analyte retention depends on the nature of the sorbent and analytes. There are many types of interactions and certain interaction are described below.

2.4.2.1 Adsorption

The adsorption mechanism occurs through van der Waals forces or hydrophobic interaction and depends on the polarity or hydrophobic/hydrophilic behaviors of sorbent and analyte.

2.4.2.2 Chelation

The chelation interaction generally occurs between the metal electron acceptor and electron donator ligand through a coordinate covalent bond. Several chelating organic molecules consist of the functional groups containing donor atom such as oxygen, nitrogen or sulfur atoms. The selectivity of ligand toward the metal ion can be basically considered by the characteristics described by hard-soft acid-base principle

(HSAB). Moreover it also depends on nature, charge and size of the metal ion; nature of the donor atoms present in the ligand; pH of solution which favors certain metal extraction and binding to active donor groups; and nature of the solid support. The Pearson HSAB species are summarized in Table 2.4.

Table 2.4 Hard and soft acid and base species [13]

	Lewis aids	**Lewis Bases**
Hard	H^+, Li^+, Na^+, K^+ Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+} BF_3, BCl_3, $B(OR)_3$ Al^{3+}, $Al(CH_3)_3$, $AlCl_3$, AlH_3, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{3+}	F^-, Cl^- H_2O, OH^-, O^{2-} ROH, RO^-, R_2O, CH_3COO^- NO_3^-, ClO_4^- CO_3^{2-},SO_4^{2-}, PO_4^{3-} NH_3, RNH_2, N_2H_4
Borderline	$B(CH_3)_3$, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Rh^{3+}, Ir^{3+}, Ru^{3+}, Os^{2+}	Br^-, NO_2^-, N_3^- SO_3^{2-}, $C_6H_2NH_2$, C_5H_5N, N_2
Soft	BH_3, Tl^+, $Tl(CH_3)_3$, Cu^+, Ag^+, Au^+, Cd^{2+}, Hg_2^{2+}, Hg^{2+}, CH_3Hg^+, Pd^{2+}, Pt^{2+}, Pt^{4+}, Br_2, I_2	H^-, I^-, H_2S, HS^-, S^{2-}, RSH, RS^-, R_2S, SCN^-, CN^-, RNC, CO, $S_2O_3^{2-}$, R_3P, $(RO)_3P$, $R_3AsC_2H_4$, C_6H_6

2.4.2.3 Ion exchange

Ion-exchange sorbents are used to extract all the cations and anions. The extractive preference depends on the functional groups on the sorbents. Ion-exchange sorbents have two types of the functional groups which are strong and weak for ion exchange. The strong ion exchange sorbents contain sulfonic acid groups (cation-exchange) or quaternary amines (anion-exchange) and can exchange ions at any pH. The weak ion exchange sorbents contain carboxylic acid groups (cation-exchange) or primary, secondary and tertiary amines (anion-exchange). After all, the drawback of ion-exchange sorbents is the lack of selectivity toward specific metal ions.

2.4.3 Selection of solid sorbents in SPE

The desired properties of sorbents in SPE are wide working pH range, high sorption capacity, fast and quantitative sorption and elution, and reusability. The sorbents can be divided into organic-based and inorganic-based sorbents as shown in Figures 2.2 and 2.3.

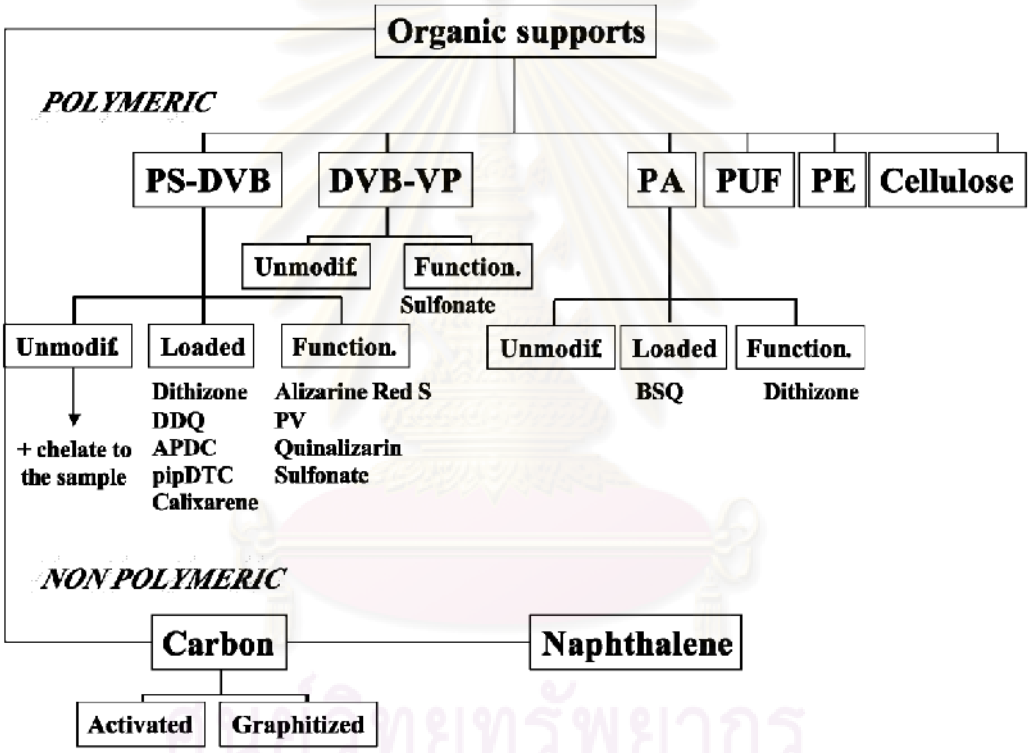


Figure 2.2 The sorbents based on organic support [12].

APDC (Ammonium pyrrolidine dithiocarbamate); BSQ (8-(Benzenesulfonamido)-quinoline); DDQ (7-Dodecenyl-8-quinolinol); pip DDTC (Piperridine dithiocarba mate); DVBVP (Divinylbenzene-vinylpyrrolidone); PA (Polyacrylate); PE (Polyethylene); PS-DVB (Polystyrene-divinylbenzene); PUF (Polyurethane foam); PV (Pyrocatechol violet).

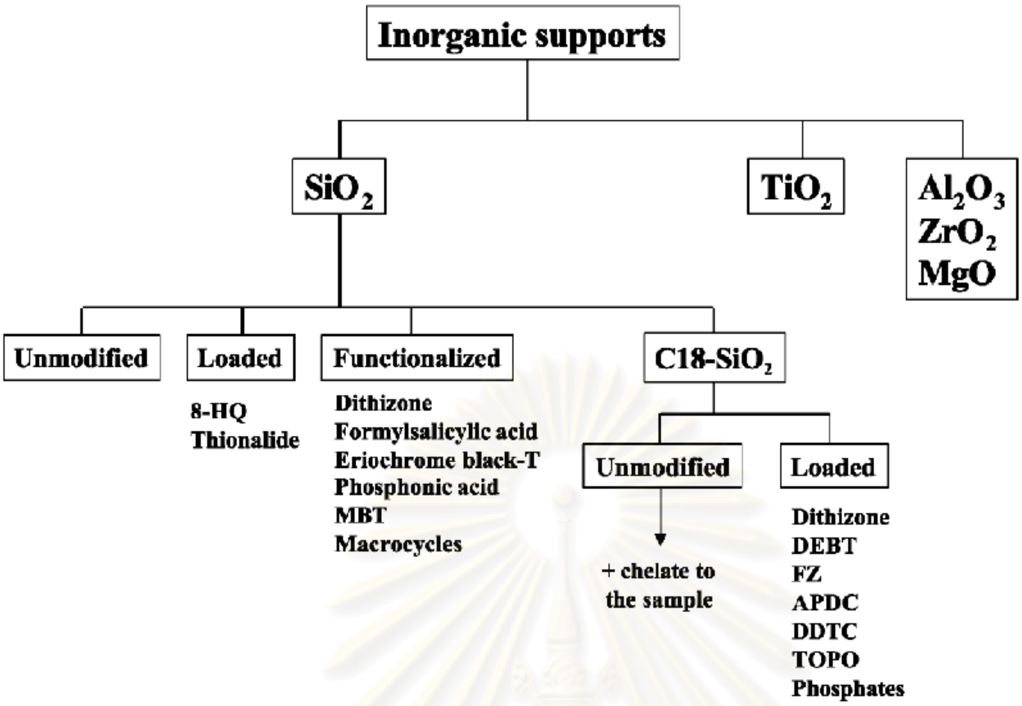


Figure 2.3 The sorbents based on inorganic support [12].

APDC (Ammonium pyrrolidine dithiocarbamate); DDTC (Diethyldithiocarbamate); DEBT (N,N’-Diethyl-N’-benzoylthiourea; FZ (Ferrozine); 8-HQ (8- Quinolinol; MBT (2-mercapto benzothiazole); TOPO (Tri-*n*-octylphosphine oxide).

In order to improve the extraction efficiency and selectivity, the solid phase is usually modified with various functional groups. There are several procedures to prepare the modified sorbents such as 1) direct physical adsorption of a complexing agent onto sorbent surface (loading), 2) modification via covalent bond between a complexing agent and sorbent (grafting). For loading procedure, it exhibits some disadvantages such as leaking out of complexing agent after elution process and complexing agent must be loaded to sorbent before each analysis. The sorbents modified through covalent bond is widely used due to the strong interaction of the functional groups and sorbent surface and can be reused several times after elution.

The organic-based sorbents are divided into polymeric and non-polymeric sorbents. The advantage of polymeric sorbents is the ability to use over the entire pH range. The selectivity of polymeric sorbent can be improved by grafting chelating groups on sorbent surface. The efficiency of polymeric sorbents depends on various physicochemical parameters, such as particle size, surface area, pore diameter and pore volume. The polymeric resin shows several disadvantages such as slow kinetics, swelling or irreversible adsorption. Thus the inorganic sorbents especially, silica gel is widely used in place of polymeric resin because they provide certain advantages over the polymeric materials such as high surface area, no swelling, rapid sorption of metal ions and good mechanical stability.

2.5 Silica gel: A solid support in metal ion preconcentration

2.5.1 The chemistry of silica gel

Silica gel is a solid, amorphous, porous and granular material with a ratio of Si:O of 1:2. Silica gel based sorbent provides many advantages such as mechanical, thermal and chemical stability under various conditions and large surface area. Furthermore, silica gel surface consists of siloxane group and several forms of silanol groups which are easily modified with functional groups.

2.5.2 Silica gel surface

Silica gel consist of silanol groups (≡Si-OH) on the surface. It is now generally accepted that surface silicon atoms tend to have complete tetrahedral configuration and that in an aqueous medium their free valence becomes saturated with hydroxyl groups, forming silanol groups. The silanol groups may be present as free silanol groups or condense to form siloxane bridges (≡Si-O-Si). Therefore, the surface composition of silica gel is made up of physically adsorbed water, chemically bound water, and silicon dioxide.

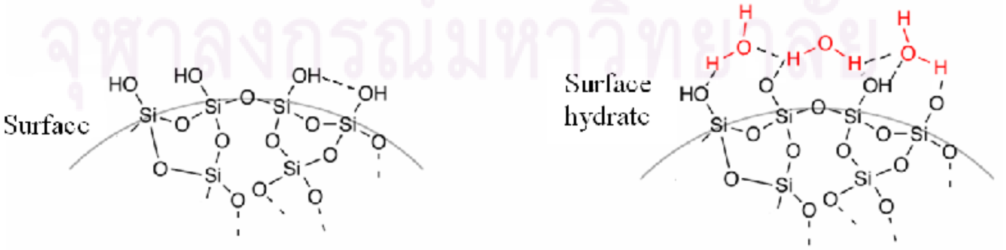


Figure 2.4 Surface of silica gel sorbent [14].

2.5.3 Modification of silica gel surface

There are two different approaches used to modify silica gel surface with the chelating organic compounds: 1) chemical sorption or chemical immobilization; a chemical bond must be formed between silica surface silanol groups and the organic compound by chemical reaction of covalent bond (grafted sorbent) and 2) physical adsorption; the organic compound is directly adsorbed on silica gel surface by passing the reagent solution through the sorbent (impregnated, coated or loaded sorbent) [12]. The advantages of chemical sorption are the strong attachment of organic functional groups on the surface and no leaching of ligand from the sorbent surface. Hence, the sorbents can be used for several times.

In addition, the silica surface consists of two types of the functional groups; siloxane (Si-O-Si) and silanol (Si-OH). The chemical modification onto silica surface may occur via the reaction of the organic functional groups with siloxane (at the Si) or the silanol (direct reaction with the hydroxyl group) groups. Between two reactions, the reaction with the silanol groups is believed to be the main modification pathway.

2.6 On-line preconcentration and determination by atomic absorption spectrometry

The most of sample preparation procedures for trace element analysis, such as preconcentration or separation by various techniques before determination with spectrometric techniques, for example FAAS, GFAAS, ICP-AES or ICP-MS, are performed manually and can be suffered from the contamination and losses of analyte. Therefore, the elimination of human interaction in the tedious stages is very important. In order to combine the sample preconcentration step with the determination step, the on-line flow injection system is often used to connect to the analytical instrument. Flow injection analysis (FIA) is the technique that has been applied and coupled with different analytical techniques such as FAAS and ICP-AES in order to reduce the analysis time and achieve the continuous determination. The typical flow injection analysis manifold usually consists of peristaltic pump, injection valve, a flow-through detector such as FAAS and column for sample separation. Thus flow injection analysis has been utilized due to its performance, such as the enhancement of sensitivity, the decrease in the risk of contamination and the continuous determination. Furthermore it can be built by low cost instrumentation available in almost all laboratories. It offers high sample throughput, low reagent and sample consumptions, better precision compared to batch methodologies and possible automated sample analysis [15].

Flow injection on-line preconcentration and determination of metals by FAAS have been developed and solid phase extraction has been coupled to FAAS to preconcentrate the analyte with simple instrument and rapid analysis. In this study, a FI on-line SPE preconcentration system was coupled to FAAS and used for the determination of lead in water samples.

2.7 Literature review

The important problem of the determination of toxic elements in environmental samples is the low concentration of the elements in the samples and preconcentration step is required in order to improve the detection limit of the analytical method. The preconcentration in the conventional approach may be performed by batch or off-line column method which are not convenient and time consuming. On the other hand, the FI on-line preconcentration based on solid phase extraction are widely used due to its advantages, such as high sample throughput, low reagent and samples consumptions and easy operation. The applications of FI on-line preconcentration coupled with FAAS systems have drawn a lot of interest.

The adsorbents used as the packing materials for off-line preconcentration purposes would not always accommodate FI on-line column preconcentration systems. Therefore, various packing materials have been developed for SPE coupled with FI system for heavy metals determination. The requirements for on-line column packing materials are 1) the mechanical properties should resist to the high flow rates through the column, 2) the kinetics should be rapid for retaining and elution of the analyte by an appropriate eluent [15].

Silica gel is one of the widely used solid phase sorbents, which has good physical and chemical properties such as porosity, high surface area and purity. Silica gel based solid phase can be prepared by chemical grafting or coating of a chelating ligand on silica surface. Research papers reporting the use of silica gel modified with many kinds of chelating agent have published. The examples of chelating agents are 2-mercaptobenzimidazole [16], 3-mercaptopropyltrimethoxysilane [17], zirconium phosphate [18], 5-formyl-3-(1’-carboxyphenylazo)salicylic acid [19], calix[4]arenes [20], 1,8-dihydroxyanthraquinone [21], *o*-dihydroxybenzene [22], 4-

phenylacetophenone 4-aminobenzoylhydrazone (PAAH) [23] and silica gel immobilized nanometer titanium dioxide [24] were also used for metal extraction.

3-mercaptopropyltrimethoxysilane is widely used as the chelating agent which contains sulfur donor atom (Fig. 2.5) it can form complex with various metal ions including Pb. There are some works reporting the use of sulfur containing ligand in Pb(II) extraction. Moreira *et al.* [16] showed in their work that the highly selective adsorption of Pb(II) and other heavy metals ions by 2-mercaptobenzimidazole was satisfactorily achieved. There were also some reports showing selectivity of thiol ligands (-SH) toward some metal ions. Arakaki *et al.* [17] studied Pb(II) and heavy metals adsorption on silica gel grafted with 3-mercaptopropyltrimethoxysilane and ethylene sulfide which contain sulfur donor atoms. The results showed that grafted silica gel was highly selective for Pb(II) determination. Liang *et al.* [25] showed the selectivity of co-condensation of 3-mercaptopropyltrimethoxysilane and tetramethoxy silane to Pb(II) and some metals in the appropriated condition and its application for selective determination of Pb(II). Celis *et al.* [26] studied Pb(II) and heavy metals adsorption on clays functionalized with 3-mercaptopropyltrimethoxysilane and 2-mercaptoethylammonium which contain sulfur donor atoms and the results showed that functionalized clays was selective for Pb(II) determination.

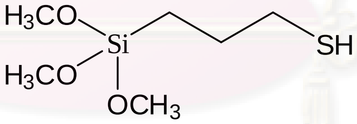


Figure 2.5 Structure of chelating ligand 3-mercaptopropyltrimethoxysilane.

The methods in SPE preconcentration and determination of heavy metal ions by atomic absorption spectroscopic reported in the previous research can be classified in two groups: off-line and on-line methods as described in detail below.

Venkatesh *et al.* [22] used batch and off-line mini-column packed with *o*-dihydroxybenzene coated on silica gel for determination of Pb(II), Cu(II), Fe(II), Zn(II), Co(II), Ni(II) and Cd(II) in tap water and biological water by flame atomic absorption spectrometry. It provided 4 µg L^{-1} of the detection limit for Pb(II). This paper showed that the coated ligand could leak out from the sorbent and the sorbent cannot be reused.

Ekinci and Köklü [27] used a mini-column packed with silica gel immobilized with 3-aminopropyltriethoxysilane for determination of V(II), Mn(II), Ag(I) and Pb(II) in seawater by off-line column method and graphite furnace atomic absorption spectrometry. The results showed the detection limit of 0.004 µg L^{-1} for Pb(II). However the use of batch and off-line column are time consuming and may increase risk of contamination.

The off-line column method exhibits the disadvantage as long analysis time and lack of continuous determination. The on-line method is suggested and developed.

Ensafi and Shiraz [28] used a mini-column packed with activated carbon coated with xylenol orange for preconcentration before determination of Pb(II) in soil and water samples by on-line column method coupled with FAAS. The results depicted the preconcentration factor and detection limit of 200 and 0.4 µg L^{-1}, respectively. The use of coating ligand is the temporary method and ligand can leak out from the sorbent. However, the proposed on-line method provides many advantages, such as low detection limit, low reagent consumption and high sample throughput.

The related publications in FI on-line SPE preconcentration coupled with FAAS using different solid phase materials are listed in Table 2.5.

Table 2.5. Comparison of the performance for FI on-line preconcentration coupled with FAAS systems for determinations of Pb

Sorbent	**Preconcentration factor**	**LOD ($\mu g\ L^{-1}$)**	**Sample throughput (h^{-1})**	**Reference**
Activated carbon loaded with xylenol orange	200	0.4	1.6	[28]
Macrocycle molecule immobilized silica gel	52	5	63	[29]
The complexation of ammonium pyrrolidine dithiocarbamate (APDC) and lead adsorbed on PCTFE-beads	220	1.2	30	[30]
Polyurethane foam loaded with 2-(2-benzothiazolylazo)-2-*p*-cresol (BTAC)	26	1	48	[31]
Amberlite XAD-2 modified by 2-2-benzothiazolyl-azo-2-*p*-cresol (BTAC)	27	3.7	26	[32]
Microcrystalline naphthalene immobilized with ammonium pyrrolidine dithiocarbamate	65	4.6	20	[33]
The complexation of ammonium pyrrolidine dithiocarbamate (APDC) and lead (Pb(II)-PDC) sorbed on PTFE micro-column	330	0.8	18	[34]
Rice husks modified with NaOH solution	46	14.1	14	[35]

No research had been employed 3-mercaptopropyltrimethoxysilane modified silica gel for the FI on-line column preconcentration and determination of Pb(II) ions in a sample before. The purpose of this work is to use an easily prepared sorbent, silica gel grafted with 3-mercaptopropyltrimethoxysilane (Si-MPTS), for determination of Pb(II) ion in water samples. The on-line preconcentration system coupled with FAAS is designed.

CHAPTER III

EXPERIMENTAL SECTIONS

3.1 Chemicals and apparatus

3.1.1 Chemicals

The reagents and solvents in all experiments were of analytical grade and summarized in Table 3.1.

Table 3.1 Chemicals and suppliers

Chemicals	**Supplier**
Silica gel, 70-230 mesh, 60 Å pore diameter	Merck
3-mercaptopropyltrimethoxysilane	Fluka
Toluene[a]	CARLO ERBA
Ethanol	Merck
Dichloromethane	Fisher Chemicals
Hydrochloric acid (37%)	Merck
Nitric acid (65%)	Merck
Thiourea	BDH SpectrosoL®
Ethylenediaminetetraacetic acid disodium salt dihydrate	Fluka
Potassium bromide	Merck
Sodium hydroxide	Merck

Table 3.1 Chemicals and suppliers (contd.)

Sodium chloride	CARO ERBA
Sodium nitrate	Fluka
Sodium sulfate	Merck
Pb standard solution (1000 mg L^{-1})	BDH SpectrosoL®
Cd standard solution (1000 mg L^{-1})	BDH SpectrosoL®
Co standard solution (1000 mg L^{-1})	BDH SpectrosoL®
Cr standard solution (1000 mg L^{-1})	BDH SpectrosoL®
Cu standard solution (1000 mg L^{-1})	BDH SpectrosoL®
Ni standard solution (1000 mg L^{-1})	BDH SpectrosoL®
Fe standard solution (1000 mg L^{-1})	BDH SpectrosoL®
Zn standard solution (1000 mg L^{-1})	BDH SpectrosoL®
Ag standard solution (1000 mg L^{-1})	BDH SpectrosoL®
Hg standard solution (1000 mg L^{-1})	BDH SpectrosoL®
Standard reference material SRM 1643e	National Institute of Standard & Technology (NIST)

[a] Toluene was dried over calcium hydride under nitrogen atmosphere for moisture removal before used.

3.1.2 Preparation of Reagents

All solutions were prepared by using de-ionized (DI) water.

a) Lead standard solutions

Lead standard solutions were prepared by dilution of 1000 mg L^{-1} stock standard solution to the desired concentrations with DI water. The pH value was adjusted using sodium hydroxide and nitric acid solutions.

b) Nitric acid solution

Nitric acid solutions (1, 5 and 10 % v/v) for pH adjustment were prepared daily by direct dilution of the concentrated solution (65%).

c) Sodium hydroxide solutions

Sodium hydroxide solutions (1, 5 and 10 % v/v) for pH adjustment were prepared daily by dissolving the appropriate amount of NaOH in DI water.

d) Hydrochloric acid solutions

Hydrochloric acid solution (0.05 M) was prepared by direct dilution of the concentrated solution (12.23 M).

e) Solutions containing different salts

The solutions containing sodium salt of different anions (NO^{3-}, SO_4^{2-} or Cl^-) of 0.1 and 1.0 M, used in the study of coexisting ions effect were prepared by dissolving the appropriate amount of sodium nitrate, sodium sulfate or sodium chloride in DI water.

f) Solution containing different metal ions

The solutions containing nitrate salt of different metal ions Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, Fe^{3+}, Zn^{2+}, Ag^+ or Hg^{2+}, used in the study of coexisting ions effect were prepared by dilution of 1000 mg L^{-1} stock standard solution with DI water to the required concentrations.

g) Lead working standard solutions

Lead working standard solutions were prepared by dilution of 1000 mg L^{-1} lead standard solution to the required concentrations with DI water. The working standard solutions were prepared freshly before used.

h) Citrate buffer solution

Citrate buffer solution (pH 7) was prepared by using 0.1 M citric acid and tri-sodium citrate 0.1 M.

3.1.3 Apparatus

The apparatuses used in this study are listed in Table 3.2.

Table 3.2 Apparatus lists

Apparatus	Model (company)	Purpose
1. Fourier transform infrared spectrometer (FT-IR)	Nicolet: Impact 410	Identification of functional groups on silica gel surface
2. Thermogravimetric analyzer (TGA)	Perkin-Elmer: Pyris 1	measurement of functional group amount on sorbent
3. Flame atomic absorption spectrometer (FAAS)	Perkin-Elmer: AAnalyst 100	metal ion determination (operating parameters are shown in table 3.3)
4. Graphite furnace atomic absorption spectrometer (GFAAS)	Perkin-Elmer: AAnalyst 4110ZL	metal ion determination (operating parameters are showed in table 3.4)
5. pH meter	Hanna instruments : pH 211	pH measurement
6. Peristaltic pump	REGLO Analog MS-4/8 model ISM 827 (ISMATEC®)	control of solution flow rate passing through the column

Table 3.3 Operating parameters the determination of Pb concentration by FAAS

Operating conditions	**Pb**
Wavelength (nm)	283.3
Slit width (nm)	0.70
Lamp current (mA)	10
C_2H_2 flow-rate (L min^{-1})	2
Air flow-rate (L min^{-1})	4

Table 3.4 Temperature program in the determination of Pb by GFAAS

Step	**Temperature (°C)**	**Ramp time (s)**	**Hold time (s)**	**Argon gas flow rate (mL min^{-1})**
1	110 (initial)	1	30	250
2	130	15	30	250
3	350	10	20	250
4	1600	0	5	0 ; Read
5	2450	1	3	250

3.2 Synthesis of silica gel functionalized with 3-mercaptopropyltri methoxysilane

In the preparation of modified silica gel, the procedure reported by Arakaki *et al.* was adopted [17]. Silica gel (12.5 g) was suspended in 100 mL of dry toluene in a 250 mL two-necked bottom flask and the mixture was refluxed and stirred under nitrogen atmosphere at 90 ^{o}C for 1 h. Then 3-mercaptopropyltrimethoxysilane (5 mL) was slowly added dropwise. The mixture was refluxed and stirred under nitrogen atmosphere at 90^{o}C for 24 h. The solid was filtered, washed continuously with toluene, ethanol and dichloromethane, respectively. This modified silica gel (Si-MPTS) was dried in vacuum at room temperature and kept in desiccator. The synthesis reaction is presented in Figure 3.1.

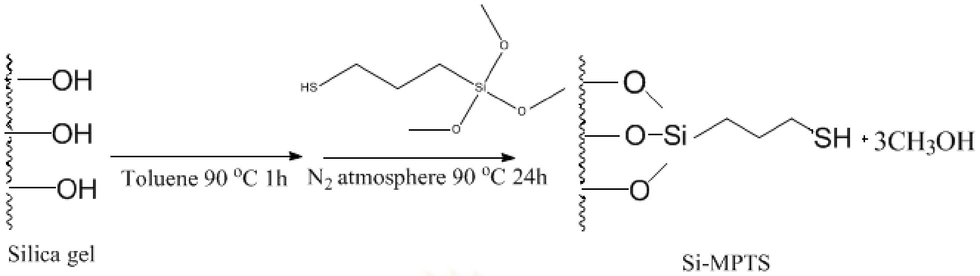


Figure 3.1 The synthesis of the Si-MPTS.

3.3 Characterization

The characterization of the synthesized Si-MPTS was performed by using fourier transform infrared spectrometer (FT-IR) and thermogravimetric analyzer (TGA). FT-IR was used to confirm the presence of functional groups on silica gel surface. The amount of 3-mercaptopropyl functionalized on silica gel sorbent was determined by TGA.

3.3.1) Fourier transform infrared spectroscopy (FT-IR)

Infrared spectra were recorded from 400 to 4000 cm^{-1} in transmittance mode by KBr pellet technique.

3.3.2) Thermal gravimetric analysis (TGA)

Thermogravimetric measurements were performed using a heating rate of 30 ºC min^{-1} under nitrogen atmosphere. The amount of 3-mercaptopropyl (mmol) per adsorbent amount (g) were calculated from the thermogram obtained.

3.4 Adsorption of metal ion onto Si-MPTS

The metal sorption properties of Si-MPTS was studied before application in on-line preconcentration. The experiment were performed using two methods : off-line column and on-line preconcentration methods. The off-line column method was used to evaluate the extraction efficiency of Si-MPTS in Pb(II) extraction before the on-line preconcentration study.

3.4.1 Off-line column method

The experiments using off-line column method were carried out to obtain the optimum conditions for extraction of Pb(II). All experiments were performed in triplicate. The process in column method consists of four steps : conditioning, extraction, washing and elution. In each step, the solution flow rate was controlled by a peristaltic pump. A homemade mini-column (2×0.4 cm i.d.) was packed with Si-MPTS and polyethylene frits were placed at both ends of the mini-column to prevent the sorbent losses. For all experiments, the Si-MPTS column was conditioned by 0.1 M citrate buffer solution at the suitable pH for extraction and washed with DI water. Then sample solution was passed to the mini-columns and the residual Pb(II) concentration in sample solution was determined by FAAS. The mini-columns were used only one time.

3.4.1.1 Effect of solution pH on Pb extraction

The effect of the pH was studied in the pH range of 2.0 to 7.0. The pH of the solution was adjusted with sodium hydroxide solutions (1, 5 and 10 % v/v) or nitric acid solutions (1, 5 and 10 % v/v) to the desired value. 5.0 mL of Pb(II) solution (2 mg L^{-1}) was passed through a mini-column packed with 30 mg Si-MPTS at a flow rate of 5.0 mL min^{-1}. The unsorbed metal ion concentration was determined by FAAS.

3.4.1.2 Effect of the amount of Si-MPTS on Pb extraction

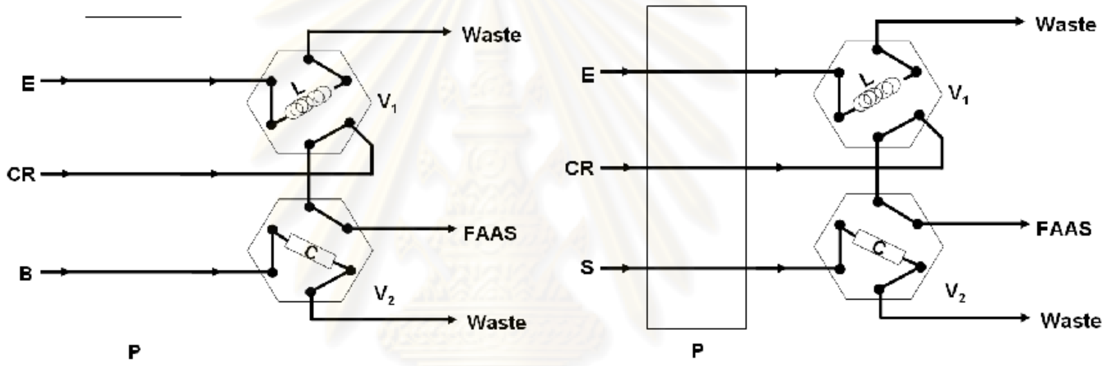
The amount of Si-MPTS packed in mini-column was varied in the range of 10–100 mg. Then 5.0 mL of Pb(II) solution (2 mg L^{-1}, pH 5.0) was passed through a mini-column at a flow rate of 5.0 mL min^{-1}. The residual Pb(II) concentration was determined by FAAS.

3.4.1.3 Selectivity of Si-MPTS

To study the selectivity of Si-MPTS in Pb extraction, 5.0 mL solution containing 0.02 mM of single Pb(II) or the binary mixture of Pb(II) with Ag(I), Cd(II), Co(II), Cu(II), Cr(III), Ni(II), Fe(II), Zn(II) or Hg(II) ions was used at pH 5.0. The solution was passed through a mini-column packed with Si-MPTS at a flow rate of 9.0 mL min^{-1}. The mini-column was used only one time or 3 injections for each metal solution. The residual Pb(II) ion in the solution was determined by FAAS.

3.4.2 On-line preconcentration method

The on-line preconcentration of Pb(II) was studied using flow injection (FI) coupled to FAAS system (FI-FAAS). This system composes of a flow injection system connected to a flame atomic absorption spectrometer (FAAS), used for preconcentration and determination, respectively. The FI manifold and steps in on-line preconcentration are shown schematically in Figure 3.2. The FI system consists of one peristaltic pump (P), two six-port valves (V_1, V_2) which are connected to each other, eluent loop (L) and a mini-column (C) for on-line preconcentration of Pb(II).


(a) Column conditioning step

(b) Extraction step

(c) Elution and determination step

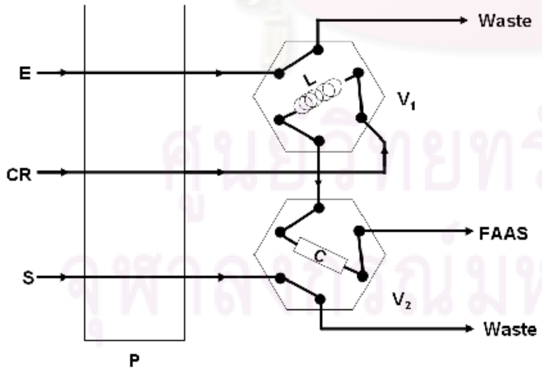


Figure 3.2 Schematic diagram for on-line preconcentration and determination of Pb(II). B, citrate buffer; S, sample; E, eluent; CR, carrier (de-ionized water); P, peristaltic pump; C, mini-column packed with Si-MPTS 30 mg; V_1 and V_2, six-port valves; L, eluent loop of 0.2 mL; W, waste, FAAS, flame atomic absorption spectrometer.

The procedures in on-line preconcentration and determination of Pb consist of three steps as described below.

(a) **Condition step:** The citrate buffer was passed through the mini-column on V_2. In this step, the surface of Si-MPTS was conditioned to activated the surface for Pb binding. The time in column conditioning was investigated.

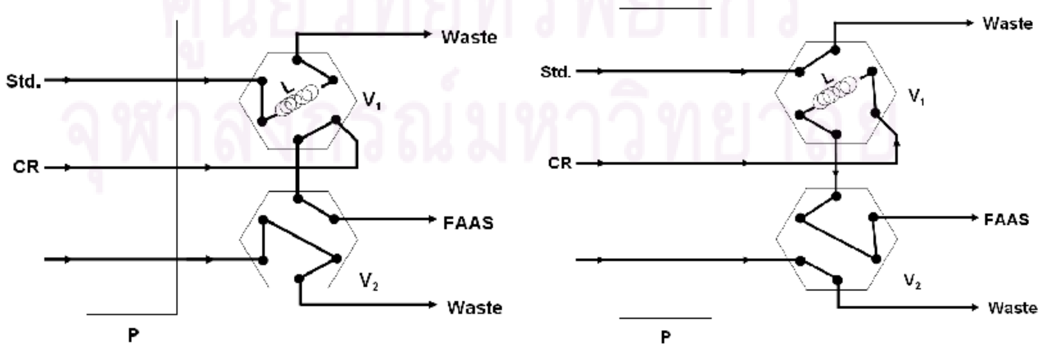
(b) **Extraction step:** A solution containing Pb(II) was pumped through the mini-column. Pb(II) was extracted on the mini-column and the effluent flowed toward waste. Carrier was taken directly to the nebulizer of the flame atomic absorption spectrometer while the eluent was filled in the eluent loop.

(c) **Elution and determination step:** When turned V_2 and V_1 simultaneously, valve V_1 was connected to V_2 and the carrier in the line was driven toward the mini-column. And the carrier transported the eluent through the mini-column. The retained Pb(II) in the mini-column was eluted and the eluate was taken directly to the nebulizer of the flame atomic absorption spectrometer for determination.

The procedures for obtaining calibration curves without preconcentration (direct determination) are shown in Figure 3.3 and consist of two steps.

(a) **Loading:** A standard Pb(II) solution having concentration in the range of 1-7 mg L^{-1} was pumped through the eluent loop, while the carrier was taken directly to the nebulizer of the flame atomic absorption spectrometer.

(b) **Determination:** V_2 and V_1 were turned simultaneously to connect V_2 to V_1 and the carrier flushed the standard Pb(II) solution to the nebulizer of the flame atomic absorption spectrometer for determination.


(a) Loading step

(b) Determination Step

Figure 3.3 The schematic diagram of direct determination of Pb(II) by FI-FAAS system. Std, standard Pb(II) solution; CR, carrier (de-ionized water); P, peristaltic pump; V_1 and V_2, six-port valves; L, eluent loop of 0.2 mL; W, waste; FAAS, flame atomic absorption spectrometer.

In this part, the on-line preconcentration of sample spiked with standard Pb(II) solution was studied and performed according to steps shown in Figure 3.2. Moreover the effect of various parameters such as sample and eluent flow rate, type and concentration of eluent and regeneration time were also investigated. All experiments were performed in triplicate.

3.4.2.1 Types and concentration of eluent

A solution (10.0 mL) containing 0.02 mg L^{-1} Pb(II) at pH 5.0 was passed through FI-FAAS system with a mini-column packed with 30 mg Si-MPTS, at a flow rate of 5.0 mL min^{-1}. The retained Pb(II) was eluted by the different eluents (0.2 mL) HCl, HNO_3 in the concentration range of 0.05-0.5 mol L^{-1}, EDTA (0.05 and 0.1 mol L^{-1}) or 1-4% thiourea in 0.05 M HCl with a flow rate of 1.4 mL min^{-1}. The concentration of Pb(II) was determined by FAAS.

3.4.2.2 Comparison of the calibration curve obtained from direct determination and preconcentration procedure

The signal of Pb solutions (1-7 mg L^{-1}) analyzed by direct determination was measured. Moreover the signal of lead working standard solutions having concentration in the range of 0.02-0.14 mg L^{-1} was recorded after preconcentration. 10.0 mL of sample and 0.2 mL of eluent (0.05 M HCl) were used in the preconcentration.

3.4.2.3 Effect of solution pH

To confirm the result of the effect of pH on Pb extraction obtained from off-line column method, in this part, the effect of the pH was also studied in the range of pH 2.0 to 7.0. The adjustment of pH was done with sodium hydroxide solution (1, 5 and 10 % v/v) or nitric acid solutions (1, 5 and 10 % v/v). 10 mL of 0.02 or 0.1mg L^{-1} Pb(II) solution was passed through a mini-column packed with 30 mg Si-MPTS at a flow rate of 5.0 mL min^{-1} controlled by peristaltic pump. In addition, 0.2 mL of 0.05 M HCl was used as the eluent and the elution flow rate was 1.4 mL min^{-1}.

3.4.2.4 Effect of eluent flow rate

0.2 mL of 0.05 M HCl was selected for elution of Pb(II) from the column. In this study, 10.0 mL of 0.02 or 0.1 mg L^{-1} Pb(II) solution (pH 5.0) was passed through a mini-column at flow rate of 5.0 mL min^{-1}. The effect of the eluent flow rate was investigated in the range of 0.5-5.0 mL min^{-1}. The concentration of Pb(II) ions in the eluate was determined by FAAS.

3.4.2.5 Effect of sample flow rate

The sample flow rate is an important parameter to be optimized in order to obtain quantitative retention of metal ion on solid adsorbent with a reasonable analysis time. 0.2 mL of 0.05 M HCl was selected for elution of Pb(II) solutions with a flow rate of 1.4 mL min^{-1} to ensure the complete elution of sorbed Pb(II) from the column. In this study, a sample solution (10.0 mL) containing 0.02 or 0.1 mg L^{-1} Pb(II) at pH 5.0 was passed through a mini-column using a flow rate in the range of 5.0-12.0 mL min^{-1}.

3.4.2.6 Effect of column conditioning

10.0 mL of Pb(II) solution (20 mg L^{-1}) at pH 5.0 was passed through an on-line system at flow rate of 9.0 mL min^{-1} controlled with peristaltic pump. The sorbed Pb(II) was eluted by 0.2 mL of 0.05 M HCl at a flow rate of 1.4 mL min^{-1}. The influence of column conditioning was also studied using 0.1 M citrate buffer and varying the times from 15 to 60 sec at room temperature. The Pb(II) ions in the eluate was determined by FAAS.

3.4.2.7 Reuse of mini-column

To evaluate the reusability of the Si-MPTS mini-column, several cycles of the extraction and the elution of Pb(II) ions was performed under the optimum conditions as shown in Table 3.5.

Table 3.5 The optimum conditions for Pb(II) preconcentration and determination by FI-FAAS

Conditions	Optimized value
Extraction conditions	
Concentration (mg L^{-1})	0.02, 0.1
Solution pH	5.0
Sample flow rate (mL min^{-1})	9.0
Sample volume (mL)	10.0
Elution conditions	
Eluent solution	0.05 M HCl
Eluent flow rate (mL min^{-1})	1.4
Eluent volume (mL)	0.2

3.4.2.8 Effect of coexisting ions

The effect of coexisting ions were examined by adding the common salt usually found in natural water such as $NaNO_3$, KNO_3 and $Mg(NO_3)_2$ and NaCl in the concentration of 0.1 and 1.0 M to Pb(II) ion solution (0.02 mg L^{-1}) at pH 5.0. Furthermore, the solutions of Pb(II) (0.02 mg L^{-1}) containing the other coexisting ions such as Ag(I), Cd(II), Co(II), Cu(II), Hg(II), Ni(II) or Zn(II) ions were also used. The levels of the tolerated concentration of coexisting ions were considered as the maximum concentration that resulted in the change in recovery of Pb(II) when analyzed the solution containing the coexisting ions, compared to the recovery of single Pb(II) solution.

3.5 Method validation

In this part, the method validation was performed by using standard Pb(II) at two concentration levels: 20 and 100 µg L^{-1}. The analysis was repeated 20 times. The calibration curve was obtained by direct injection of 0, 1, 2, 3, 4, 5, 6 and 7 mg L^{-1} Pb(II) solution. Then, the sample solution (10.0 mL) spiked with 20 or 100 µg L^{-1} Pb(II) (pH 5.0) was pass through the on-line preconcentration system with a flow rate of 9.0 mL min^{-1}. The sorbed Pb(II) on the column was eluted by 0.2 mL of 0.05 M HCl at a flow rate of 1.4 mL min^{-1} and determined by FAAS. The accuracy and the precision were presented as recovery (%) and the relative standard deviation (%), respectively. The limit of detection was calculated from the standard deviation of 20 measurements of reagent blank using the on-line preconcentration system.

3.6 Real sample analysis

To demonstrate the performance of the FI-FAAS system in the determination of Pb(II) in real samples, water samples spiked with standard Pb(II) at two concentration levels: 20 and 100 µg L^{-1} were analyzed. The calibration curve was obtained by direct injection of 0, 1, 2, 3, 4, 5, 6 and 7 mg L^{-1} Pb(II). All water samples were filtered with the membrane (0.45 µm) before analysis. Furthermore the concentrations of Pb in real sample solutions determined by this proposed method were compared to the results from graphite furnace atomic absorption spectrometry (GFAAS) method. For analysis of water samples, the water samples used in the experiment were drinking water from 5 sources, tap water, seawater, ground water, canal water, river water and wastewater, spiked with standard Pb(II) at two concentration levels: 20 and 100 µg L^{-1} and adjusted the pH to 5.0 was passed through the on-line preconcentration system with a flow rate 9.0 mL min^{-1}. The retained Pb(II) on the column was eluted by 0.2 mL of 0.05 M HCl at a flow rate of 1.4 mL min^{-1} and determined by FAAS. The experiment was performed in 7 replicates for each sample.

3.7 Analysis of certified reference material

The accuracy of the proposed method was evaluated by analyzing Pb(II) content in certified reference material (SRM 1643e) compared with graphite furnace atomic absorption spectrometry method. The experiment was performed in 5 replicates.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis and characterization of silica gel functionalized with 3-mercaptopropyltrimethoxysilane

In this work, 3-mercaptopropyltrimethoxysilane was chosen as the chelating ligand for Pb(II) ion extraction because it contains sulfur donor atoms which form metal-ligand complex with Pb(II) selectively. The silica gel functionalized with 3-mercaptopropyltrimethoxysilane (Si-MPTS) could be obtained in one step synthesis The characterization was performed to identify and confirm the product from the synthesis. The functionalized silica gel was characterized by FT-IR and TGA before the sorption studies. The results are shown in the following topics.

4.1.1 Fourier transforms infrared spectroscopy

Fourier transform infrared spectroscopy (FT-IR) was used to confirm the presence of 3-mercaptopropyl group on silica gel adsorbent. The IR spectrum of Si-MPTS is compared to that of unmodified silica gel. The results and IR spectra are presented in Table 4.1 and Figure 4.1.

Table 4.1 FT-IR vibration band position assigned for unmodified and modified silica gel [36-38]

Adsorbents	**Absorption frequency (cm^{-1})**	**Remark and assignments**
Unmodified silica gel	3462.74	O-H bond stretching of the silanol groups / the remaining adsorbed water molecule
	1638.46 and 1098.12, 1093.16	Asymmetric stretching vibrations of Si-O-Si bridge
	800.68, 810.60	Si-O bridge symmetric stretching vibrations
Modified silica gel (Si-MPTS)	3437.95	O-H bond stretching of the silanol groups / the remaining adsorbed water molecule
	2942.23 and 2852.99	C-H symmetric stretching vibrations
	2581.32	S-H stretching

The additional peaks observed in the IR spectrum of Si-MPTS at 2942.23 and 2852.99 cm^{-1} correspond to the aliphatic C-H stretching vibration [17]. A very weak S-H stretching peak was also observed at 2581.32 cm^{-1} in the spectra of silica gel containing 3-mercaptopropyl groups [17,39]. In conclusion, FT-IR results show the success of the synthesis and confirm the attachment of mercaptopropyl on the silica gel support.

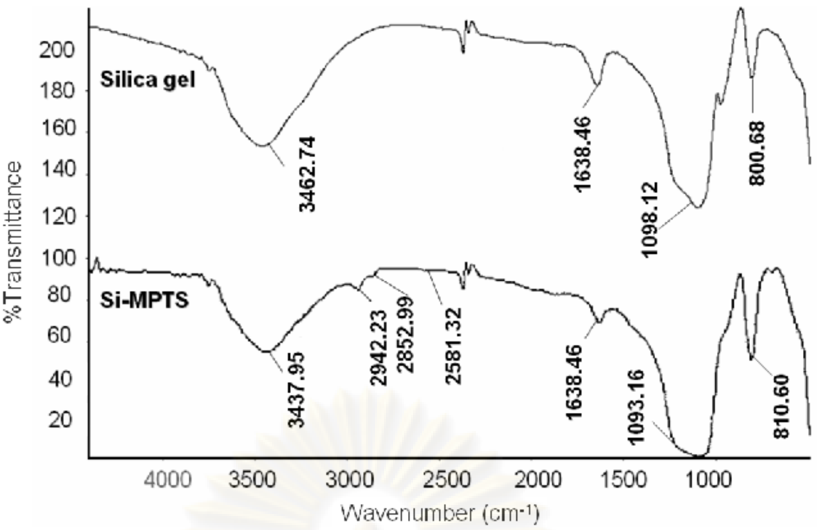
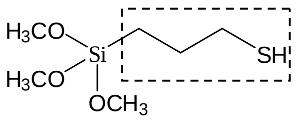


Figure 4.1 Infrared spectrum of Si-MPTS and the bare silica gel.

4.1.2 Thermogravimetric analysis

The TGA profiles of the Si-MPTS and unmodified silica gel, illustrated in Figures 4.2, showed the different decomposition temperature of the functionalized and bare silica gel. For the starting material silica gel, a weight loss of 2.05 % was observed in the temperature range of 30-150 °C, due to the evaporation of adsorbed water. The TGA curve of the final product (Si-MPTS) showed the weight loss in two steps. In the first step, a mass loss of 1.55 % observed at the temperature lower than 200°C was attributed to sorbed water evaporation. In the second step, the mass loss of about 11.30 %, started at 300 to 600 °C, corresponding to the decomposition of 3-mercaptopropyl groups. The TGA results confirm the presence of 3-mercaptopropyl groups on the silica gel surface. The loading of 3-mercaptopropyl on the silica sorbent was calculated using the weight loss data from TGA curve of Si-MPTS. The loading capacity of mercaptopropyl functional group on the obtained adsorbent was calculated using weight loss data from TGA curves (Figure 4.2) and the equation 4-1. the calculated loading capacity of mercaptopropyl was 1.54 mmol g^{-1}.

$$\text{Loading capacity (mmol Ligand/g adsorbent)} = \frac{\text{Ligand (g)}}{\text{M.W. of } (CH_2)_3SH \times \text{Adsorbent (g)}} \qquad 4\text{-}1$$



$(CH_2)_3SH$ M.W. = 75 g/mol

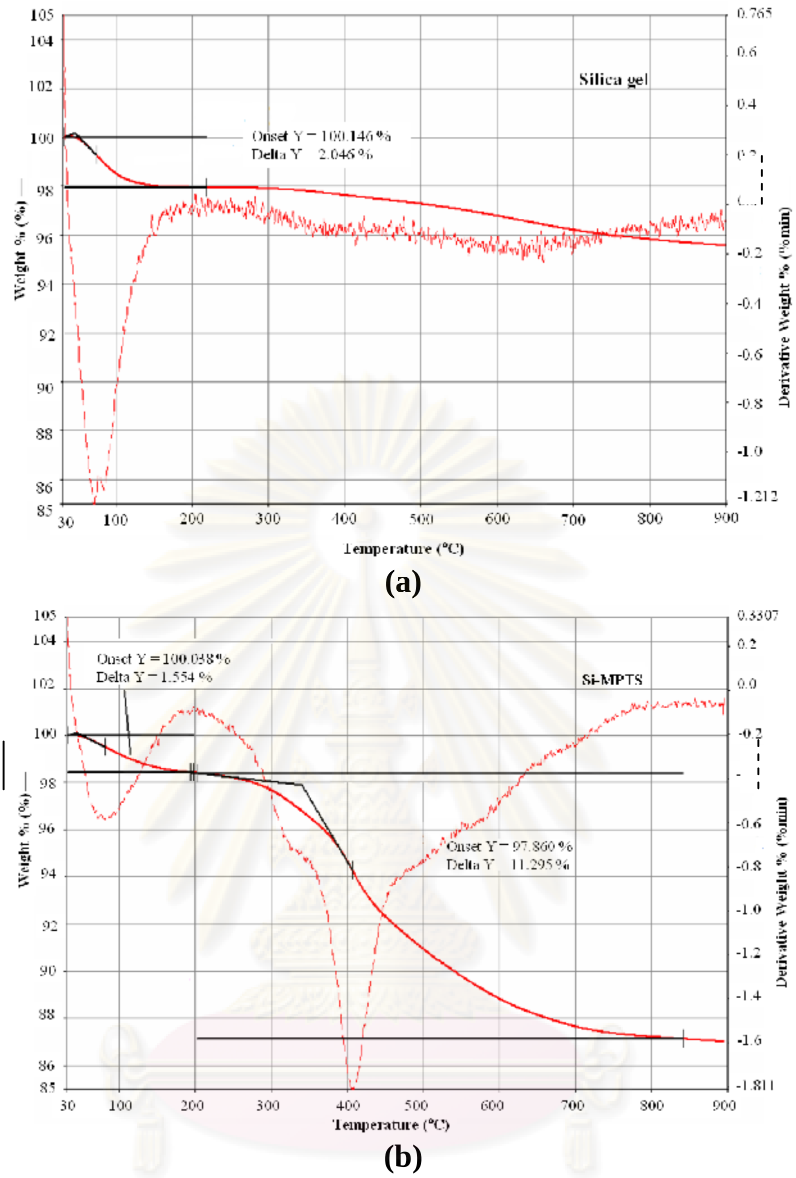


Figure 4.2 Thermograms of (a) silica gel and (b) Si-MPTS.

4.2 Adsorption of metal ion onto Si-MPTS

4.2.1 Off-line column method

4.2.1.1 Effect of solution pH

The pH of the solution is an important parameter which affects the efficiency of the metal ions extraction. In acidic medium, the binding sites can be protonated and the protonated ligand may not form complex with Pb ions in the solution. In basic medium, the metal ions would precipitate as metal hydroxide instead of forming complexes with the ligand. In this study, the thiol groups of Si-MPTS are the binding sites and sulfur atoms act as electron donor in complex formation with various metal ions. The pH effect was studied in the pH range of pH 2.0-7.0. The adsorption experiments at pH higher than 7.0 were not performed due to the precipitation of Pb as lead hydroxide. The results are shown in Figure 4.3.

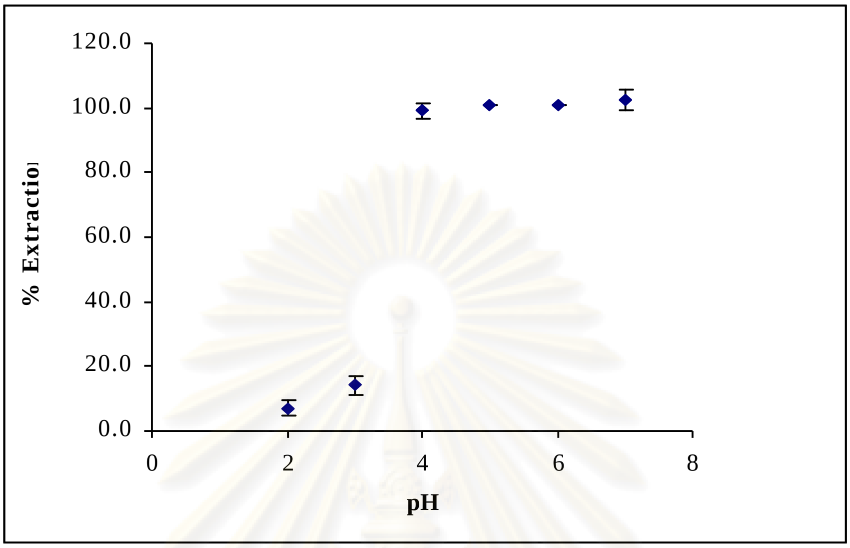


Figure 4.3 Effect of the solution pH on metal extraction.

The low extraction efficiency was observed at pH 3 and lower. At pH $\leq$ 3.0, the binding site of Si-MPTS was possibly protonated by proton in the solution (H^+) and has less affinity toward Pb(II) in complexation. The recovery of Pb(II) increased with increasing the solution pH to the pH 4 and higher. However the experiments at pH 7.0 and higher were not performed due to the precipitation of $Pb(OH)_2$ [40,41]. Thus, the suitable pH for extraction was pH 5.0.

4.2.1.2 Effect of the amount of Si-MPTS

The amount of Si-MPTS in the range of 10-100 mg was used in the determination of 2 mg L^{-1} Pb(II) 5.0 mL. The results are shown in Figure 4.4. The quantity of 20 mg of Si-MPTS was enough to retain Pb(II) ions. However, 30 mg was used to ensure the total retention of the analytes.

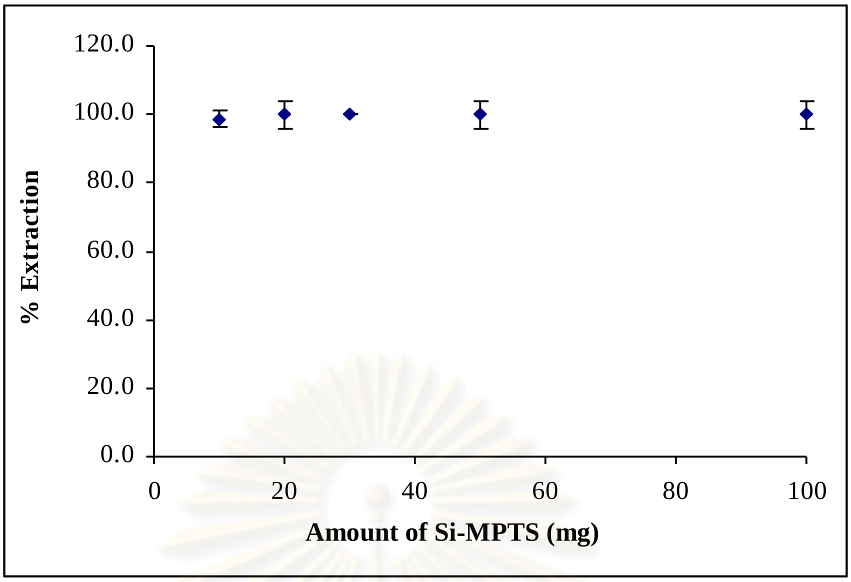


Figure 4.4 Effect of the amount of Si-MPTS on Pb extraction (Pb 2 mg L^{-1} 5.0 mL).

4.2.1.3 Selectivity of Si-MPTS in Pb extraction

In order to examine the selectivity of Si-MPTS in Pb extraction, the solution of Pb(II) (0.02 mM) and the solution of Pb(II) (0.02 mM) containing Ag(I), Cd(II), Co(II), Cu(II), Cr(III), Ni(II), Fe(II), Zn(II) or Hg(II) ions in a concentration of 0.02 mM as binary mixture at pH 5.0 were used in the experiment. Silica gel and Si-MPTS were used as the adsorbent. The results are shown in Figures 4.5 and 4.6. According to the results, Si-MPTS could extract Pb with higher extraction efficiencies compared to silica gel sorbent, especially in the presence of other metal ions in the binary mixture. The significant decrease in extraction percentage of Pb(II) was observed in the binary mixture of Pb(II)/Ag(I) and Pb(II)/Hg(II). Considering the hard-soft acid-base theory, Ag(I) and Hg(II) are soft acids and have good affinity in complexation with mercaptopropyl ligand which is a soft base ligand. Therefore, the competitive adsorption occurred and interfered the extraction of Pb(II). However, the percentage of Pb(II) extraction is higher than 80% in all solution, indicating that Si-MPTS has good selectivity toward Pb extraction over the other metal ions studied and Si-MPTS is suitable for the use as solid phase for the extraction and determination of Pb(II).

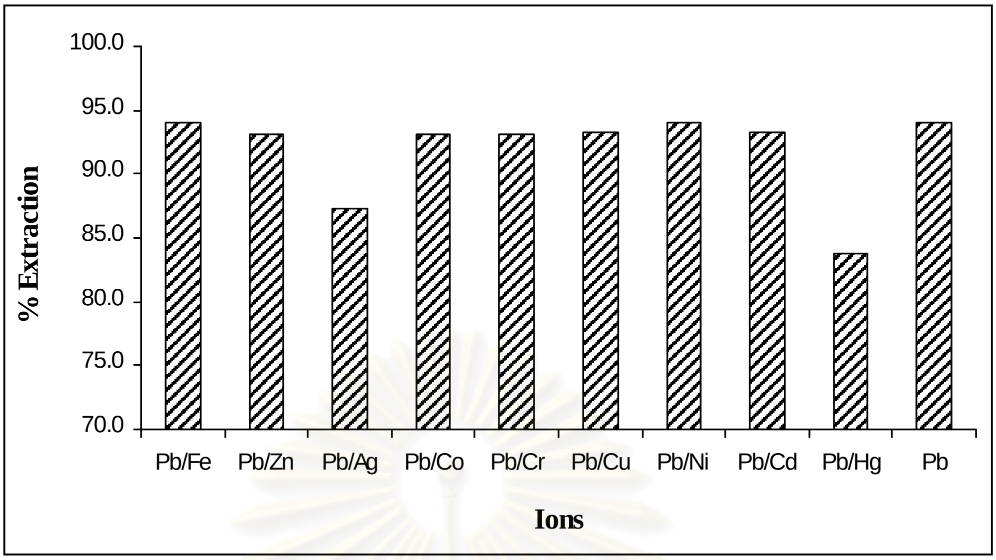


Figure 4.5 Extraction of Pb(II) ions in single ion solution and binary mixture solution by Si-MPTS. Initial concentration of metal ions: 0.02 mM; sample flow rate 9.0 mL min^{-1}; pH 5.0.

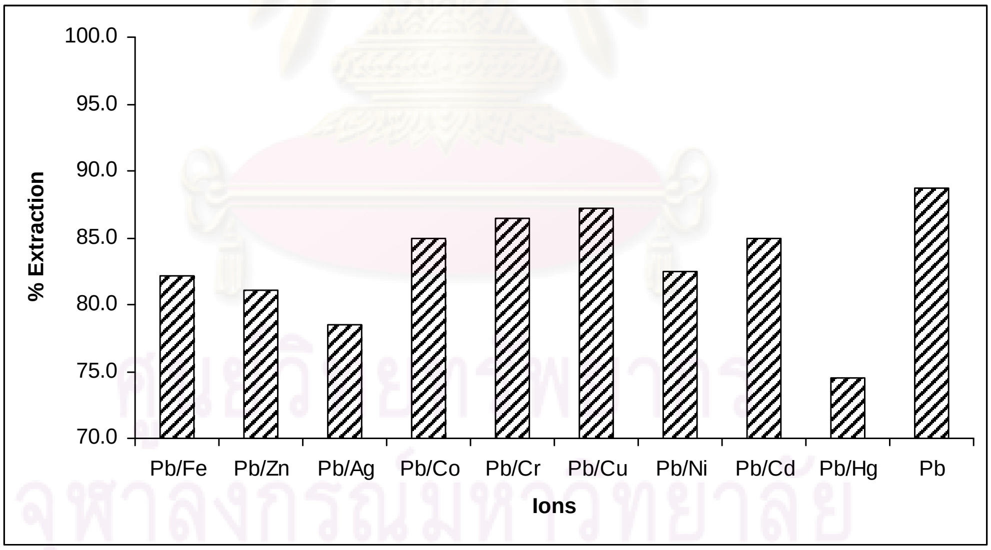


Figure 4.6 Extraction of Pb(II) ions in single ion solution and binary mixture solution by silica gel. Initial concentration of metal ions: 0.02 mM; sample flow rate 9.0 mL min^{-1}; pH 5.0.

4.2.2 On-line column method

4.2.2.1 Types of eluent

In this experiment, various eluents were used to recover the adsorbed metal ions from Si-MPTS. Nitric acid and hydrochloric acid, which are compatible for the determination of Pb(II) by FAAS, were firstly selected as eluent. The selection criterion is based on the results observed in the study of pH effect that Si-MPTS could not extract Pb(II) ions at pH 2.0-3.0. The concentration of nitric acid or hydrochloric acid was varied in the range of 0.05-0.5 mol L^{-1} in order to obtain enough quantity of proton to protonate the chelation sites. The results are plotted between the percentage of recovery which was calculated by using equation 4-1, versus the concentration of nitric acid or hydrochloric acid, as shown in Figure 4.7.

$$\% \text{ Recovery} = \frac{C_f}{C_i} \times 100 \qquad 4\text{-}2$$

C_i and C_f represent the initial concentration of Pb(II) ion before extraction by Si-MPTS (mg L^{-1}) and the final concentration of Pb(II) ion eluted from Si-MPTS (mg L^{-1}), respectively.

The results show that the concentration of 0.05 mol L^{-1} of HNO_3 and HCl was sufficient for the quantitative elution of Pb(II) ions with recovery higher than 99 %.

Furthermore the alternative way for desorption is the use of chelating agent that could form complex with Pb(II) ions better than mercaptopropyl functional group. EDTA (0.05 and 0.1 mol L^{-1}), which is a well-known complexing agent that can form complexes with many metal ions with high formation constants, was selected for elution Pb(II) ions from Si-MPTS. Moreover, thiourea (1-4%) in 0.05 mol L^{-1} HCl solution was also used to eluted the retained Pb(II). The results are shown in Figure 4.8 and 4.9, respectively. The results show that EDTA solution could not quantitatively elute Pb(II) from Si-MPTS while 4% thiourea in 0.05 M HCl could elute Pb(II) from the column. Nevertheless, thiourea may not suitable due to the contamination of thiourea eluent in Si-MPTS column. When passed the new sample to the contaminated column, Pb(II) ions in the sample may from complex with thiourea and not retain in the column.

In this research, HCl in the concentration of 0.05 mol L^{-1} was chosen as eluent because acid solution with higher concentration could damage the column.

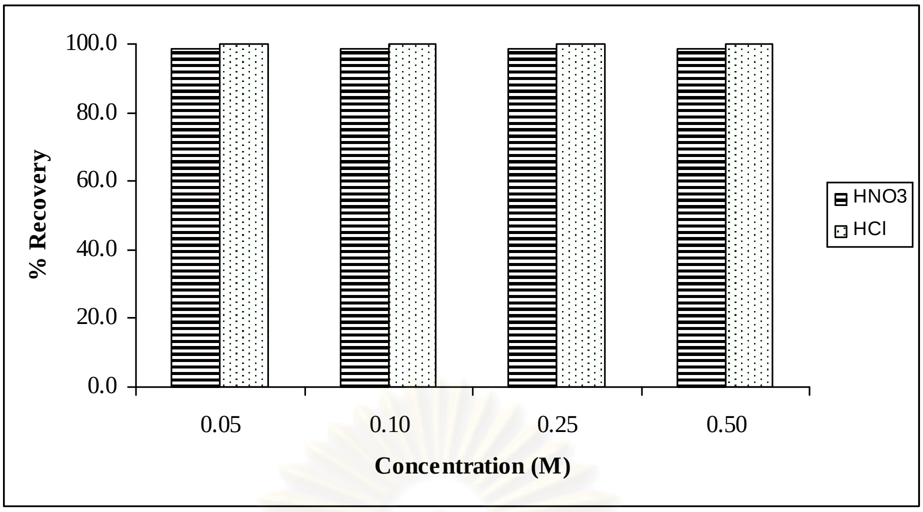


Figure 4.7 Effect of HNO_3 and HCl concentration on Pb recovery (Pb(II) 0.02 mg L^{-1}).

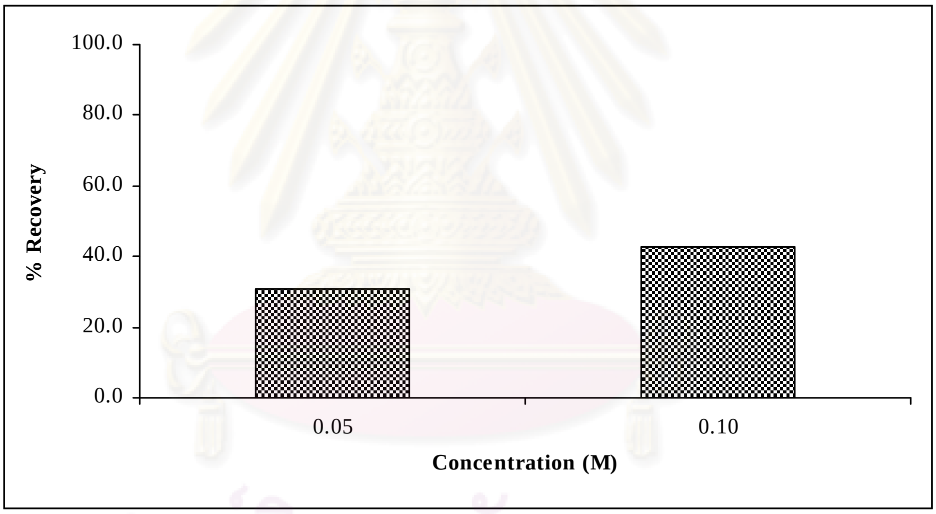


Figure 4.8 Effect of EDTA concentration on Pb recovery (Pb(II) 0.02 mg L^{-1})

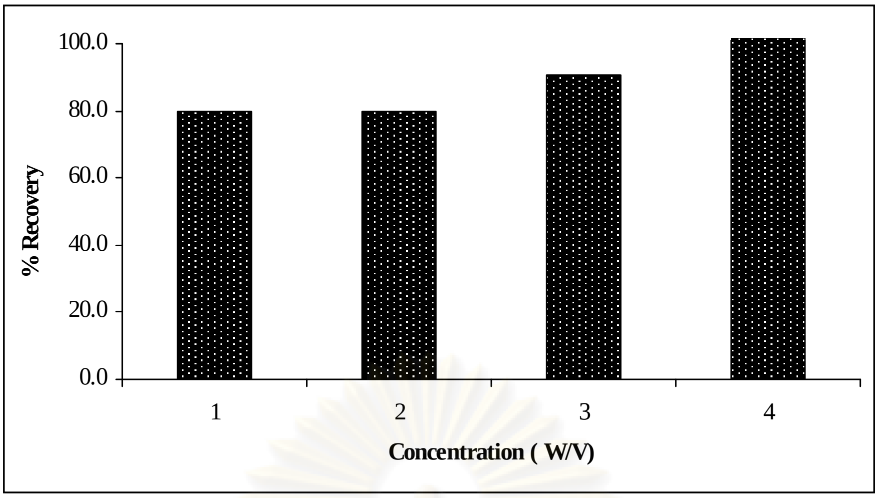


Figure 4.9 Effect of thiourea concentration in 0.05 mol L^{-1} HCl on Pb recovery (Pb(II) 0.02 mg L^{-1}).

4.2.2.2 Comparision of the calibration curve obtained from direct determination and preconcentration procedure

In order to check the preconcentration performance, the calibration curves obtained from direct determination of standards and from preconcentration and determination of standards are compared. The calibration curves were obtained by using two different concentration ranges; a) concentration range of 1-7 mg L^{-1} for direct determination calibration curve and b) concentration range of 0.02-0.14 mg L^{-1} for calibration curve obtained from preconcentration procedure. The results are shown in Table 4.2.

Table 4.2 Comparison of calibration curve obtained from direct determination and preconcentration procedure.

Calibration curve	Linear equation
Direct determination of standards	$y = 0.0027x - 0.0002$ $R^2 = 0.9958$
Preconcentration and determination of standards	$y = 0.0028x - 0.0002$ $R^2 = 0.9931$

When compare the calibration curve obtained by both procedures, the calibration curves for Pb determination were not significantly different. The results indicate that the preconcentration procedure has a good performance in standards preconcentration and that the calibration curve obtained from direct determination of standards could be used in the quantification instead of the calibration curve from preconcentration procedure to reduce the analysis time.

4.2.2.3 Effect of solution pH

The effect of sample solution pH on the on-line determination of Pb(II) was evaluated by varying the pH from pH 2.0 to pH 7.0 (Figure 4.10.). Solution containing 0.02 and 0.05 mg L^{-1} Pb(II) were applied as samples regarding the allowable concentration of Pb(II) in discharged industrial wastewater and in drinking water set by the Ministry of Public Health of Thailand. The result shows very low recovery of Pb(II) from solution at low pH and increased with increasing the pH to 4 and higher values. The results are in agreement with those observed in off-line column study. It may be explained by the low affinity of the binding site of Si-MPTS toward Pb(II) in strong acid solution. The optimum pH for Pb(II) determination is pH 4-7. A pH of 5.0 was chosen for the analysis in the further experiments.

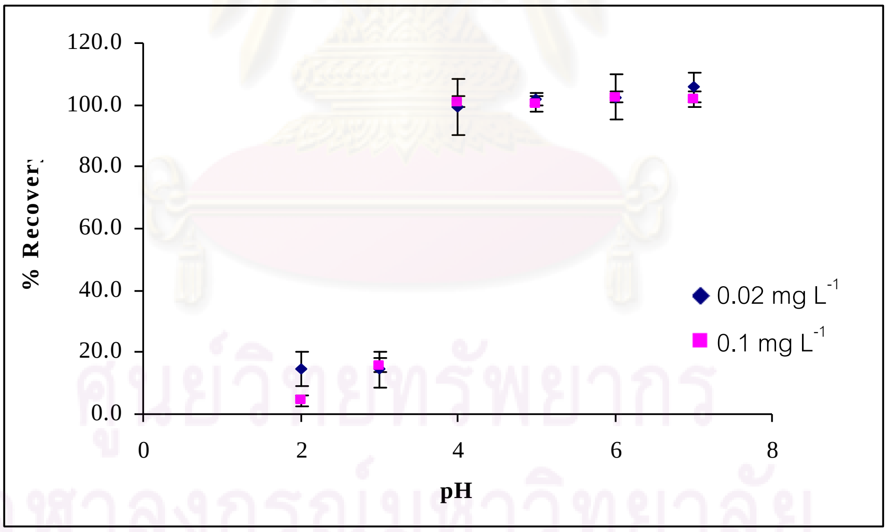


Figure 4.10 Effect of sample pH on Pb recovery (Pb(II) 0.02 and 0.1 mg L^{-1}).

4.2.2.4 Effect of eluent flow rate

In order to maintain the high elution efficiency and shorten the analysis time, the eluent flow rate was studied. From the previous results from the off-line column experiments, 0.05 mol L^{-1} HCl could quantitatively elute Pb(II) from Si-MPTS. In this study, 0.2 mL of 0.05 mol L^{-1} HCl was used as eluent with a flow rate ranging from 0.5-5.0 mL min^{-1} (Figure 4.11). The results indicate that the low eluent flow rate could recover the quantitative amount of Pb(II) from the column. The results in the determination of Pb(II) in both concentrations are in the same trend. When used the eluent flow rate higher than 1.4 mL min^{-1}, the analytical recovery decreased significantly because the eluent had less contact time with adsorbents surface. Consequently, an elution flow rate of 1.4 mL min^{-1} was selected.

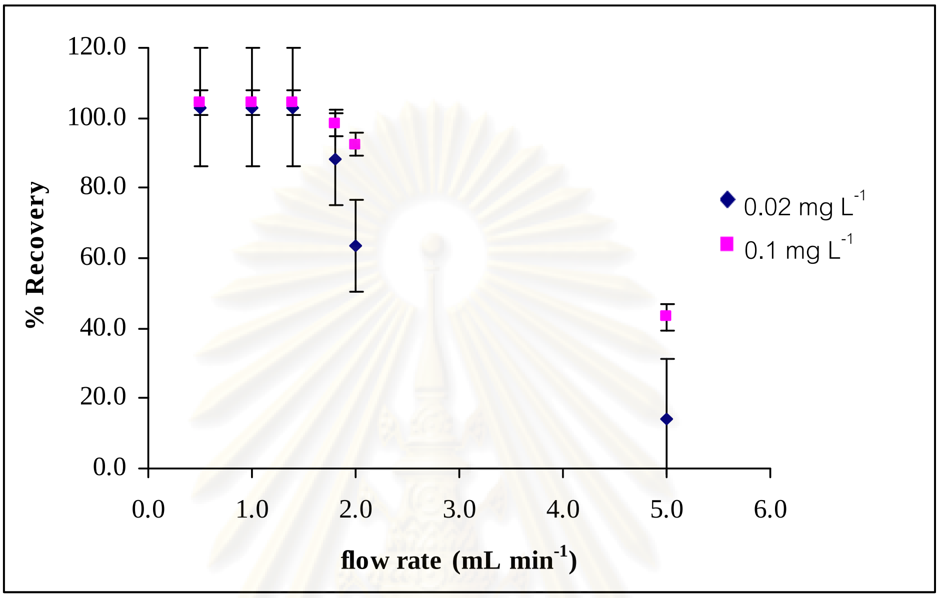


Figure 4.11 Effect of eluent flow rate on Pb determination. (Condition: Si-MPTS 30 mg, metal solution volume 10.0 mL, Pb 0.02 and 0.1 mg L^{-1} at pH 5.0 and sample flow rate 9.0 mL min^{-1}).

4.2.2.5 Effect of sample flow rate

The extraction efficiency depends on the contact time between the analyte and the solid phase. At the high sample flow rate, the solution is passed through the column quickly and the contact time between adsorbent and the metal ions in the solution may not sufficient for the complete metal retention. When use low sample flow rate, the solution passes through the column for long time resulting in a quantitative retention of metal on solid phase but the analysis time also increases. In order to maintain the high extraction efficiency and shorten the analysis time, the sample flow rate was optimized.

The influence of sample flow rate on the determination of Pb was studied at the flow rate ranging from 5.0 to 12.0 mL min^{-1}. The results are shown in Figure 4.12. When used sample flow rate of 10 mL min^{-1} and higher, the analyte recovery decreased due to the short contact time between the solid phase and Pb(II) ions in the solution, resulting in low extraction efficiency. Moreover, there was a high back pressure in mini-column that led to the leak of sample solution at the junction of the column. Therefore, the sample flow rate of 9.0 mL min^{-1} was chosen to reduce the analysis time.

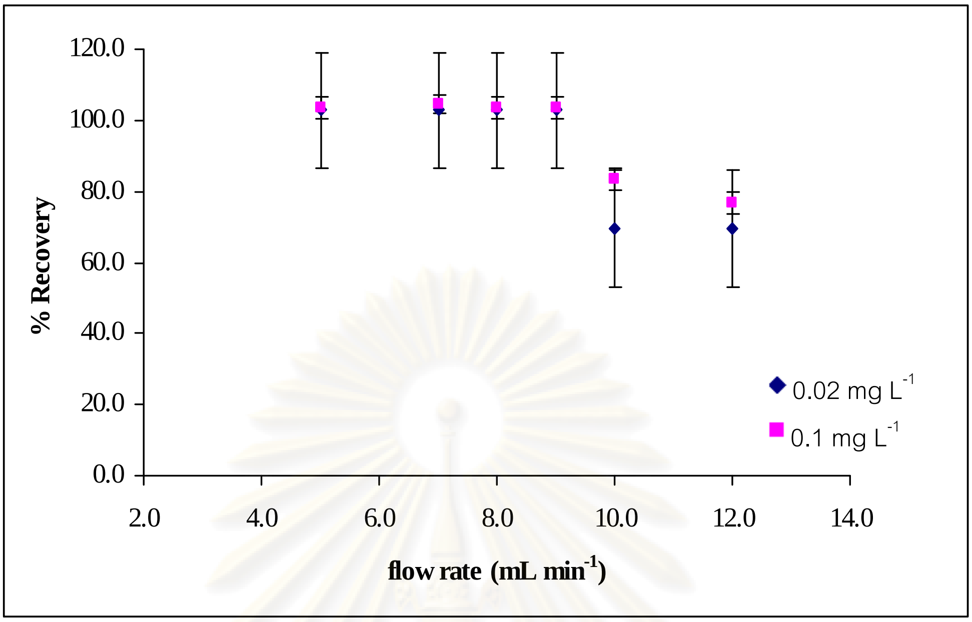


Figure 4.12 Effect of sample flow rate on Pb analysis. (Condition: Si-MPTS 30 mg, metal solution volume 10.0 mL, Pb 0.02 and 0.1 mg L^{-1} at pH 5.0, HCl (0.05 mol L^{-1}) eluent 0.2 mL and eluent flow rate 1.4 mL min^{-1}).

4.2.2.6 Effect of condition time

After the elution, the Si-MPTS phase should be conditioned to prepare the surface before another extraction. The conditioning time of Si-MPTS column for the preconcentration of 0.02 mg L^{-1} Pb(II) was investigated. After elution, Si-MPTS column was conditioned with citrate buffer solution (pH 7.0) at a flow rate of 5.0 mL min^{-1} for 15, 30 or 60 seconds. Afterwards the column was washed with de-ionized water before the preconcentration of another sample. The results are shown in the Figure 4.13. When conditioned the Si-MPTS column for 30 or 60 seconds, the acceptable recovery of Pb(II) in the determination of samples could be obtained. At the condition time of 60 seconds, the total analysis time also increased. In attempt to reduce the analysis time and achieve high sample throughput, the condition time of 30 seconds was chosen.

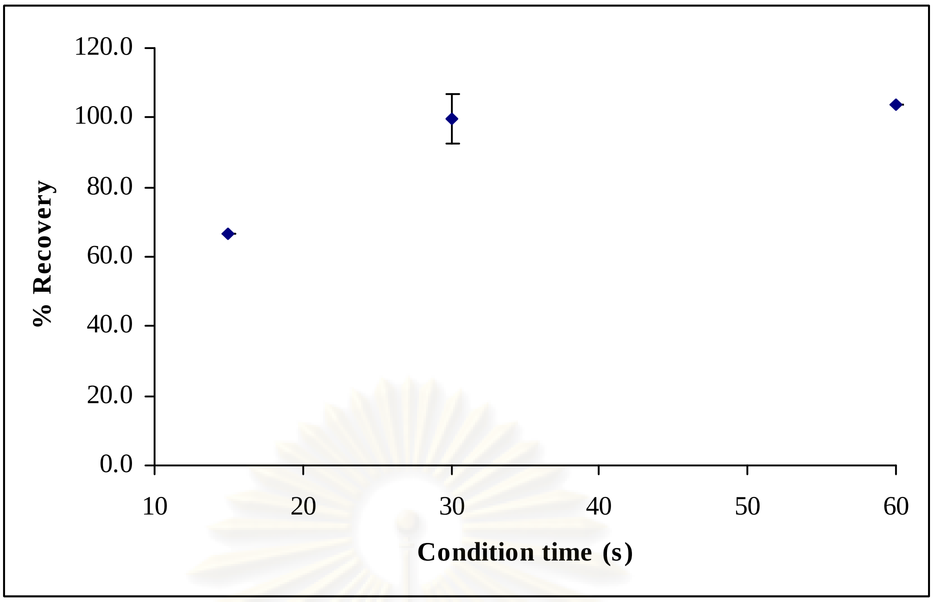


Figure 4.13 Effect of condition time on Pb(II) analysis.

4.2.2.7 Reuse of mini-column

To investigate the reusability of the Si-MPTS column, several cycles of preconcentration-determination of Pb(II) were performed using one column. The recovery of Pb(II) in the analysis of 0.02 and 0.1 mg L^{-1} Pb(II) solutions are shown in Figure 4.14 and Table 4.3. The results indicate that the percentage of Pb(II) recovery in the determination of solutions by each Si-MPTS column did not change significantly within 20 determinations. After 20 time use, the efficiency of the column decreased and recovery of lower than 80% was observed. When compare the performance between three Si-MPTS columns, the recovery of Pb in the determination of solutions by using the three Si-MPTS columns were not significantly different. The results indicate that the mini-column could be used for 20 cycles of Pb(II) determination.

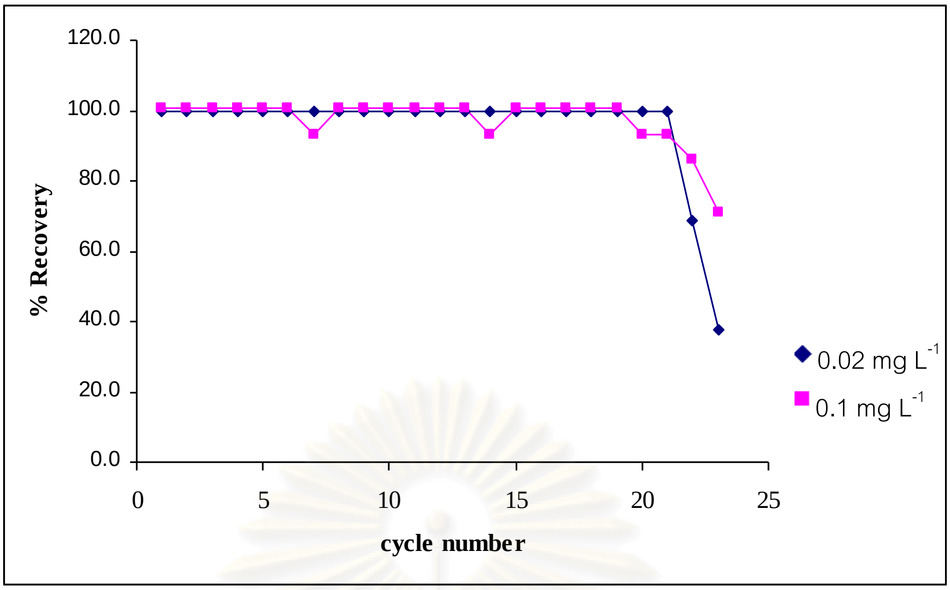


Figure 4.14 Reuse of Si-MPTS column for Pb(II) analysis.

Table 4.3 The performance of the Si-MPTS mini-column when reused 20 times

Concentration (mg L^{-1})	Column number	% Recovery[a]
Pb(II) 0.02 mg L^{-1}	1	98.4 ± 7.0
	2	100.0±10.3
	3	100.0±11.4
Pb(II) 0.1 mg L^{-1}	1	99.6±2.7
	2	100.2±3.8
	3	100.0±3.0

[a] Mean±SD, (n=20)

(Condition: Si-MPTS 30 mg, metal solution volume 10.0 mL, Pb 0.02 and 0.1 mg L^{-1} at pH 5.0, sample flow rate and eluent flow rate 9.0 and 1.4 mL min^{-1}, 0.05 mol L^{-1}HCl (eluent 0.2 mL).

4.2.2.8 Effect of coexisting ions

The effect of the presence of several anions and cations on the determination of Pb(II) (0.02 mg L^{-1}) at pH 5 was examined using the FI-FAAS system. The result reported regarding the criterion that the coexisting ions would interfere the determination of Pb when the recovery of Pb decreases to lower than 80%. The tolerated concentration of coexisting ions is considered as the maximum concentration of coexisting ions present in the solution that does not result in the deviation of the recovery of Pb(II) more than

20% of the signal in the absence of the coexisting ions. The tolerance limits are shown in Table 4.4.

Table 4.4. Tolerance limits of coexisting ions in the determination of Pb (0.02 mg L^{-1})

Ions	**Tolerance limit (mg L^{-1})**
Na^+	>85,010
K^+	>101,100
Mg^{2+}	>24,305
Cl^-	>58.5
Hg^{2+}	0.18
Ag^+	1
Cd^{2+}	2
Co^{2+}	1
Cu^{2+}	1
Ni^{2+}	1
Zn^{2+}	2

4.3 Method validation

After the optimum condition for the preconcentration of Pb(II) ions in the solution using FI-FAAS was achieved, the method was validated by demonstrating the performance characteristics related to the accuracy and precision of the method, reported in the term of the recovery (%) and relative standard deviation (%), respectively. The detection limit was also determined. In this study, standard solutions of Pb(II) were used.

The results are summarized in Table 4.5. The results show that the accuracy and precision of this method in Pb(II) determination are acceptable, according to the widely used criteria of analyte recovery and precision at different concentrations [42] (Table 4.6).

Table 4.5 Accuracy, precision and limit of detection of the proposed on-line preconcentration system for Pb(II) determination

Pb concentration (mg L^{-1})	Recovery (%)[a]	RSD (%)[a]	LOD (µg L^{-1})
0.02	106.8	9.5	11
0.1	102.2	4.7	

[a]Mean value (n=20)

Table 4.6 Acceptable values of analyte recovery and relative standard deviation of the determination of analyte at different concentrations [42]

Analyte, %	Analyte ratio	Unit	Mean recovery, %	RSD, %
100	1	100%	98-102	1.3
10	10^{-1}	10%	98-102	2.8
1	10^{-2}	1%	97-103	2.7
0.1	10^{-3}	0.1%	95-105	3.7
0.01	10^{-4}	100 ppm	90-107	5.3
0.001	10^{-5}	10 ppm	80-110	7.3
0.0001	10^{-6}	1 ppm	80-110	11
0.00001	10^{-7}	100 ppb	80-110	15
0.000001	10^{-8}	10 ppb	60-115	21
0.0000001	10^{-9}	1 ppb	40-120	30

Table 4.7. Comparison of the performance for FI on-line preconcentration coupled with FAAS systems for determinations

Analyte	Sorbent	Preconcentration factor	LOD ($\mu g\ L^{-1}$)	Sample throughput (h^{-1})	Reference
Pb(II)	Activated carbon loaded with xylenol orange	200	0.4	1.6	[28]
Pb(II)	Macrocycle molecule immobilized silica gel	52	5	63	[29]
Pb(II)	PCTFE-beads for extraction of lead-ammonium pyrrolidine dithiocarbamate (APDC) complexes	220	1.2	30	[30]
Pb(II)	Polyurethane foam loaded with 2-(2-benzothiazolylazo)-2-*p*-cresol (BTAC)	26	1	48	[31]
Pb(II)	Amberlite XAD-2 modified by 2-2-benzothiazolylazo-2-*p*-cresol (BTAC)	18 18 27	3.7	26	[32]
Pb(II)	Microcrystalline Naphthalene immobilized with ammonium pyrrolidine dithiocarbamate	65	4.6	20	[33]
Pb(II)	PTFE micro-column for extraction of lead-ammonium pyrrolidine dithiocarbamate (APDC) complexes	330	0.8	18	[34]
Pb(II)	Rice husks modified with NaOH solution	46	14.1	14	[35]
This work		50	11	37	-

The results from Table 4.7 demonstrate that the performance of the proposed system was relatively good compared to the methods reported by the other researchers. The developed method permitted high sample throughput with high preconcentration factor with low detection limit.

4.4 Analysis of certified reference material

The accuracy of the proposed method was tested by analyzing Pb(II) content in certified reference material (SRM 1643e) compared to GFAAS standard method. The results and recovery values are shown in Table 4.8. The values obtained by using the proposed method are not different from the certified values, indicating the good accuracy of the proposed method. There is also no significant differences between results obtained from the proposed method and the standard method. Therefore, the proposed method can be applied to the analysis of water samples with the acceptable accuracy.

Table 4.8 Analytical results of Pb determination in certified reference material by FI-FAAS method and GFAAS standard method

Element	Certified (µg/L)	Found[a] (µg/L)		% Recovery	
		FI-FAAS	GFAAS	FI-FAAS	GFAAS
Pb	19.63±0.21	20.4±1.9	20.6±0.5	103.9	104.9

[a] Mean ± SD (n=5)

4.5 Real sample analysis

The FI-FAAS method was applied to determine Pb(II) in real water samples (drinking water, ground water, canal water, river water, seawater, tap water and wastewater) using spiked method. The results are compared to the results obtained by using graphite furnace atomic absorption spectrometry (GFAAS) reference method. These experiments were performed in 7 replicates. The results of the proposed method presented as percentage of recovery are shown in Table 4.9.

Table 4.9 Determination of Pb(II) in real samples

Sample	Added ($\mu g\ L^{-1}$)	Found[a] ($\mu g\ L^{-1}$)		Recovery (%)	
		Proposed method FI-FAAS	Reference method GFAAS	Proposed method FI-FAAS	Reference method GFAAS
Drinking water 1	-	n.d.	n.d.	n.d.	n.d.
	20	21.1±0.9	20.8±0.2	105.3	104.0
	100	102.2±0.9	103.2±1.9	102.2	103.2
Drinking water 2	-	n.d.	n.d.	n.d.	n.d.
	20	21.0±0.5	20.6±0.2	105.0	103.0
	100	101.8±2.7	101.5±2.4	101.8	101.5
Drinking water 3	-	n.d.	n.d.	n.d.	n.d.
	20	20.7±0.9	20.5±0.2	103.5	102.5
	100	102.2±2.1	102.1±1.9	102.2	102.1
Drinking water 4	-	n.d.	n.d.	n.d.	n.d.
	20	20.7±1.1	20.6±0.6	103.5	103.0
	100	103.4±1.9	101.7±3.0	103.4	101.7

Table 4.9 Determination of Pb(II) in real samples (contd.)

Sample	Added ($\mu g\ L^{-1}$)	Found[a] ($\mu g\ L^{-1}$)		Recovery (%)	
		Proposed method FI-FAAS	Reference method GFAAS	Proposed method FI-FAAS	Reference method GFAAS
Drinking water 5	-	n.d.	n.d.	n.d.	n.d.
	20	20.4±1.4	20.7±0.5	102.0	103.5
	100	103.5±1.7	102.7±2.5	103.5	102.7
Seawater	-	n.d.	n.d.	n.d.	n.d.
	20	20.8±0.9	20.7±0.4	104.0	103.5
	100	102.2±2.1	102.3±1.5	102.2	102.3
Tap water	-	n.d.	n.d.	n.d.	n.d.
	20	21.1±0.4	20.4±0.3	105.5	102.0
	100	102.8±1.8	102.5±1.0	102.8	102.5
Ground water	-	n.d.	n.d.	n.d.	n.d.
	20	21.5±2.1	20.8±0.2	105.7	104.0
	100	103.5±1.1	102.3±1.3	103.5	102.3
Canal water	-	n.d.	n.d.	n.d.	n.d.
	20	20.4±1.3	20.2±0.5	102.0	101.0
	100	103.2±2.2	103.4±1.5	103.2	103.4
River water	-	n.d.	n.d.	n.d.	n.d.
	20	21.7±1.1	20.9±0.5	108.5	104.5
	100	102.2±1.6	102.4±1.3	102.2	102.4
Waste water	-	31.2±4.8	30.2±0.9	-	-
	20	52.6±4.3	50.2±0.5	107	100.0
	100	130.7±2.6	130.3±0.7	99.5	100.1

n.d. = non detectable

[a] Mean ± SD (n=7)

The recoveries of Pb from samples spiked with Pb standard of both concentration levels (20 and 100 µg L^{-1}) are acceptable. The values obtained from the proposed method (FI-FAAS) and the reference method (GFAAS) was not significantly different. Therefore, the proposed method can be applied for the determination of Pb(II) in water samples with acceptable accuracy.

CHAPTER V

CONCLUSIONS

The silica gel functionalized with 3-mercaptopropyltrimethoxysilane was successfully prepared by one step synthesis. The product was characterized by fourier transforms infrared (FT-IR) and thermal gravimetric analysis (TGA). The Pb(II) extraction properties were studied by off-line column method. The suitable pH for Pb(II) extraction was pH 5.0. The appropriate amount of Si-MPTS for Pb(II) extraction was 30 mg. The Si-MPTS showed a good selectivity toward Pb (II) extraction over the other metal ions. Furthermore, the Si-MPTS column was used in on-line preconcentration and determination of Pb(II) by FAAS.

The flow injection on-line preconcentration system coupled with FAAS was proposed. The condition in the determination of Pb(II) by the proposed system were optimized. The characteristics and performance of the proposed method are shown in Table 5.1.

Table 5.1 The analytical performance of Pb analysis.

Features	
Detection limit (3S) (µg L^{-1})	11
Precision (R.S.D., n=20) (%)	9.5 (Pb 20 µg L^{-1}) 4.7 (Pb 100 µg L^{-1})
Accuracy (Recovery, n= 20) (%)	106.8±10.2 (Pb 20 µg L^{-1}) 102.2±4.8 (Pb 100 µg L^{-1})
Linear range (µg L^{-1})	20-140
sample volume	10.0 mL
eluent volume	0.2 mL
sample flow rate	9.0 mL min^{-1}
eluent flow rate	1.4 mL min^{-1}
preconcentration factor	50
Analysis time (sec sample^{-1})	97
Sampling frequency (sample h^{-1})	37

The accuracy of the proposed method was tested by analyzing standard solution and a certified reference material. The obtained results indicate that the method could be used with high accuracy. Finally, the method was successfully applied for the determination of Pb(II) in water samples.

Suggestions for future work

To obtain more effective and convenient system, the on-line preconcentration coupled with FAAS system proposed in this study should be developed to automated on-line analysis controlled by computer software.

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