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HOLLOW FIBER SUPPORTED LIQUID MEMBRANE FOR INORGANIC
ARSENIC SPECIATION

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Chemistry
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FOR INORGANIC ARSENIC SPECIATION

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ขนิษฐา โตสันติกุล : เมมเบรนเหลวที่พยุงด้วยเส้นใยกลวงสำหรับการวิเคราะห์รูปแบบ
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เทคนิคเมมเบรนเหลวที่พยุงด้วยเส้นใยกลวงถูกพัฒนาขึ้นสำหรับการวิเคราะห์รูปแบบทาง
เคมีและเพิ่มความเข้มข้นของอาร์เซนิกอนินทรีย์ในน้ำดื่ม การสกัดแบบ 3 เฟสถูกนำมาประยุกต์ใช้
ในเทคนิคนี้ ประกอบด้วยสารละลายตัวอย่างทำหน้าที่เป็นเฟสให้ ของผสมระหว่าง
methyltrialkylammonium chloride (Aliquat 336) ในตัวทำละลาย kerosene ที่ถูกบรรจุอยู่ในรู
พรุนของเมมเบรนชนิดเส้นใยกลวงทำหน้าที่เป็นเฟสที่ใช้ทำการสกัด และสารละลายโซเดียมไฮดรอก
ไซด์ทำหน้าที่เป็นเฟสรับ เทคนิคนี้สารละลายตัวอย่างถูกปรับให้มีค่าพีเอชเท่ากับ 6 ทำให้ As(V) อยู่
ในรูปประจุลบ ($H_2AsO_4^-$) ขณะที่ As(III) อยู่ในรูปที่ไม่มีประจุ (H_3AsO_3) ในขั้นตอนการสกัด As(V)ที่
อยู่ในเฟสให้จะถูกสกัดไปยังเฟสรับโดยอาศัยกลไกของการแลกเปลี่ยนไอออนลบ หลังการสกัดเสร็จ
สิ้น As(V) ถูกนำมาตรวจวัดหาปริมาณด้วยวิธี molybdenum blue ในระบบวิเคราะห์แบบไหล
สำหรับการวิเคราะห์ As(III) As(III) จะถูกออกซิไดส์ให้อยู่ในรูป As(V) โดยโพแทสเซียมเปอร์แมงกา
เนตและถูกตรวจวัดในรูปแบบของผลรวมของอาร์เซนิก จากนั้นนำเอาปริมาณของ As(V)ลบออก
จากปริมาณรวมของอาร์เซนิก เทคนิคนี้ถูกนำมาประยุกต์ใช้กับตัวอย่างน้ำดื่มตามท้องตลาด พบว่า
สามารถเพิ่มความเข้มข้นได้มากกว่า 250 เท่า ช่วงความเป็นเส้นตรงอยู่ที่ความเข้มข้นระหว่าง 30
ถึง 110 ไมโครกรัมต่อลิตรและให้ค่าสัมประสิทธิ์ความเป็นเส้นตรงมากกว่า 0.99 ขีดจำกัดต่ำสุดของ
วิธีการตรวจวัดอยู่ที่ระดับความเข้มข้นประมาณ 5 ไมโครกรัมต่อลิตร สำหรับการตรวจวัด As(III)
และ As(V) พบว่าให้ค่าการคืนกลับอยู่ในช่วง 86 ถึง 102 เปอร์เซ็นต์ และ 92 ถึง 112 เปอร์เซ็นต์
ตามลำดับ และมีค่าเบี่ยงเบนมาตรฐานสัมพัทธ์ของ As(III) และ As(V) น้อยกว่า 5 เปอร์เซ็นต์ เมื่อ
เปรียบเทียบผลกับวิธีตรวจวัดด้วยอินดักทีฟคูเปิลพลาสมา-อะตอมมิคอิมิชชันสเปคโทรสโกปีพบว่า
ความเข้มข้นของอาร์เซนิกอนินทรีย์ในรูปของผลรวมของอาร์เซนิกของทั้งสองวิธีไม่แตกต่างกันอย่าง
มีนัยสำคัญ (P > 0.05, Paired t-Test) เทคนิคนี้เป็นเทคนิคที่ง่าย ราคาถูก ลดการใช้ปริมาณตัวทำ
ละลาย และสามารถวัดหาปริมาณของอาร์เซนิกอนินทรีย์ในระดับต่ำได้

ภาควิชา	เคมี	ลายมือชื่อนิสิต
สาขาวิชา	เคมี	ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก
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KANIDTHA TOSUNTIKUL: HOLLOW FIBER SUPPORTED LIQUID MEMBRANE FOR INORGANIC ARSENIC SPECIATION. ADVISOR: ASST.PROF.PAKORN VARANUSUPAKUL, Ph.D., 54 pp.

Hollow fiber supported liquid membrane (HF-SLM) was developed for speciation and preconcentration of inorganic arsenic in drinking water. The three-phase extraction mode was applied, where the sample solution was a donor phase; the Aliquat 336 in kerosene impregnated in the pores of the membrane was an extracting phase; and NaOH was an acceptor phase. The sample solution was adjusted to pH 6, so As(V) was in anion form ($H_2AsO_4^-$) while As(III) was in neutral form (H_3AsO_3). The As(V) in the donor phase was extracted into the acceptor phase via anion-exchange mechanism. After extraction, As(V) was determined by the flow-based molybdenum blue method. For the determination of As(III), As(III) was oxidized to As(V) by $KMnO_4$ and determined as total As. Then the amount of As(III) was obtained by subtracting of As(V) from the total amount of As. The method was applied for speciation of inorganic arsenic in drinking water from local market. The enrichment factor more than 250 was obtained. The linear range was 30-110 μg L^{-1}, which provided the correlation coefficients (R^2) of more than 0.99. The detection limit was about 5 μg L^{-1}. The recoveries for determination of As(III) and As(V) were 86 to 102% and 92 to 112%, respectively and relative standard deviations of As(III) and As(V) were less than 5%. The method was compared with the ICP-AES method for the determination of total As. The concentration of total As from both methods were not significantly different ($P > 0.05$, Paired t-Test). This method is simple, low cost, uses less solvent and can be used for determination of inorganic arsenic at trace level.

Department   Chemistry   Student's Signature ....

Field of Study   Chemistry   Advisor's Signature ....

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LIST OF ABBREVIATIONS AND SYMBOLS

AU	Absorbance Unit
cm	centimeter
g	gram
ID	Inner Diameter
L min^{-1}	liter per minute
mg L^{-1}	milligram per liter
min	minute
mL	milliliter
mL min^{-1}	milliliter per minute
nm	nanometer
OD	Outer Diameter
R^2	correlation coefficient
RSD	Relative Standard Deviation
rpm	round per minute
sec	second
v/v	volume per volume
w/v	weight per volume
µg L^{-1}	microgram per liter
µL	microliter

CHAPTER I

INTRODUCTION

1.1 Motivation of Proposer

Arsenic contamination in natural water is a major problem in different areas of the world. Sources of arsenic contamination in natural water are such as petroleum production, semi-conductor manufacturing, smelting of metal ores, the production of pesticide and herbicide [1-2]. The toxicology of arsenic to humans is well known. These health effects include cancerous *i.e.*, skin, lung, liver, kidney and nasal passages cancer and non-cancerous effects *i.e.*, pulmonary, neurological, endocrine, cardiovascular and immunological effects [1, 3-4]. Contamination of arsenic in drinking water has been reported in more than 70 countries such as Bangladesh, India and some other countries of South and South-East Asia etc, posing a serious health hazard to estimated 150 million people worldwide [5].The World Health Organization (WHO) and US Environmental Protection Agency (US EPA) have set a maximum contamination level of total arsenic in drinking water at 10 µg L^{-1} [2, 5-7].

Arsenic exists in an environment in both organic and inorganic forms. Generally, the most common inorganic arsenic forms *i.e.*, arsenates As(V) and arsenite As(III), are found in the natural water and about 100 times more toxic than organic arsenic forms (e.g. monomethylarsonate [MMA] or dimethylarsinate [DMA]) [1]. As(III) is about 60 times more toxic than As(V) [1, 8]. Thus, speciation of inorganic arsenic forms in water is important.

Normally, techniques for determination of inorganic arsenic include non-specific determination techniques and specific determination techniques. Non-specific determination techniques such as atomic absorption spectroscopy (AAS), atomic fluorescence spectrometry (AFS), inductively coupled plasma mass spectrometry (ICP-MS) and inductively couple plasma atomic emission spectrometry (ICP-AES) determine inorganic arsenic species as total arsenic. Therefore, separation techniques such as ion chromatography (IC), liquid chromatography (LC) and capillary electrophoresis (CE) are necessary for separation of each species before determination

by the non-specific techniques. Specific determination techniques are selective to one inorganic arsenic species such as molybdenum blue technique (selective to As(V)) and voltammetric technique (selective to As(III)). However, direct determination As(III) and As(V) by these techniques are often difficult due to the complexity of sample matrix and the low concentration of arsenic in water sample resulting in that significant errors may be experienced in these techniques [8-9]. Therefore, sample preparation techniques that enable separation, preconcentration, and clean-up of inorganic arsenic species, are required.

The most methods for speciation of As(III) and As(V) that combine sample preparation techniques with sensitive detection techniques reported in the literatures are liquid-liquid extraction (LLE) [10-11] and solid phase extraction (SPE) [12-15]. However, these sample preparation techniques have some disadvantages such as time consuming processes, unsatisfactory enrichment factors, and use of large volume of organic solvent, that make them less attractive.

Liquid phase microextraction (LPME) is one of the most recent trends in sample preparation techniques, which involve a great reduction of organic solvent consuming. Single drop microextraction (SDME) is the LPME technique that uses much less organic solvent and provides high preconcentration factor but the major problem is the stability of the organic solvent drop. Then, hollow fiber membrane liquid phase microextraction (HF-LPME) has been brought in to overcome such a problem. In HF-LPME, the organic solvent is protected by the hollow fiber membrane. The small volume of the organic solvent is contained inside the lumen of the porous hollow fiber membrane. HF-LPME for the speciation of As(III) and As(V) reported in the literatures were based on three phase extraction referred to as supported liquid membrane (SLM) [5, 16-17]. Typically, the SLM system consists of a liquid membrane (an organic solvent impregnated in the pores of the hollow fiber membrane), a donor phase (a sample containing analytes of interest usually located outside the membrane) and an acceptor phase (a final destination to where the analytes of interest are transferred). The main advantages of SLM extraction are low consumption of organic solvents and high enrichment factor [18]. Hollow fiber supported liquid membrane (HF-SLM) has been used mostly for removal of inorganic arsenic. There have been a few HF-SLM applications for speciation of inorganic

arsenic. Therefore, development of HF-SLM method for speciation of As(III) and As(V) in water sample has became our interest.

Molybdenum blue method is the specific analytical method for determination of inorganic arsenic in As(V) form [19]. In this technique, As(V) with form complex with ammonium molybdate in acidic condition. Then the complex is reduced by a suitable reducing agent at 100 °C for 10 min, the sample turned into a blue solution, which was detected by UV-Visible spectrometer at 840 nm. The molybdenum blue method is simple and low cost but the drawback of this method is time consuming processes. Flow injection analysis (FIA) is interesting technique for combination with molybdenum blue method, which is brought in to overcome such a problem. Principle of FIA system is the injection of a sample solution into carrier stream, after the sample form disperses in the carrier stream of reagent and transports into detector. The FIA technique is simple, high sampling rate (about 1sample/min) and reduces consumption sample and reagents (microliters) [20-21]. Therefore, the development of the FIA combination with molybdenum blue method for determination of inorganic arsenic has became our interest because it provides high sample throughput and the cost is lower than sensitive analytical instruments.

1.2 Objective

To develop the hollow fiber supported liquid membrane (HF-SLM) method for speciation and preconcentration of inorganic arsenic in drinking water and determination by the flow-based molybdenum blue method.

1.3 Scopes of this research

The method for speciation of As(III) and As(V) is developed using HF-SLM technique. As(III) and As(V) are speciated by adjusting the pH of the sample solution into an appropriate pH for one arsenic species and extracted into the HF-SLM via anion exchange process. Methyltrialkylammonium chloride (Aliquat 336) is used as extracting solvent in the HF-SLM system. The HF-SLM system is designed to enable the determination of arsenic by the flow-based molybdenum blue method. Parameters are studied to obtain sufficient sensitivity for determination of arsenic in drinking

water samples. The method is evaluated and applied for speciation of inorganic arsenic in drinking water samples. The results were compared with those determined by the conventional ICP-AES method.

1.4 The benefit of this research

A method for speciation and preconcentration of As(III) and As(V) is obtained providing high enrichment factor, high sample throughput, which is suitable for determination of arsenic contamination in drinking water.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Speciation analysis of inorganic arsenic

Speciation analysis is defined as the analytical identification and quantitative determination of the different physico-chemical forms of the elements present in a sample [22]. Several elements such as Au, Se, Cr, Hg, Sb, Pb, Fe and As etc are speciated [23].

Normally, inorganic arsenic can be determined by atomic spectroscopic methods such as AAS and ICP. Since these methods cannot differentiate arsenic species, therefore in speciation analysis of inorganic arsenic, separation of each species is required by using chromatographic methods such as IC, LC, and CE. In addition, speciation analysis of inorganic arsenic can be done by using a specific determination method of one species such as molybdenum blue method (specific to As(V)) or electrochemical method (specific to As(III)), while the other species is determined by first turning it into the former one by oxidation or reduction and determined as a total, and then subtraction of the total by the former ones.

In speciation analysis of inorganic arsenic in natural water, As(V) is commonly determined because As(III) is usually found at much lower concentration and relatively difficult to be determined [24]. Thus, oxidation of As(III) into As(V) is required.

2.2 As(III) oxidation

Common oxidants that are reported in the literature for oxidizing As(III) to As(V) are such as hydrogen peroxide (H_2O_2), sodium hypochlorite (NaOCl), Iron(III) chloride ($FeCl_3$), and potassium permanganate ($KMnO_4$) [25]. The efficiency of these oxidizing agents can be quantified by calculation of electron stoichiometric ratio (r) [26]. For r = 1, the oxidation reaction fits the stoichiometry of the reaction; when r < 1 or r > 1, the need of oxidant quantity to achieve oxidation reaction is lower or higher

than what the stoichiometry predicts, respectively. The electron stoichiometric ratio (r) is calculated by (Eq.1).

$$r = \frac{n \times [Ox] \times V_{ox}}{2 \times [As] \times V_{As}} \tag{1}$$

Where n is the number of electrons involved in the oxidant half-reaction. [Ox] and V_{ox} are the molar concentration of oxidant solution and volume of oxidant solution, [As] and V_{As} are the molar concentration of As(III) and volume of As(III) solution.

At pH below 7 the oxidation reaction can be written as (Eq.2):

$$H_3AsO_3 + H_2O \leftrightarrow H_2AsO_4^- + 3H^+ + 2e^- \tag{2}$$

The oxidation reactions of As(III) by various oxidants are listed in Table 2.1 and their advantages and drawbacks are summarized in Table 2.2. It suggests that $FeCl_3$ and $KMnO_4$ provide relatively high efficiency (r < 1) and have fewer drawbacks when compared to other oxidants.

Table 2.1 Oxidation reactions of As(III) by various type of oxidants [26].

Type of oxidant	The oxidation reaction	Eq.
H_2O_2	$H_3AsO_3 + H_2O_2 \rightarrow H_2AsO_4^- + H_2O + H^+$	(3)
NaOCl	$H_3AsO_3 + HClO \rightarrow H_2AsO_4^- + Cl^- + 2H^+$	(4)
$FeCl_3$	$H_3AsO_3 + 2Fe^{3+} + H_2O \rightarrow H_2AsO_4^- + 2Fe^{2+} + 3H^+$	(5)
$KMnO_4$	$2MnO_4^- + 3H_3AsO_3 \rightarrow 2MnO_2 + 3H_2AsO_4^- + H_2O + H^+$	(6)

Table 2.2 Advantages and drawbacks of each oxidant for oxidation of As(III) [26].

	H_2O_2	NaOCl	$FeCl_3$	$KMnO_4$
Time stability on field application	No	No	Yes	Yes
Oxidant quantity	Very high excess	Excess (r = 4)	Less than stoichmetry (r < 1)	Less than stoichmetry (r < 1)
Health risks	No	Yes	No	No
Sludge production	No	No	Yes	Yes
Costs	High	Low	Low	Low
Efficiency	No	No	Yes	Yes

2.3 Determination of As(V) by molybdenum blue method

Molybdenum blue method is a specific method for determination of As(V). As(V) reacts with ammonium molybdate to form a heteropolymolybdiarsenate complex in acidity condition. The complex is then reduced giving a strongly blue color "molybdenum blue" by a suitable reducing agent [19, 27]. The blue solution can be detected by UV-Visible spectrophotometer at 840 nm. The reaction between As(V) and reagents is shown in (Eq.7) and (Eq.8).

$$AsO_4^{3-} + 12MoO_4^{2-} + 3NH_4^+ + 24H^+ \rightarrow (NH_4)_3[AsMo_{12}O_{24}] \cdot 12H_2O \qquad (7)$$

$$Mo(VI) + e^- \rightarrow Mo(V) \qquad (8)$$
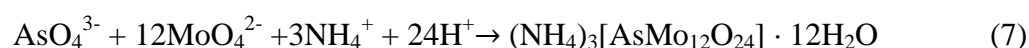
Generally, types of reducing agent reported in the literatures are stannous chloride (SnCl$_2$), hydrazine sulfate and ascorbic acid. SnCl$_2$ is less attractive because of the yellowish color and its instability. Ascorbic acid is also relatively instable in the air while hydrazine sulfate is more stable (usually for 24 hrs). Therefore, hydrazine sulfate is considered the best reducing agent for As(V) in the molybdenum method.

The reduction reaction in the molybdenum blue method usually requires acidic condition. Types of acid solution reported in the literatures are sulfuric acid (H_2SO_4), hydrochloric acid (HCl) and perchloric acid ($HClO_4$), which also depend on the type of reducing agent. Besides, since the reaction proceeds very slowly at room temperature, it can be accelerated by heating. Table 2.3 summarizes type of reducing agent, type of acid solution, heating temperature and heating time used in the molybdenum blue method.

Table 2.3 Type of reducing agent, type of acid and heating condition in the molybdenum blue method [19].

Reducer	Acid	Heating temperature (°C)	Reaction time (min)
Hydrazine sulfate	H_2SO_4	100	10
Ascorbic acid	H_2SO_4	No heating	20
$SnCl_2$	HCl	No heating	20
Hydrazine sulfate	HCl	100	10
Ascorbic acid	$HClO_4$	100	10

2.4 Flow injection analysis

Flow injection analysis (FIA) was first described in 1975 by Ruzicka and Hansen [28]. The technique is based on the injection of a sample solution into a carrier stream of a suitable liquid. Then, the sample is mixed with a stream of reagent and transports toward a detector. Basic components of the FIA system consists of pump, which is used to transfer the carrier stream through a narrow tubing; an injection vale, which is used to inject a defined volume of the sample solution into the carrier stream in the system; a reaction coil, which is used to allow the sample to disperse and react with the reagent of the carrier stream; and a detector, which is used to detect the analyte that flows through the flow cell and give a signal to be recorded. The simple diagram of the FIA system is illustrated in Figure 2.1
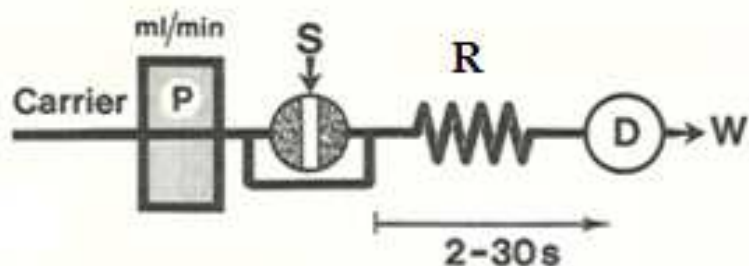
Figure 2.1 A shematic diagram of typical FIA system. P: pump; S: injection vale; R: reaction coil; D: detector; and W: waste [28].

The signals such as absorbance and electrical potential are continously monitored as the sample stream is passing through the flow cell. Figure 2.2 demonstrates a typical output signal chracteristic obtained from the FIA system. The peak is related to the concentration of analyte. The time between the sample injection (S) and the peak height measurement is the residence time (T) during which the reaction takes place.
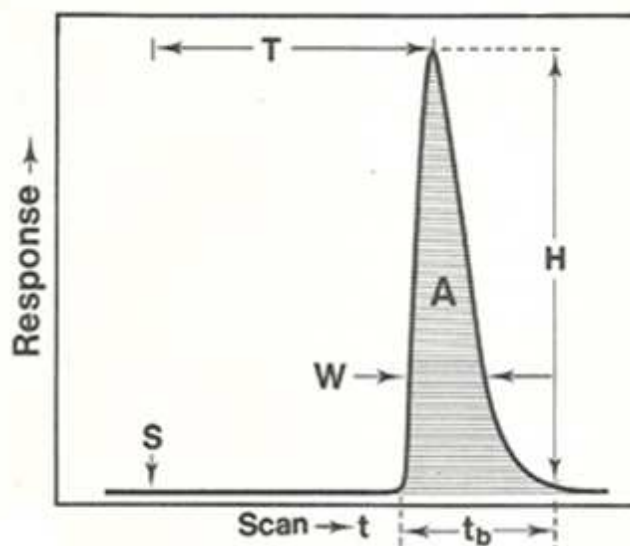
Figure 2.2 The output signal characteristic from the FIA system. (S: recording starting at time of injection t_0; H: peak height; W: peak width at selected level; A: peak area; T: residence time corresponding to the peak height measurement; t_b: peak width at the baseline [28].

The FIA system has been designed for extremely rapid reaction; typical reaction time is in the range of 5-20 sec. The injected sample volumes usually range between 1-200 µL (typically 25 µL), which requires no more than 0.5 mL of reagent/sampling cycle. The FIA system can be designed to couple with several detection techniques including atomic and molecular spectrometers and electrochemical detectors. FIA system is a simple, automated microchemical technique, and capable of high sampling rate with minimum sample and reagent consumption [28].

2.5 Separation and preconcentration method in speciation analysis of arsenic

For determination of metals at trace level, of which the concentration does not meet the limit of detection of the analytical instrument, preconcentration step is usually required prior to determination. The sample preparation techniques that have been commonly used for separation and preconcentration of metals are liquid-liquid extraction (LLE), solid phase extraction (SPE), solid phase microextraction (SPME), and single-drop microextration (SDME). The metal after preconcentration can be determined by atomic spectroscopic detectors. Examples of sample preparation techniques for separation and preconcentration of metals are summarized in Table 2.4

Table 2.4 Sample preparation methods for separation and preconcentration of metals.

Species	Sample	Extraction conditions	Detection technique	Ref
LLE method				
Se(VI) and Se(IV)	Environmental waters	Extraction with organic chelating reagent APDC.	ETV-ICP-MS	[29]

Au(I) and Au(III)	Wastewater	Formation of an ion pair between $AuCl_4^-$ and 1-(3,5-diamino-6-chloropyrazinecar boxyl) guanidine hydrochloride monohydrate. The ion pair was extracted into 4-metthyl pentan-2-one.	GF-AAS	[30]
SPE method				
Cr(III) and Cr(VI)	Seawater	Selective retention on Dowex-1. The resin adsorbs Cr (VI) selectively (99%), eluting out Cr(III).	ET-AAS	[31]
Fe(II) and Fe(III)	Environmental waters	Preconcentration with a micro-column packed with BPHA loaded on microcrystalline naphthalene.	ETV-ICP-OES	[32]
SDME method				
Sb(III) and Sb(V)	Natural waters	Drop of chloroform with BPHA to extract Sb(III). To obtain the total Sb content, pre-reduction of Sb(V) to Sb(III) was performed before extraction. The concentration of Sb(V) was calculated by subtractting the Sb(III) concentration from the total Sb concentration.	ET-AAS	[33]

ET-AAS, Electrothermal atomic absorption spectrometry; ETV-ICP-OES, Electrothermal vaporization inductively coupled plasma optical emission spectroscopy; ETV-ICP-MS, Electrothermal vaporization inductively coupled plasma mass spectrometry; GF-AAS, Graphite furnace atomic absorption spectrometry.

The sample preparation techniques such as LLE and SPE are widely used methods for separation/speciation and preconcentration of inorganic arsenic. Since the presence of inorganic arsenic species in water samples depends on pH of the samples [24] as illustrated in Figure 2.3, by adjusting the pH, As(V) in the form of charged monovalent ($H_2AsO_4^-$) or divalent ($H_2AsO_4^{2-}$) anion can be selectively separated and speciated from the neutral species of As(III) (H_3AsO_3) via ion exchange process. The neutral species of As(III) can be oxidized to As(V), extracted and determined as a total As and subtracted by the As(V) for speciation of As(III).
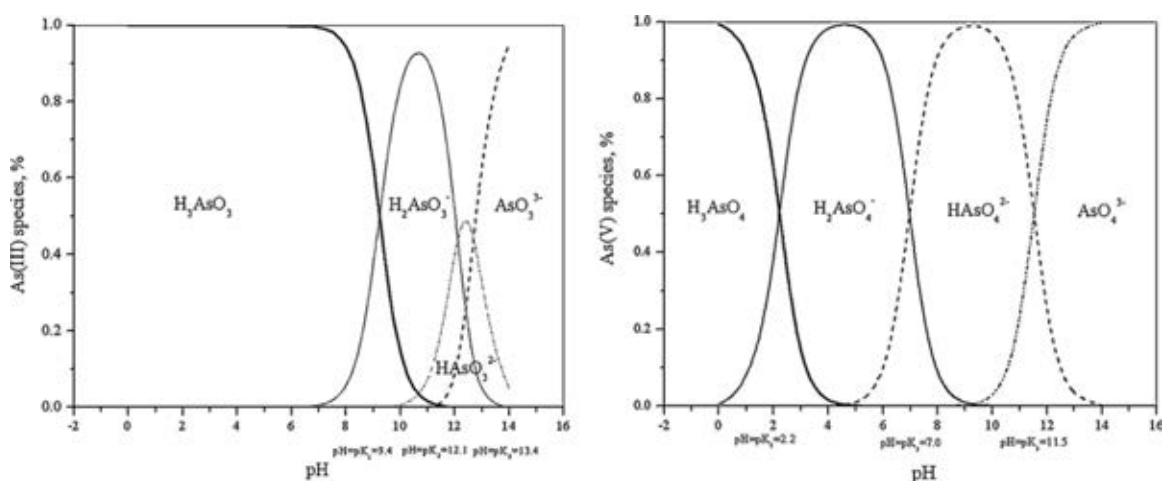
Figure 2.3 Speciation profile of As(III) and As(V) as a function of pH of the solution [24].

2.5.1 Liquid-liquid extraction (LLE)

Liquid-liquid extraction (LLE) [10-11] is the conventional sample preparation technique that separates analyte from other constituents of sample solution based on affinity of the analyte between two different immiscible liquid phases; aqueous solution and organic solvent. Generally, the sample solution and organic solvent are mixed using a separatory funnel. After a certain time, partitioning of the analytes between two phases reaches equilibrium. LLE technique is simple and widely used. However, there have been drawbacks such as high consumption of toxic organic solvent, time consuming and formation of emulsion. For these reasons, new sample preparation techniques have been developed.

2.5.2 Solid phase extraction (SPE)

Solid phase extraction (SPE) [12-15] is a sample preparation technique that analytes are extracted from a liquid phase (sample solution) into a solid phase, and then, the retained analytes in the solid phase are removed by eluting with an appropriate solvent. Despite the SPE technique is simple, low cost and using less volume of organic solvents than that of LLE technique, the volume of organic solvent is still in milliliter level.

2.5.3 Hollow fiber liquid phase microextraction (HF-LPME)

Recently, liquid phase microextraction (LPME) has been brought in to overcome such problems. This technique uses less volume of organic solvent (a few microliters) and gives high enrichment factor when compared to LLE and SPE. Liu and Dasgupta introduced the first paper of LPME in 1996 [34]. The major idea of this technique is a great reduction in the volume of organic solvent. Single drop microextraction (SDME) is the first LPME technique, where the analyte is extracted into an immiscible microdrop of organic solvent that is suspended at a tip of a microsyringe. The SDME technique is simple and consumes less volume of organic solvent (a few microliters). However, it suffers from organic drop stability, so the analyte in the microdrop is easily lost during extraction [23, 35].

A new LPME technique called hollow fiber liquid phase microextraction (HF-LPME) was presented by Pedersen-Bjergaard and Rasmuseen in 1999 [36]. Hollow fiber membrane provides much higher surface area per unit volume than other kinds of membranes. The hollow fiber membrane has been used in the extraction system as shown in Figure 2.4. The microvolume of the extracting solvent is contained within the lumen of the porous hollow fiber membrane, so the extracting solvent is not in direct contact with the sample solution. The major advantage of the hollow fiber membrane in LPME technique is that the sample solution may be stirred without any loss of extracting solvent. Therefore, the hollow fiber membrane has been widely used for separation and preconcentration in sample preparation technique.
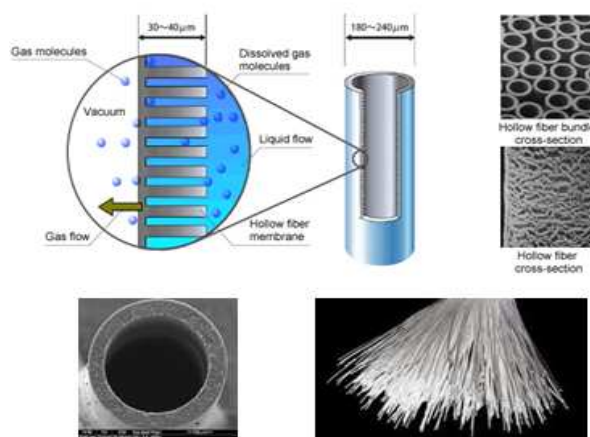
Figure 2.4 Hollow fiber membrane and its application in the liquid phase microextraction technique [37].

Normally, the extraction of HF-LPME includes two modes; two-phase and three-phase modes. In two-phase mode or so-called microporous membrane liquid-liquid extraction (MMLLE), analytes are extracted from an aqueous sample (donor phase) into an organic solvent (acceptor phase) immobilized in the pores and in the lumen of the hollow fiber membrane. In three-phase mode or so called supported liquid membrane (SLM), analytes are extracted from an aqueous sample into an organic solvent immobilized inside the pores of the porous hydrophobic hollow fiber membrane and then back-extracted into an acceptor solution contained inside the lumen of the hollow fiber membrane. The driving force of extraction in two-phase and three-phase HF-LPME system is the diffusion, which is promoted by high partition coefficients.

There are many setups for HF-LPME technique. U-shape setup, illustrated in Figure 2.5 has been widely used in HF-LPME technique. Two medical syringe needles are inserted through a septum. Both ends of the hollow fiber membrane are connected with needle tip. The membrane is then immersed into the vial containing the sample solution. In two-phase mode, the organic solvent is contained in the pores and filled in the lumen of the membrane as the acceptor solution. In three-phase mode, the organic solvent is impregnated in the pores of the membrane while the lumen of the membrane is filled with the acceptor solution. After

extraction is completed, the acceptor solution is withdrawn and transferred into a micro insert vial for further analysis.
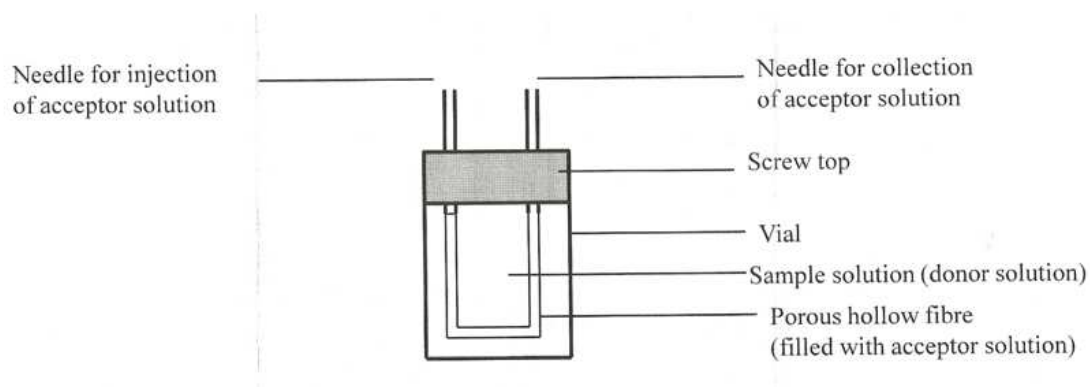
Figure 2.5 Schematic representation of U-shape HF-LPME [38].

The efficiency of the extraction is essentially determined by two parameters such as the enrichment factor (EF) and extraction efficiency (EE) [31]. The enrichment factor (EF) is defined as the ratio of analyte concentration in the acceptor solution to that in the donor solution. The EF was calculated by (Eq.9).

$$EF = \frac{C_a}{C_d} \tag{9}$$

Where C_a and C_d are concentrations of the analyte in the acceptor solution and the donor solution, respectively.

The extraction efficiency (EE) is defined as the fraction of analyte that is extracted into the acceptor solution, and can be represented in (Eq.10).

$$EE = \frac{C_a V_a}{C_d V_d} \tag{10}$$

Where V_a and V_d are the volumes of the acceptor solution and the donor solution, respectively.

The HF-LPME technique employs much less acceptor volume, so it provides high preconcentration factor.

2.6 Literature review

In 1999, Muñoz et al. [10] reported the LLE technique for extraction of As(III) and As(V) in seafood products. In this report, the sample containing As(V) or As(III) was digested in hydrochloric acid, after reduction by hydrobromic acid and hydrazine sulfate. The inorganic arsenic was extracted into chloroform, back-extracted in hydrochloric acid and determined total As by HG-AAS.

In 2003, Iberhan and Wiśniewski [11] studied the removal of As(III) and As(V) from sulfuric acid solution by LLE. In this report, extraction efficiency using various extractants such as Cyanex$^®$ 923, Cyanex$^®$ 925, dialkyldithiophosphinic acids (Cyanex$^®$ 301), hydrophobic glycol (2-ethylhexane-1,3-diol), and hydroxamic acids were studied and compared.

In 2005, Jitmanee et al. [7] reported the SPE technique for speciation of As(III) and As(V) in freshwater samples and determination by ICP-AES. The system included two miniature columns with solid phase anion exchange resin. In the pH range 3.0-6.9, As(V), which exits as a monovalent anionic form ($H_2AsO_4^-$) was retained in the first column while As(III), which exits as a neutral form (H_3AsO_3) passed though the first column going into the second column. Prior to entering to the second column, As(III) was oxidized to As(V) by $KMnO_4$ so that it could be retained by the second column. Then, the retained As(V) in both columns was eluted by nitric acid and introduced into ICP-AES.

In 2010, Issa et al. [24] reported a method for separation and preconcentration of As(III) and As(V) in natural water using ion exchange and hybrid resins and determined by ICP-MS. This work consisted of two columns; a strong base anion exchange (SBAE) and a hybrid (HY) resin. The pH value of sample solution was adjusted to less than 8, so As(V) would be in a monovalent anionic form ($H_2AsO_4^-$) and As(III) would be in a neutral form (H_3AsO_3). The SBAE resin was used for separation of As(V) from As(III) in the water by retaining As(V) via anion exchange process while As(III) was allowed to pass through. The hybrid (HY) resin was used for retaining all inorganic arsenic species over a wide range of pH values from 5 to 11. So total arsenic (As(III) and As(V)) could be determined.

In 2001, Rupasinghe et al. [39] presented the flow injection method for determination of inorganic arsenic based on hydride generation and the molybdenum blue reaction. This system, As(V) was reduced to As(III) and converted to arsine that was pervaporated across a semi-permeable membrane into an acceptor phase containing oxidizing agent and oxidized to As(V). The acceptor stream was merged with reagent stream containing $SnCl_2$, hydrazine sulfate, and ammonium molybdate at 70 °C. The concentration of arsenomolybdenum blue was determined by UV-Visible spectrophotometer at 840 nm. This method gave a sampling frequency of 8 h^{-1} and a detection limit of 15 $\mu g\,L^{-1}$.

In 2007, Sangtumrong et al. [40] presented the method for separation of mixture of Hg(II) and As(III) ions from chloride media via HF-SLM. This method, tri-n-octylamine (TOA) in toluene was used as an extractant; sodium hydroxide was used as a stripping solution. Hg(II) and As(III) were present in different forms in hydrochloric feed solution. Hg(II) ions could be extracted with TOA in liquid membrane while the neutral As(III) remained in the feed solution. Therefore, the HF-SLM can be used to extract Hg(II) from As(III).

In 2007, Perez et al. [41] studied HF-SLM for extraction of As(V). Trioctylphosphine oxide (Cyanex 921) in kerosene was used as an extractant and Na_2SO_4 was used as a stripping solution. As(V) in 2 M H_2SO_4 feed solution existing in neutral form (H_3AsO_4) could be extracted. Arsenic concentrations in the feed and stripping solutions were determined by UV-Visible spectrophotometry using the molybdenum blue method.

In 2008, Hylton and Mitra [42] developed a microfluidic device using hollow fiber membrane for extraction of As(V), using dibutyl butyl phosphonate (DPPP)/tributyl phosphate (TBP) as an extractants and NaCl as an acceptor phase. As(V) was determined by a spectrophotometric method employing the colorimetric reagent molybdenum blue. The enrichment factors of this method were close to 30, and the limit of detection was 27 $\mu g\,L^{-1}$.

In 2008, Prapasawat et al. [16] evaluated the separation of As(III) and As(V) by HF-SLM. This method, As(III) and As(V) was separated from sulphate media based on mass transfer theory. In the system, Cyanex 923 in toluene was used as an extracting solvent and water was used as a stripping solution. The concentration of arsenic was determined by ICP-AES. The extractability of As(V) was higher than that of As(III).

In 2009, Pancharoen et al. [43] studied types of extractants for removal efficiency of arsenic ion from water samples. Five extractants such as Cyanex® 923, Cyanex® 301, TBP, TOA, and Aliquat 336 were studied. The concentration of arsenic ions was determined by ICP. Aliquat 336 was reported as a suitable extractant for removal of arsenic ion from water samples.

In 2009, Jiang et al. [17] developed HF-LPME combined with ET-AAS for the speciation As(III) and As(V) in fresh waters and human hair extracts. At pH range of 3.0 to 4.0, As(III), existing in neutral form (H_3AsO_3), could form complex with ammonium pyrrolidine dithiocarbamate (APDC) that was extracted into toluene in the hollow fiber membrane. After 10 min extraction time, the organic solvent was withdrawn into microsyringe and injected into ET-AAS for determination of As(III). This method, As(V) could not form complex with APDC, so As(V) was reduce to As(III) by L-cysteine before forming complex with APDC. The enrichment factor of 78 was achieved in this method.

In 2010, Bey et al. [44] presented the HF-SLM for removal of As(V) using PVDF hollow fiber membrane and Aliquat 336 as an extractant. The schematic of the experimental setup is shown in Figure 2.7. The concentration of arsenic in the feed samples was determined by ICP-OES. The removal of arsenic around 70% was achieved after 6 h of operation.
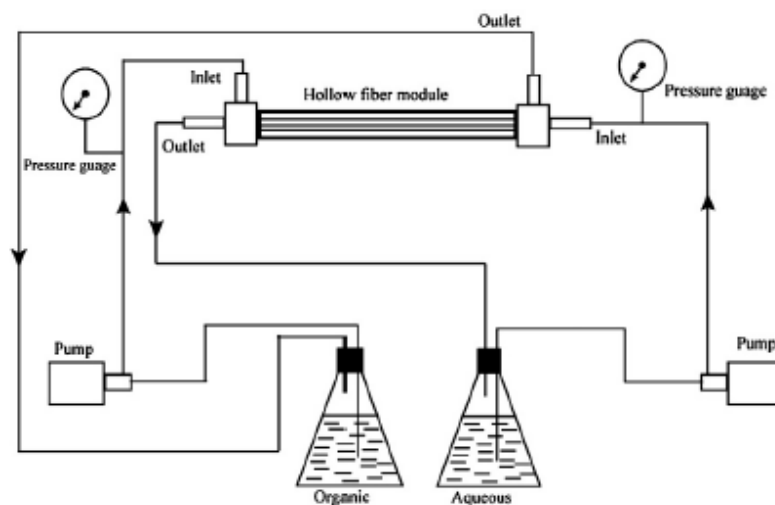
Figure 2.6 The schematic of the HF-SLM system removal of arsenic [44].

In 2010, Güell et al. [5] presented the supported liquid membrane (SLM) method for speciation of As(III) and As(V) based on their different kinetic behaviors. This method, The feed solution of As(V) and As(III) was adjusted to pH 13 so that As(V) and As(III) exist in AsO_4^{3-} and $HAsO_3^{2-}$, respectively. A 0.5 M Aliquat 336 in dodecane modified with 4% 1-dodecanol was used as an extracting solvent. A 0.1 M HCl was used as a stripping phase. The result demonstrated the rate of transportation of As(V) was higher than that of As(III). The concentration of arsenic was determined by ICP-AES. This method was applied for the removal of As(V) from real samples such as tap water and river water.

According to the reviewed literatures, the hollow fiber membrane has been used mostly for removal of inorganic arsenic. The applications of the hollow fiber membrane for speciation of inorganic arsenic are few and involve many steps and time consuming. This research attempts to develop a simple and rapid HF-SLM method for speciation of As(III) and As(V). Besides, the flow injection system based on molybdenum blue method is also developed for rapid determination of inorganic arsenic providing high sample throughput.

CHAPTER III

EXPERIMENTAL

3.1 Instrument and equipment

1. Spectrophotometer model V-325-XS (Shanghai LW scientific, China)
2. Fiber optic UV-Visible spectrophotometer with micro flow Z-cell (path length 10 cm) (Aventes BV, the Netherlands)
3. Inductively coupled plasma atomic emission spectrometer (ICP-AES) iCAP 6000 series (Thermo Scientific, USA)
4. Peristaltic pump, Masterflex$^{®}$ L/S^{TM} model 7519-20, 4 channel (Cole-parmer, USA)
5. Tygon tubing, 2-stop, 0.51 mm ID (Cole-parmer, USA)
6. Teflon tubing, 1/16" OD x 0.02" ID (IDEX Health & Science, USA)
7. Halogen lamp (230V) (Philips, China)
8. DC power supply YG 3005D (YUGO$^{®}$)
9. HPLC micro syringe 50 µL (Hamilton, Switzerland)
10. Six-port valve, model: V-451, V-541 (Upchurch Scientific, Oak Harbor, WA, USA)
11. Polypropylene hollow fiber membrane, Accurel$^{®}$ PP Q3/2 with ID 600 µm, wall thickness 200 µm and pore size 0.2 µm (Membrana, Wuppertal, Germany)
12. Magnetic stirrer, IKA$^{®}$ RCT basic safety control (IKA, Germany)
13. Medical syringe, 3 and 5 mL (Becton Dickinson, Singapore)
14. Headspace vial, 30 mL (Vertical Chromatography, Thailand)
15. Medical syringe needle, 0.7 x 25 mm o.d. (Nipro, Thailand)
16. Autopipettes and tips, 100 µL, 1000 µL and 10 mL (BRAND, Germany)
17. Volumetric flasks, 10, 25, 50, 100 and 250 mL (class A, witeg, Germany)
18. Micro insert vial, 300 µL (Vertical Chromatography, Thailand)
19. pH meter model 744 (Metrohm, Switzerland)

3.2 Chemicals and reagents

1. Sodium hydrogen arsenate heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$) (BDH Chemicals, UK)

2. Sodium meta-arsenite ($NaAsO_2$) (BDH Chemicals, UK)

3. Sodium hydroxide (Merck, Germany)

4. Methyltrialkylammonium chloride (Aliquat 336) ($CH_3N(C_8-C_{10}$ n-Alkyl$)_3Cl$) (Merck, Germany)

5. Kerosene (Carco Chemical CO., LTD., Thailand)

6. Potassium permanganate ($KMnO_4$) (Suksapan,Thailand)

7. Sulfuric acid (H_2SO_4) (J.T. Baker, Thailand)

8. Hydrazinium sulfate ($N_2H_6SO_4$) (Merck, Germany)

9. Ammonium heptamolybdate tetrahydrate (($NH_4)_6Mo_7O_{24} \cdot 4H_2O$) (Merck, Germany)

10. di-sodium hydrogen phosphate (Na_2HPO_4) (Merck, Germany)

11. Hydrochloric acid (J.T. Baker, Thailand)

12. Nitric acid 65% (Merck, Germany)

3.3 Experiment

3.3.1. Flow-based molybdenum blue method for determination of inorganic arsenic As(V)

3.3.1.1 Preparation of chemical solutions

3.3.1.1.1 Ammonium molybdate solution 1.5% (w/v)

The 1.5% ammonium molybdate solution was prepared by dissolving 1.5 g of ammonium heptamolybdate tetrahydrate (($NH_4)_6Mo_7O_{24} \cdot 4H_2O$) in 100 mL Milli-Q water.

3.3.1.1.2 Hydrazine sulfate solution in 1.5 mol L^{-1} sulfuric acid solution

The hydrazinium sulfate solution was prepared by dissolving 1.0 g of hydrazinium sulfate ($N_2H_6SO_4$) in 100 mL 1.5 mol L^{-1} H_2SO_4 solution.

3.3.2.2 The flow-based molybdenum blue method

Flow system for molybdenum blue method is schematically shown in Figure 3.1. A 40 µL of sample solution containing As(V) was injected into a six-port valve. The sample stream was mixed with 0.5% hydrazine sulfate in 1.5 M sulfuric acid solution (R2) and 1.5% ammonium molybdate solution (R3), successively. Then, the mixture was heated in the heating coil (120 cm), which was controlled temperature at 80 °C. The absorbance of the blue solution was measured by the fiber optic UV-Visible spectrometer with micro flow Z-cell at 830 nm. The flow rates of all streams were 0.5 mL min^{-1}.
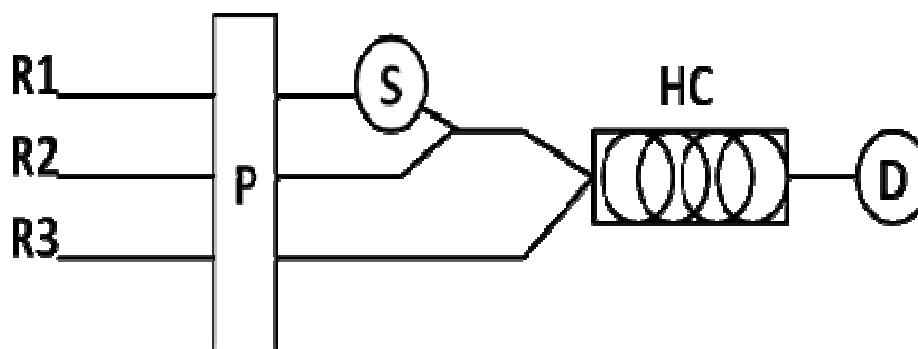
Figure 3.1 Schematic of the flow-based molybdenum blue system; R1 = Milli Q water, R2 = 0.5% hydrazine sulfate in 1.5 mol L^{-1} H_2SO_4, R3 = 1.5% Ammonium molybdate, P = peristaltic pump, S = six-port valve, HC = heating coil, D = detector (Fiber optic UV-Visible spectrophotometer with micro flow Z-cell).

3.3.2. Hollow fiber supported liquid membrane (HF-SLM) method for speciation and preconcentration of inorganic arsenic

3.3.2.1 Preparation of chemical solutions

3.3.2.1.1 Stock standard solution of As(V)

The stock 1000 mg L^{-1} standard solution of As(V) was prepared by dissolving 0.4160 g of Sodium hydrogen arsenate heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$) in a 100-mL volumetric flask and made up to the volume with Milli-Q water.

3.3.2.1.2 Stock standard solution of As(III)

The stock 1000 mg L^{-1} standard solution of As(III) was prepared by dissolving 0.1732 g of Sodium meta-arsenite ($NaAsO_2$) in a 100-mL volumetric flask and made up to the volume with Milli-Q water.

3.3.2.1.3 Potassium permanganate ($KMnO_4$) solution 0.01 mol L^{-1}

The 0.01 mol L^{-1} $KMnO_4$ solution was prepared by dissolving 0.1580 g of $KMnO_4$ in a 100-mL volumetric flask and made up to the volume with Milli-Q water.

3.3.2.1.4 Sodium hydroxide (NaOH) solution 1.0 mol L^{-1} as acceptor phase

The 1.0 mol L^{-1} NaOH solution was prepared by dissolving 4.0 g of NaOH in a 100-mL volumetric flask and made up to the volume with Milli-Q water.

3.3.2.1.5 Sodium hydroxide solution 0.1 mol L^{-1} for pH adjustment

The 0.1 mol L^{-1} NaOH solution was prepared by appropriate dilution of 1.0 mol L^{-1} NaOH with Milli-Q water.

3.3.2.1.6 Hydrochloric acid (HCl) solution 0.1 mol L^{-1} for pH adjustment

The 0.1 mol L^{-1} HCl solution was prepared by appropriate dilution of concentrated HCl with Milli-Q water.

3.3.2.1.7 10% (v/v) Aliquat 336 in kerosene

The 10% (v/v) Aliquat 336 in kerosene was prepared by dissolving 1 mL of Aliquat 336 in 10 mL of kerosene.

3.3.2.2 HF-SLM for speciation and precocentration of As(V)

The setup of HF-SLM is shown in Figure 3.2. The sample solution containing As(V) or As(III) was first adjusted to pH 6 with 0.1 M HCl and 0.1 M NaOH. A 28 mL of the sample solution was transferred into a 30-mL sample vial. The hollow fiber membrane was cut in a piece of 21-cm length, cleaned by sonication with acetone for 10 min to remove contaminants, dried and soaked in Aliquat 336: kerosene mixture overnight to ensure that the extracting phase was completely filled the pores of the membrane. The remaining solvent in the lumen was removed using air blowing and replaced by 50 µL NaOH solution by using a 3-mL medical syringe. The hollow fiber was coiled into a double loop configuration (2x U-shapes), as schematically shown in Figure 3.2. Both ends of the membrane were connected with stainless steel needle tips that were pierced through a septum cap. The membrane was immersed into sample solution. The solution was stirred for a certain time. Then, the acceptor solution in the lumen was withdrawn and transferred into a micro insert vial. The concentration of As(V) was determined by the flow-based molybdenum blue method as described in section 3.3.1. This procedure, only As(V) species was determined.
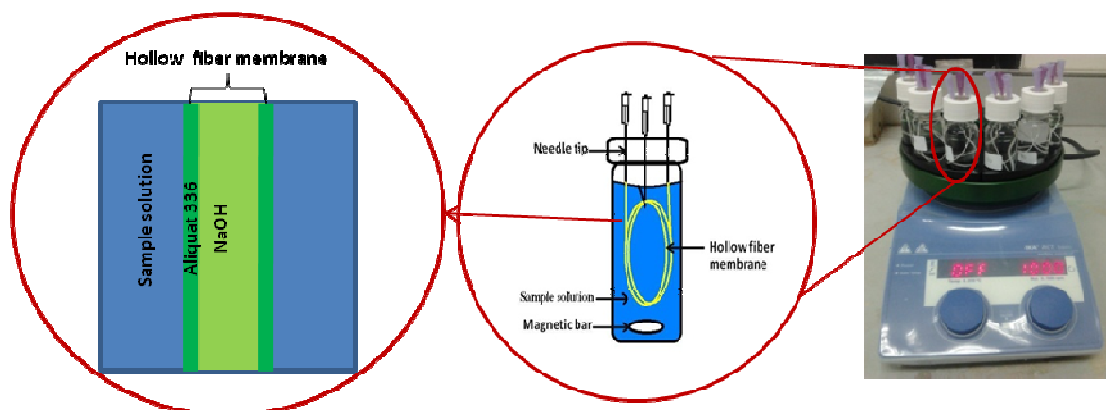
Figure 3.2 Complete setup and schematic diagram of HF-SLM for speciation of inorganic arsenic.

3.3.2.3 HF-SLM for speciation and preconcentration of As(III)

As(III) in the sample solution could not be extracted into the acceptor phase by the previous procedure (3.3.2.2) because at pH 6, As(III) existed in neutral form, which was not able to undergo anion exchange with Aliquat 336. Therefore, in speciation of As(III), As(III) would be oxidized to As(V) prior to preconcentration and determination by the flow-based molybdenum blue method. In our study, $KMnO_4$ was used as oxidizing agent. An aliquot of 40 µL $KMnO_4$ was added into a 28 mL of sample solution. The solution was then adjusted to pH 6, and placed at room temperature overnight before extraction. The extraction procedure was done according to Section 3.3.2.2. This procedure, the total As was determined. The concentration of As(III) was calculated by the difference between the total concentration of As and the concentration of As(V) as shown in the following equation.

$$[As(III)] = [Total As] - [As(V)]$$

3.3.3 Real samples

The method was applied for determination of As(III) and As(V) in drinking water. Five brands of drinking water were purchased from local markets. The extraction procedures were done according to Section 3.3.2.2 for As(V) and Section 3.3.2.3 for As(III), respectively.

3.3.4. Determination of inorganic arsenic by ICP-AES method

A 10-mL of drinking water was acidified to pH value less to 2.0 with 2 drop of concentrated nitric acid prior to analysis by ICP-AES method. The determination of arsenic in drinking water was followed by US EPA method 200.15 [45]. The optimal instrumental operating conditions are shown in Table 3.1.

Table 3.1 Optimal instrumental (iCAP 6000 series) operating conditions.

Sample Pump:	
Flush Pump Rate :	100 rpm
Analysis Pump Rate:	50 rpm
Pump Stabilization Time:	5 sec
Pump Tubing Type:	Tygon Orange/White
Source settings:	
Wavelength Range:	189.042
RF Power:	1150 W
Auxiliary Gas Flow:	0.5 L min^{-1}
Nebulizer Gas Flow:	0.70 L min^{-1}
Coolant Gas Flow:	12 L min^{-1}

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Optimization of the flow-based molybdenum blue method for the determination of inorganic arsenic (As(V))

In typical molybdenum blue method (batch), the blue color is slowly generated and accelerated when the mixture is heated for 10 min. Nevertheless, in the flow-based molybdenum blue method, the mixture is continuously flowed; therefore, the heating time of less than 10 min would be encountered and the sensitivity of the method would be optimized. The sensitivity of the method depends on the concentration of ammonium molybdate, the concentration of reducing agent, the temperature and the flow rate.

4.1.1 Concentration of ammonium molybdate

The sensitivity of the molybdenum blue method depends on the intensity of the blue color obtained. Since the blue color is slowly developed, the concentration of the reactant would kinetically accelerate the reaction. At the given time of reaction, the higher concentration of ammonium molybdate would give more intense blue color than the lower concentration. Moreover, the amount of ammonium molybdate should be in excessive of the amount of As(V). In this work, the concentrations of ammonium molybdate were varied from 0.5 to 2.5% (w/v). The results are shown in Figure 4.1. The absorbances increased with increased concentrations of ammonium molybdate. The concentrations of ammonium molybdate above 1.5 % (w/v) did not alter the absorbance significantly. Therefore, 1.5% (w/v) of ammonium molybdate was used in this work.

Figure 4.1 Absorbance of 20 mg L^{-1} As(V) obtained by using various concentrations of ammonium molybdate. (0.5% hydrazine sulfate in 1.5 mol L^{-1} H$_2$SO$_4$; flow rates of all streams: 0.5 mL min^{-1}).

4.1.2 Concentration of hydrazine sulfate in 1.5 mol L^{-1} H$_2$SO$_4$

Hydrazine sulfate in H$_2$SO$_4$ was used as a reducing agent in molybdenum blue reaction of As(V). According to the slow formation of the blue color, at the given time of reaction, the concentration of the reducing agent would affect the intensity of the blue color. Besides, the amount of hydrazine sulfate and the concentration of H$_2$SO$_4$ should be sufficient for the reaction. The H$_2$SO$_4$ concentration of 1.5 mol L^{-1} was appropriated concentration for the system because it gave stable baseline signal. The concentration of hydrazine sulfate between 0.1–1.25% (w/v) in 1.5 mol L^{-1} H$_2$SO$_4$ were investigated. The results are shown in Figure 4.2. The absorbance increased with increased hydrazine sulfate concentrations. At concentrations of hydrazine sulfate above 0.5% (w/v) gave stable blue color in the flow system. Therefore, 0.5% (w/v) of hydrazine sulfate in 1.5 mol L^{-1} H$_2$SO$_4$ was chosen for this work.
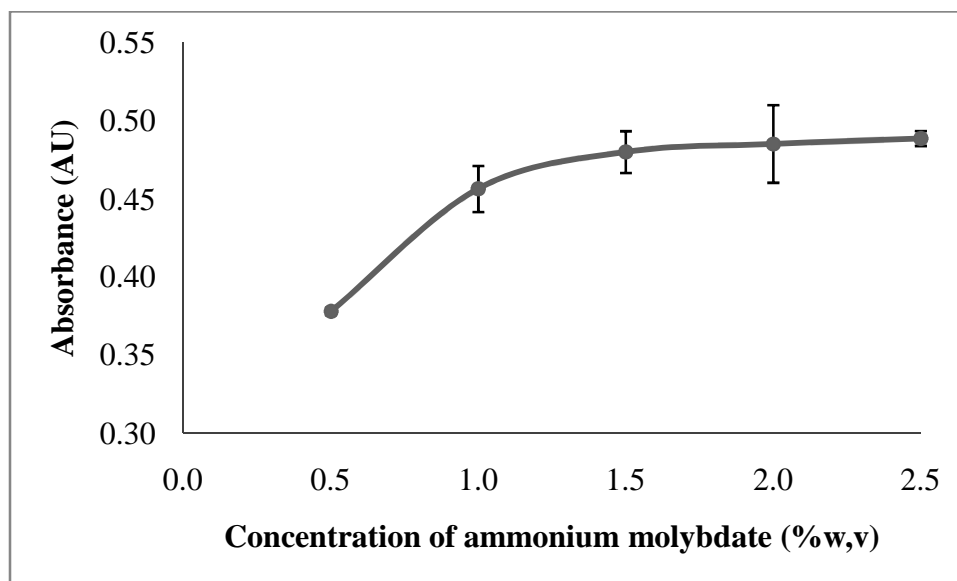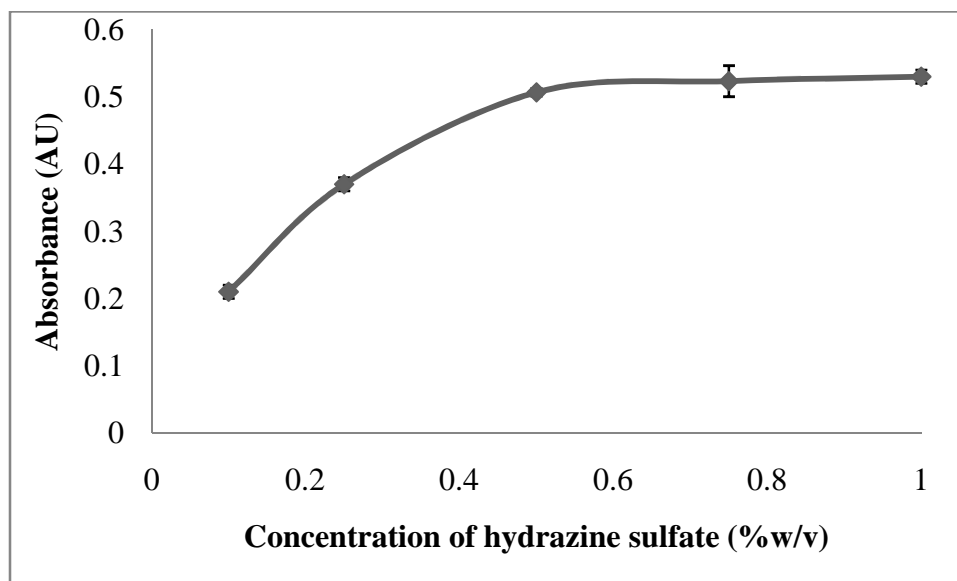
Figure 4.2 Absorbance of 20 mg L^{-1} As(V) obtained by using various concentrations of hydrazine sulfate in 1.5 mol L^{-1} H$_2$SO$_4$. (1.5% ammonium molybdate; flow rates of all streams: 0.5 mL min^{-1}).

4.1.3 Temperature and flow rate of reagents

In molybdenum blue method, the formation of the blue color complex can be accelerated by heating. Since the mixture in the flow system was flowed through the heating coil, the temperature and time that the mixture being heated in the heating coil was optimized. The heating temperature is typically 70-100 °C. The higher heating temperature can shorten the heating time. The time that the mixture spent in the heating coil also depends on the flow rate of the system; therefore, the slower flow rate would lengthen the heating time. In the flow-based molybdenum blue system, the heating temperature at 80 °C was the maximum temperature that could be used because the maximum DC power supply had been reached. The flow rate of 0.5 mL min^{-1} provided the heating time of 30 sec and allowed satisfactorily intense blue color. The flow rates of all streams of 0.5 mL min^{-1} and the heating temperature at 80 °C was chosen.

4.1.4 Performance of the flow-based molybdenum blue method for determination inorganic arsenic As(V)

The calibration curve for determination of inorganic arsenic As(V) is shown in Figure 4.3. The linear calibration curve was obtained from As(V) solutions in concentration range of 10-30 mg L^{-1} and provided correlation coefficients (R^2) $\geq$ 0.999. The limit of detection (LOD) based on 3SD + $\bar{X}$ (SD = standard deviation of absorbance of blank and $\bar{X}$ = average absorbance of blank) was below 2 mg L^{-1}.
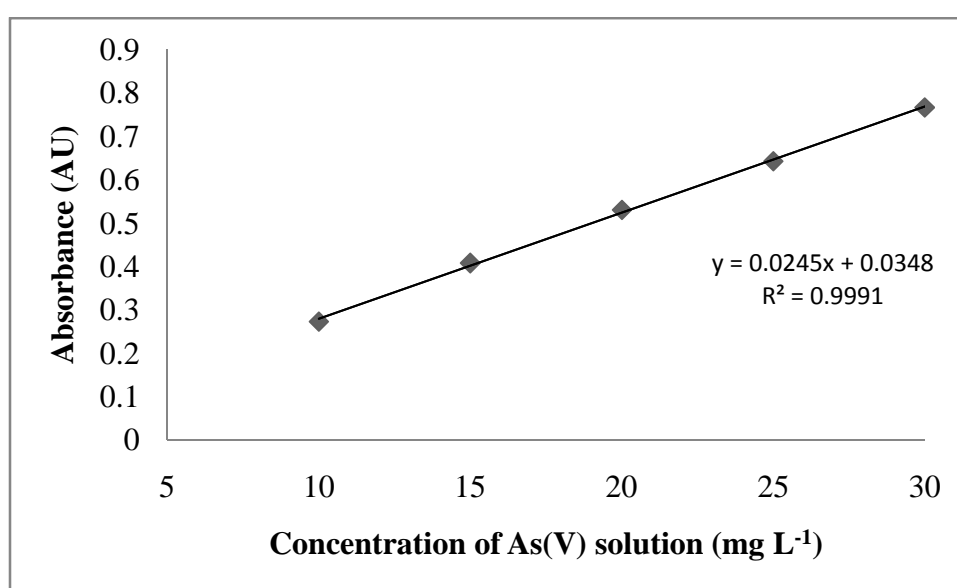
Figure 4.3 The calibration curve of As(V) determined by the flow-based molybdenum blue method. (0.5% hydrazine sulfate in 1.5 mol L^{-1} H$_2$SO$_4$; 1.5% ammonium molybdate; flow rates of all streams: 0.5 mL min^{-1}).

4.2 Optimization of HF-SLM of inorganic arsenic

The HF-SLM was applied for preconcentration of As(V). Several parameters affecting the enrichment factor (EF) or method sensitivity were investigated and optimized.

4.2.1 Length of the hollow fiber membrane

The volume of the accepter solution is relative to the length of hollow fiber membrane. The shorter membrane, the smaller volume of the acceptor solution can be filled. The smaller volume may yield the higher enrichment factor. For our experiment, too short membrane did not give sufficient volume of the acceptor solution for injection into the flow-based molybdenum blue system. Therefore, 21-cm membrane was used.

4.2.2 Aliquat 336: kerosene ratio

Methyltrialkylammonium chloride or Aliquat 336 ($CH_3R_3N^+Cl^-$) was used as extractant based on anion exchange process. The sample solution was adjusted to pH 3-7, so As(V) was dominantly present in the form of monovalent ion ($H_2AsO_4^-$). The ion exchange process of As(V) ion with Aliquat 336 is described by the equilibrium equation below [46].

$$H_2AsO_4^- + CH_3R_3N^+Cl^- \rightleftharpoons (CH_3R_3N^+)(H_2AsO_4^-) + Cl^-$$
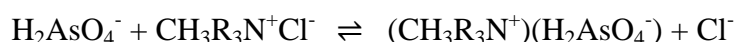
Since Aliquat 336 is so viscous that it is difficult to thoroughly fill in the pores of the hollow fiber membrane easily, dilution of Aliquat 336 with a solvent is necessary. In this work, kerosene was used because it was available at low cost. The optimum Aliquat 336: kerosene ratio should provide sufficient active site for ion exchange process with As(V) ion. The Aliquat 336: kerosene ranging from 10% to 50% (v/v) was studied.

The results are shown in Figure 4.4. The Aliquat 336: kerosene ratio of 10% (v/v) gave the highest enrichment factor. The enrichment factors were decreased as increased Aliquat 336: kerosene ratios. The reason might be that increased Aliquat 336: kerosene ratios are so viscous that the mass transfer of As(V) ion into the acceptor phase be difficult.
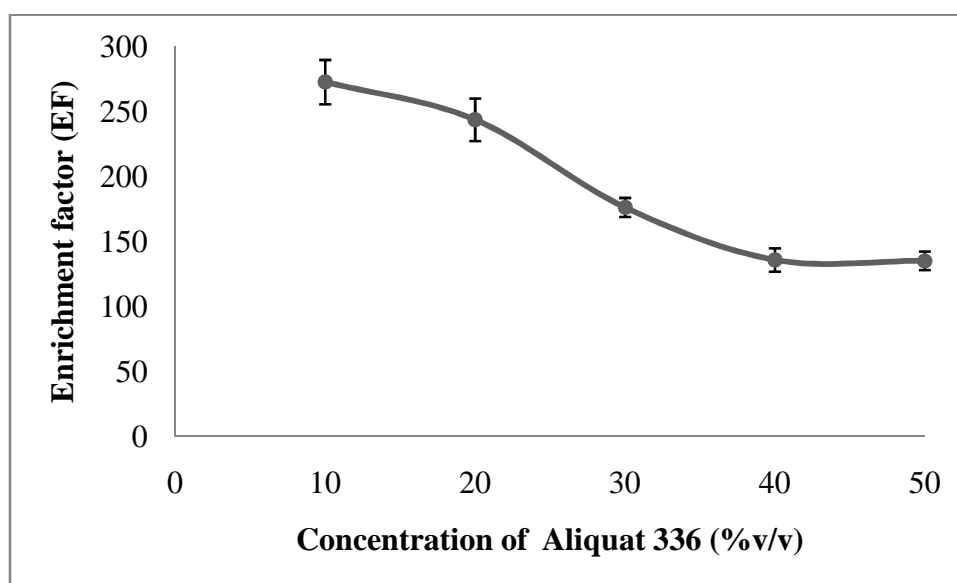
Figure 4.4 The enrichment factor of As(V) obtained by the HF-SLM at various Aliquat 336: kerosene ratios. (100 µg L^{-1} of As(V) solution; Acceptor phase: 1.0 mol L^{-1} NaOH; Extraction time: 20 min; Stirring rate: 1000 rpm; pH 6).

4.2.3 Concentration of NaOH

Sodium hydroxide was used as the acceptor solution. It provided hydroxide ion (OH$^-$) for ion exchange process with As(V) ion. The amount of As(V) ion in the acceptor phase can be driven by the amount of OH$^-$ as described by the equilibrium equation below [46].

$$(CH_3R_3N)(H_2AsO_4^-) + NaOH \rightleftharpoons CH_3R_3N \cdot OH + NaH_2AsO_4$$
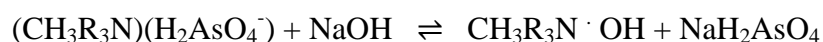
In this study, the concentrations of NaOH varied from 0.25 to 1.25 mol L^{-1} were studied. The results are shown in Figure 4.5. The enrichment factors were increased with increased NaOH concentrations. The NaOH concentration of 1.0 mol L^{-1} was chosen because it gave the highest enrichment factor.

Figure 4.5 The enrichment factor of As(V) obtained by the HF-SLM at various concentrations of NaOH. (100 µg L^{-1} of As(V) solution; Aliquat 336: kerosene ratio: 10% (v/v); Extraction time: 20 min; Stirring rate: 1000 rpm; pH 6).

4.2.4 Stirring rate

One important parameter that affects the extraction efficiency is stirring rate. Stirring creates the convection of the solution that enhances the transfer of the As(V) ion from the donor phase to the acceptor phase where the mass transfer occurs. Stirring rates ranging from 200 to 1000 rpm were tested. The results are shown in Figure 4.6. The enrichment factor increased as increased stirring rates. Nevertheless, the stirring speeds of higher than 1000 rpm cause too vigorous convection. Therefore, the stirring rate of 1000 rpm was selected.

Figure 4.6 The enrichment factor of As(V) obtained by the HF-SLM at various stirring rates. (100 µg L^{-1} of As(V) solution; Aliquat 336: kerosene ratio: 10% (v/v); Acceptor phase: 1.0 mol L^{-1} NaOH; Extraction time: 20 min; pH 6).

4.2.5 Extraction time

Extraction time is the time that As(V) ion transfers into the extracting phase, which also relates to the sensitivity of the method. In this study the extraction time was varied in the range of 5 to 30 min. Figure 4.7 shows that the enrichment factor increased with increased extraction time. The extraction time was optimized between the sensitivity of the method and the speed of the analysis. The extraction time of 20 min was selected because it gave the limit of detection below the maximum contamination level of total arsenic in drinking water set by the World Health Organization (WHO) and the US Environmental Protection Agency (US EPA).

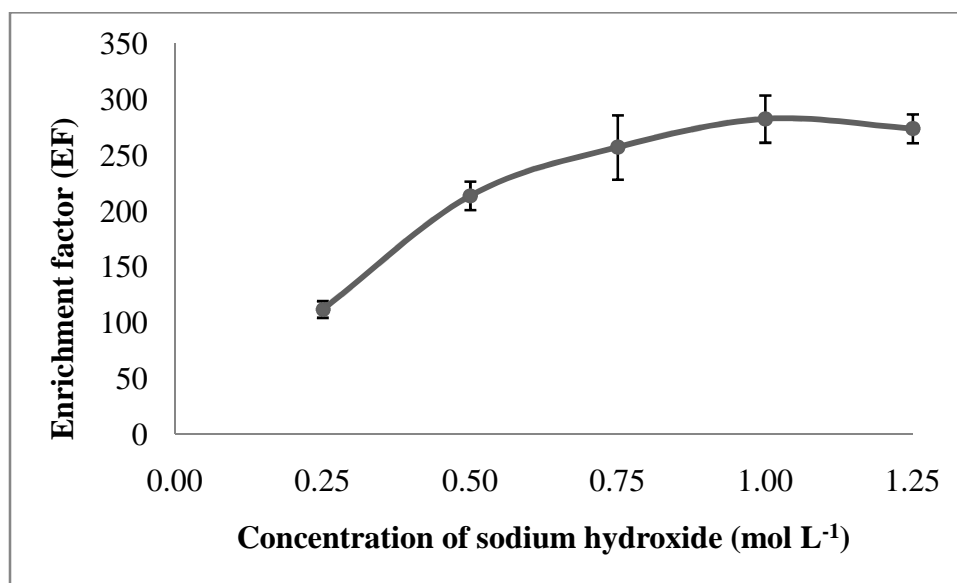**Figure 4.7** The enrichment factor of As(V) obtained by the HF-SLM at various extraction times. (100 µg L^{-1} of As(V) solution; Aliquat 336: kerosene ratio: 10% (v/v); Acceptor phase: 1.0 mol L^{-1} NaOH; Stirring rate: 1000 rpm; pH 6).

4.2.6 Effect of pH

This method, As(V) was extracted into Aliquat 336 based on anion exchange process, so As(V) must exist in the anion form. Generally, As(V) can be present in natural water in many forms depending on the pH values. The pH of water sample is one important parameter that affects the anion exchange process between Aliquat 336 and As(V). Therefore, various pH of sample solution were tested. The pH of sample solution (donor phase) was varied from pH 3 to pH 7 because at pH more than 7, As(III) is present in the anion form and it can be extracted with Aliquat 336 via anion exchange process as well. The results are shown in Figure 4.8. At pH 3, the enrichment factor was small because some of As(V) might be present in neutral form. At pH more than 3, the enrichment factor was increased and not independent on the pH value. However, pH 6 was employed in the experiment because it would be required for the oxidation procedure of As(III) to As(V) by KMnO$_4$.
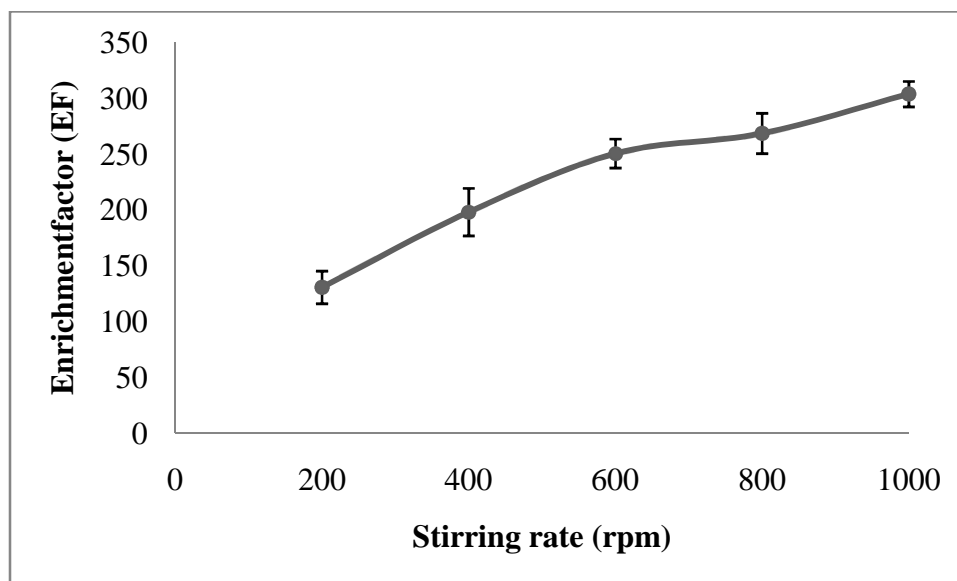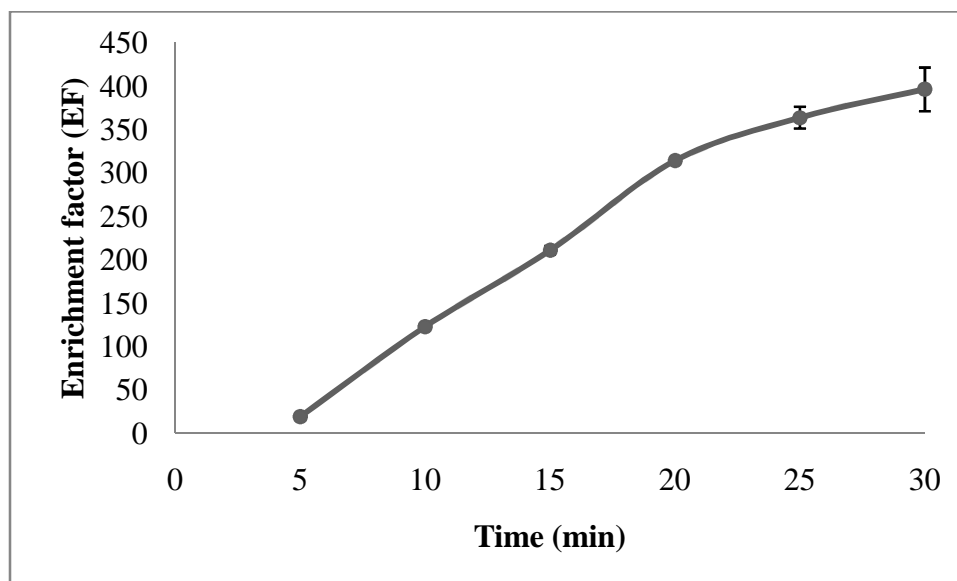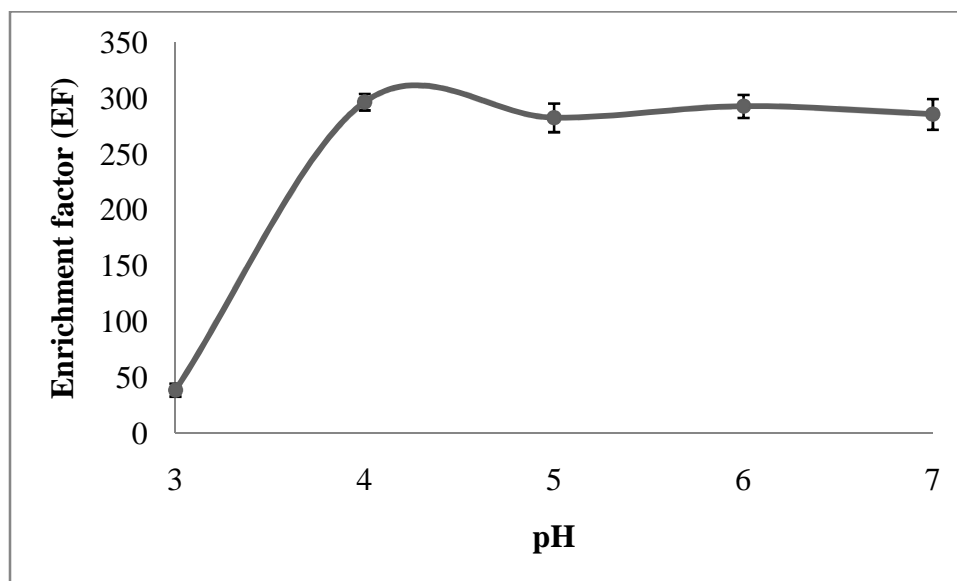
Figure 4.8 The enrichment factor of As(V) obtained by the HF-SLM at various pH values. (100 µg L^{-1} of As(V) solution; Aliquat 336: kerosene ratio: 10% (v/v); Acceptor phase: 1.0 mol L^{-1} NaOH; Extraction time: 20 min; Stirring rate: 1000 rpm).

4.3 Oxidation of As(III) to As(V)

The common form of As(III) in water samples is present in neutral form (H_3AsO_3), so it cannot be exchanged with Aliquat 336. Thus, in speciation of As(III), As(III) is oxidized to As(V) prior to extraction and determination as total As. The concentration of As(III) is then calculated by the difference between the total concentration of As and the concentration of As(V) as described in Section 3.3.2.3. The extraction efficiency in this method depends on the oxidizing efficiency. Therefore, concentration of oxidizing agent was optimized.

4.3.1 Concentration of KMnO$_4$

Potassium permanganate was used as oxidizing agent for oxidation of As(III) to As(V) because it gave high efficiency [30] and it was available in the laboratory at low cost. The oxidation reaction of KMnO$_4$ with As(III) at pH 6 is shown in Section 2.2 (Eq.6).

In this work, an electron stoichiometric ratio (r) was used to indicate the oxidizing efficiency of $KMnO_4$. Lenoble et al. [30] reported that complete oxidation of As(III) by $KMnO_4$ can be achieved when (r) was greater than 30. An electron stoichiometric ratio (r) was calculated by (Eq.1) in Section 2.2. In the experiment, 3.85×10^{-6} M $KMnO_4$ was added to a mixture of the same concentrations of As(III) and As(V) (25 µg L^{-1}) giving the electron stoichiometric ratio (r) = 30. Figure 4.9 shows the absorbance of a mixture of the same concentrations of As(III) and As(V) (25 µg L^{-1}) before and after oxidation. A mixture of inorganic arsenic after oxidation gave the absorbance almost 2 times more than that of a mixture of inorganic arsenic before oxidation. The oxidation efficiency of As(III) to As(V) was studied by calculation of yield that As(III) could be oxidized to As(V). It was calculated based on the equation below:

$$yield\ (\%) = \frac{A_{tot.\ As} - A_{As(V)}}{A_{As(V)}\ *} \times 100$$

where
$A_{tot.\ As}$ is the absorbance of total arsenic in As(V) form

$A_{As\ (V)}$ is the absorbance of As(V)

$A_{As(V)}\ *$ is the absorbance of As(V) as the absorbance of As(III)

at same concentration

The oxidation efficiency of As(III) to As(V) was about 93%. So the oxidation method was effective for oxidizing As(III). Therefore, concentration of $KMnO_4$ when r > 30 was used for oxidation of As(III) to As(V) in this experiment.
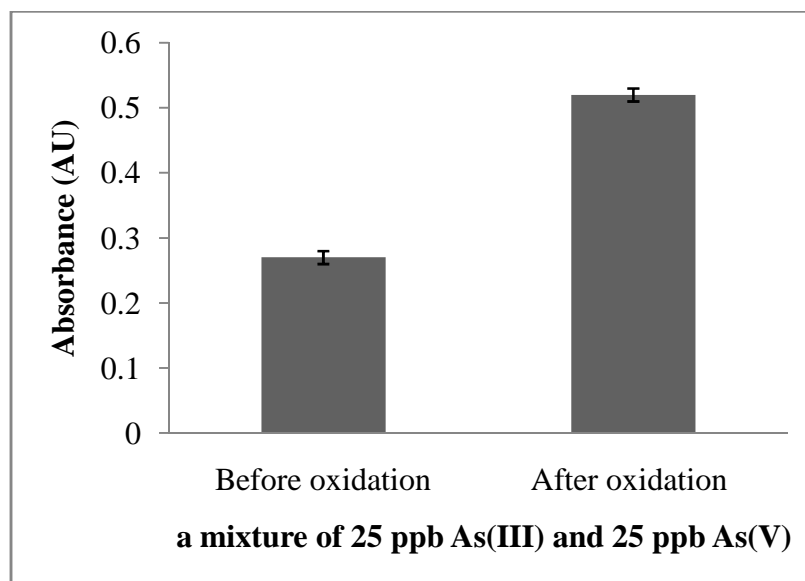
Figure 4.9 Comparison between the absorbances of mixture of As(III) and As(V) (25 µg L^{-1}) before and after oxidation (the solutions were preconcentrated by the HF-SLM).

4.4 Interference study

4.4.1 Phosphate interference

Phosphate is the major interference for the molybdenum blue method because it gives the same color as As(V). In natural water, phosphate usually exists in anion form (PO$_4^{3-}$). Thus, phosphate may be extracted via anion exchange process with Aliquat 336. Absorbances in Figure 4.10 obtained from 100 µg L^{-1} of As(V) solution and 100 µg L^{-1} of phosphate solution indicated that phosphate ion could be extracted with Aliquat 336. Although, the absorbance of phosphate was lower than the absorbance of As(V), influence of the presence of phosphate to the determination of As(V) in the sample was studied. In the experiment, absorbances of 100 µg L^{-1} of As(V) mixed with various concentrations of phosphate were studied. The results are shown in Figure 4.11. Phosphate concentrations of more than 10 µg L^{-1} might have affected the absorbance of 100 µg L^{-1} As(V). This could be a limitation of the method that can be used for samples containing phosphate less than 0.1 times concentration of As(V).
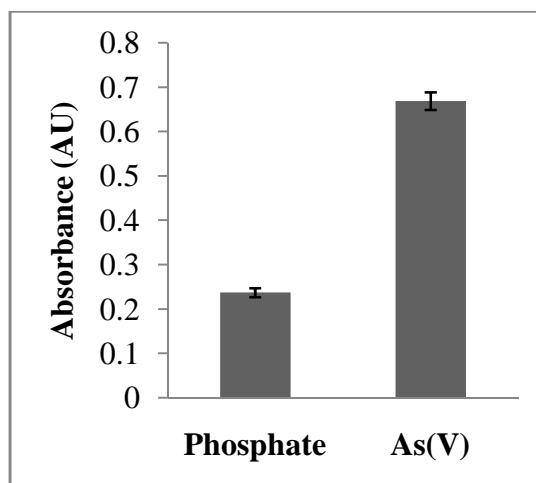
Figure 4.10 Comparison between the absorbances of phosphate and As(V) at 100 µg L^{-1} each (both solutions were preconcentrated by the HF-SLM).
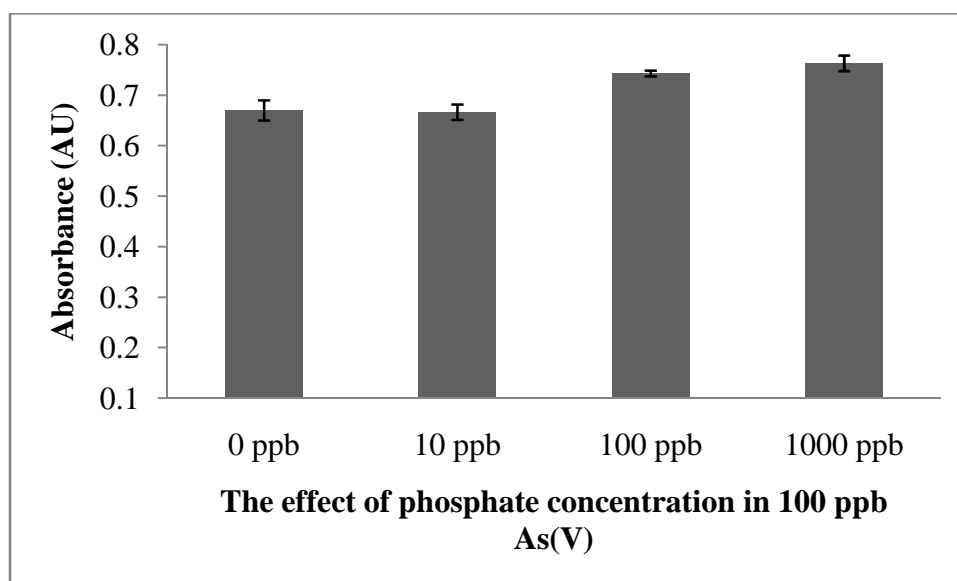
Figure 4.11 Comparison between the absorbances of solution containing 100 µg L^{-1} As(V) mixed with various concentrations of phosphate (solutions were preconcentrated by the HF-SLM).

4.4.2 Matrix effect

In the real sample, other anions may affect extraction efficiency. Figure 4.12 shows that the enrichment factor of As(V) in drinking water was diminished compared to that in Milli-Q water at the same extraction condition. It suggested that the sensitivity of the method might be matrix dependent. Decrease in enrichment factor leads to raise limit of detection (poorer sensitivity).
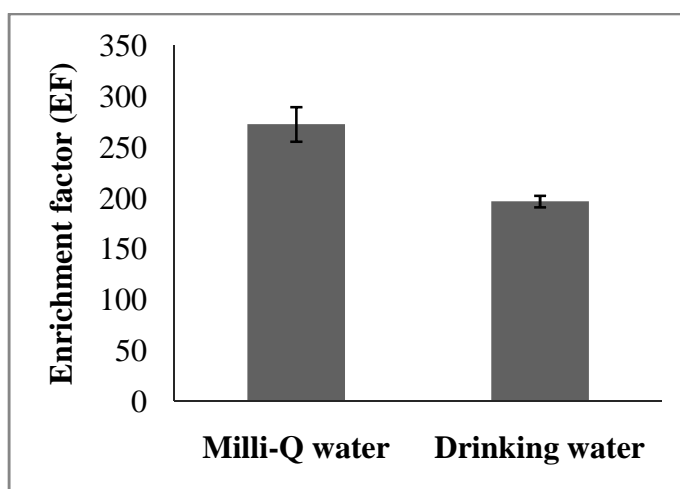
Figure 4.12 The enrichment factors of 100 µg L^{-1} As(V) spiked in different kinds of water samples obtained by the HF-SLM at the same extraction (20 min).

However, the sensitivity of the method can be improved by extending the extraction time. Prolonging extraction time allows more analytes to be extracted resulting in improvement of enrichment factor (better sensitivity). Extraction time ranging from 20 to 90 min was tested for drinking water samples. The results are shown in Figure 4.13. The extraction time of 40 min was selected for drinking water samples because it gave the limit of detection below 10 µg L^{-1}; the maximum contaminant level of arsenic in drinking water recommended by the World Health Organization (WHO) and US Environmental Protection Agency (US EPA).
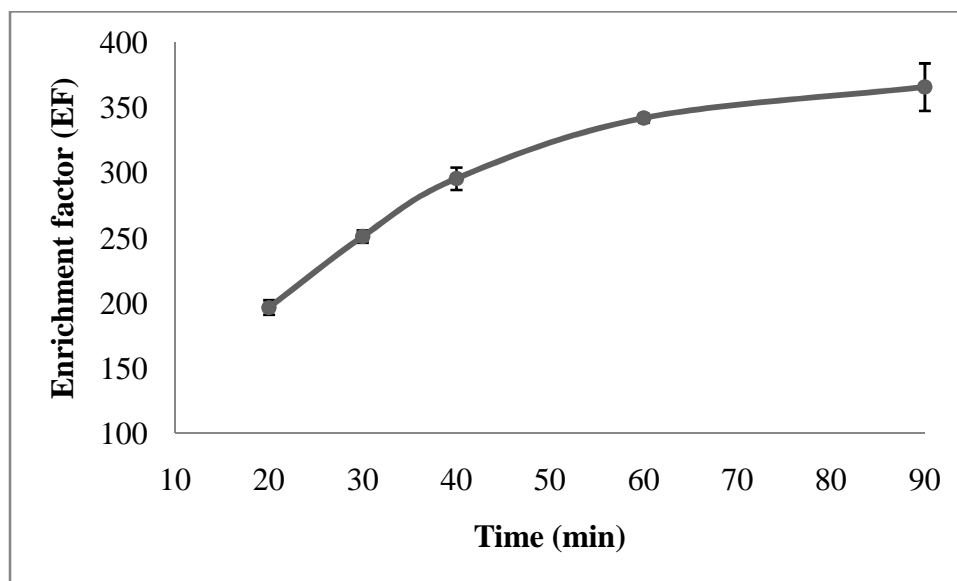
Figure 4.13 The enrichment factor of As(V) in drinking water obtained by the HF-SLM at various extraction times. (100 µg L^{-1} of As(V) solution; Aliquat 336: kerosene ratio: 10% (v/v); Acceptor phase: 1.0 mol L^{-1} NaOH; Stirring rate: 1000 rpm; pH 6).

4.5 Method evaluation for speciation and preconcentration of inorganic arsenic by HF-SLM and determination by flow-based molybdenum blue system

4.5.1 Calibration curve and linearity for determination of inorganic arsenic

The calibration curve was used for quantitative determination of As(V) in water samples. Since the method could be influenced by ions in the matrix, matrix matched calibration method was considered. The calibration curve was prepared on a matrix of drinking water sample and extracted for 40 min. The calibration curve is shown in Figure 4.14. The calibration curve for As(V) solution was established for concentrations of As(V) ranging from 30 to 110 µg L^{-1}. The linearity of this method provided the linear regression equation: y = 0.0086x + 0.0151 with correlation coefficient (R^2) = 0.9984.
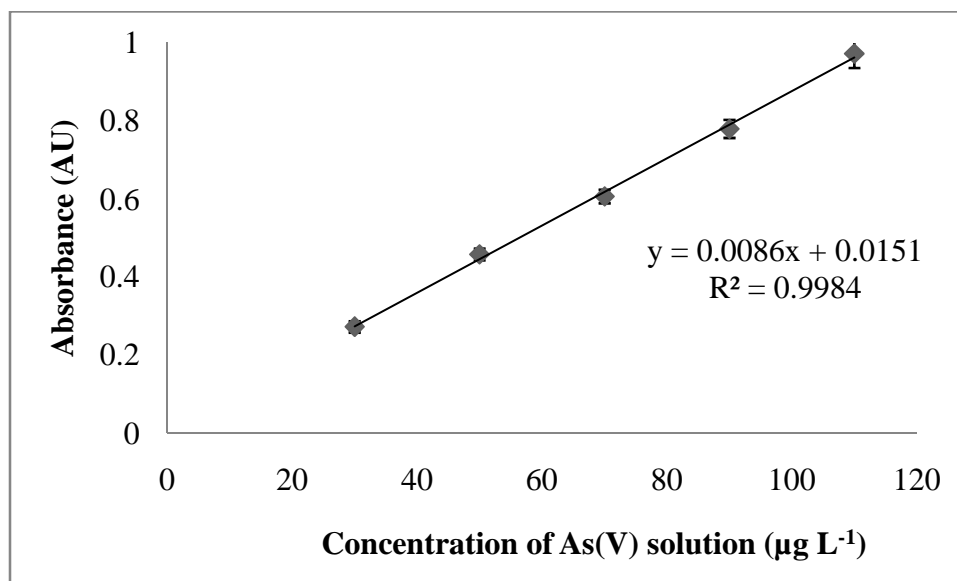
Figure 4.14 Working concentration range of the HF-SLM with flow-based molybdenum blue method for speciation and preconcentration of inorganic arsenic in drinking water (extraction time: 40 min).

4.5.2 Limit of detection (LOD)

The limit of detection (LOD) is defined by the concentration of As(III) and As(V) in drinking water calculated from the absorbance at $3SD + \bar{X}$ (SD = standard deviation of the absorbance of blank and $\bar{X}$ = average absorbance of blank). The absorbances of blank were obtained by injections of the acceptor solutions after extraction of blank solutions (40 min for drinking water) into the flow-based molybdenum blue method. This method gave the limit of detection about 5 µg L^{-1}, which was lower than the maximum contaminant level of arsenic in drinking water recommended by the World Health Organization (WHO) and US Environmental Protection Agency (US EPA).

4.5.3 Accuracy and precision

Accuracy is the difference between the concentration of analyte determined and the known concentration of analyte, which can be determined by calculating the %recovery. Precision is the repeatability of the measurement, which can be determined by calculating the %RSD.

This experiment, 40 µg L^{-1} of As(III) and As(V) were spiked into five brands of drinking water samples. The extraction procedures were done according to Section 3.3.2.2 for As(V) and Section 3.3.2.3 for As(III), respectively. The results of % recoveries and % RSD of As(III) and As(V) are summarized in Table 4.1. The recoveries of As(III) ranged from 86 to 102% and the recoveries of As(V) ranged from 92 to 112%. The %RSD of As(III) and As(V) were less than 5%. Both %recovery and %RSD were in the acceptable ranges [47].

The results in Table 4.1 show that there were no As(V) and As(III) found in all five brands of drinking water samples.

Table 4.1 % Recoveries and % relative standard deviation of As(V) 40 µg L^{-1} and As(III) 40 µg L^{-1} were spiked in drinking waters (n=3).

Sample	Spiked (µg L^{-1})		Found (µg L^{-1}) (SD)		Recovery (%RSD)	
	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
drinking water 1	-	-	ND	ND	-	-
	40	40	35 (1)	38 (2)	86(1)	94(3)
drinking water 2	-	-	ND	ND	-	-
	40	40	35 (2)	45 (1)	87(3)	112(1)
drinking water 3	-	-	ND	ND	-	-
	40	40	41 (1)	39 (1)	102(2)	98(2)
drinking water 4	-	-	ND	ND	-	-
	40	40	40 (1)	37 (1)	99(1)	92(3)
drinking water 5	-	-	ND	ND	-	-
	40	40	40 (5)	44 (2)	100(4)	111(4)

ND = non detected.

4.5.4 Method comparison with ICP-AES method

The ICP-AES method was used for comparison of the accuracy of the method. Since the ICP-AES was not able to differentiate As species; therefore, total As was reported and compared. In this experiment, 40 µg L^{-1} of As(III) and As(V) were spiked in five brands of drinking water samples. The total As was determined by the proposed method and the ICP-AES method. The results are summarized in Table 4.2. The concentrations of total As obtained by both methods were not significantly different ($P > 0.05$, Paired t-Test).

Table 4.2 Comparative determination of total As(V) in drinking waters by the proposed method and the ICP-AES method.

sample	[total As] (µg L^{-1}) (SD)	
	The proposed method	The ICP-AES method
Drinking water 1	72 (1)	76 (3)
Drinking water 2	80 (2)	75 (3)
Drinking water 3	80 (1)	90 (3)
Drinking water 4	76 (1)	71 (3)
Drinking water 5	84 (4)	74 (2)

CHAPTER V

CONCLUSION AND SUGGESTION OF FUTURE WORK

5.1 Conclusion

The hollow fiber supported liquid membrane (HF-SLM) technique has been developed for speciation of As(III) and As(V) in drinking water. As(III) and As(V) in sample solution are speciated by first adjusting the solution to pH 6. As(V), which exists in anion form ($H_2AsO_4^-$), is extracted into the HF-SLM via anion exchange process. Methyltrialkylammonuim chloride (Aliquat 336) is used as the extracting solvent. Sodium hydroxide solution is used as the acceptor solution. The concentration of As(V) in acceptor solution is determined by the flow-based molybdenum blue method. As(III), which exists as neutral form (H_3AsO_3), is oxidized to As(V) by $KMnO_4$ before extracted and determined as total As. Concentration of As(III) can be calculated by the difference between the total concentration of As and the concentration of As(V).

In the real sample, other anions in the matrix may affect extraction efficiency by decreasing the enrichment factor of As(V) resulting in downgrading limit of detection. Extraction time is important parameter involving extraction efficiency. Extending the extraction time can improve sensitivity and limit of detection of the method. Furthermore, the presence of phosphate may be the limitation of the method that can be applied to samples containing less concentration of phosphate such as drinking water.

The HF-SLM has been applied for speciation and preconcentration of inorganic arsenic in drinking water from local market. The proposed method provides high enrichment factor (up to 250) and give the method detection limit lower than the maximum contamination level of total arsenic in drinking water values of WHO and US EPA regulation. The method evaluation shows that %recoveries and %RSD are in the acceptable ranges (86-112% recovery, %RSD < 5%) for determination of As(III) and As(V) in drinking water samples. Furthermore, the results of total As obtained

from our method are comparable and not significantly different (P > 0.05, Paired t-Test) with the ICP-AES method.

The HF-SLM setup is so simple that several samples can be performed simultaneously. In addition, the flow-based molybdenum blue method also can reduce analysis time (about 10 times shorter than conventional molybdenum blue method (batch)). The method enables high sample throughput (5 min sample^{-1} based on 16 samples) and uses less solvent, which is environmental friendly and can be considered green chemistry.

5.2 Suggestion of future work

Since phosphate has affected the determination of As(V) by the method, other extraction mechanism may be considered. Extraction solvent based on partition of As in neutral form may be studied. In addition, design of HF-SLM for other applications either for speciation of metal ions, inorganic anions or organic compounds is interesting. Finally, incorporation of HF-SLM into an automated flow-based system is still challenging.

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APPENDIX

Appendix

Table A-1 A statistical test for difference between concentration of total As in drinking water from the proposed method and the ICP-AES method by using Paired *t*-Test at P = 0.05.

t-Test: Paired Two Sample for Means

	The proposed method	The ICP-AES method
Mean	78.449768	76.856228
Variance	19.5029084	55.9125473
Observations	5	5
Pearson Correlation	0.145709402	
Hypothesized Mean Difference	0	
df	4	
t Stat	0.43929955	
P(T<=t) one-tail	0.341566906	
t Critical one-tail	2.131846782	
P(T<=t) two-tail	0.683133811	
t Critical two-tail	2.776445105	

VITA

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Poster presentation and proceeding

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