SPECIATION OF ARSENIC USING SULFUR CONTAINING LIGAND AND COTTON WOOL BY ICP-OES

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การวิเคราะห์รูปแบบของอาร์เซนิกด้วยลิแกนด์ที่มีซัลเฟอร์เป็นองค์ประกอบและสำลีโดยใช้
ICP-OES

นายกวีร์ ไตรตียะประเสริฐ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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                    CONTAINING LIGAND AND COTTON WOOL BY
                    ICP-OES
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องค์ประกอบและสำลีโดยใช้ ICP-OES. (SPECIATION OF ARSENIC
USING SULFUR CONTAINING LIGAND AND COTTON
WOOL BY ICP-OES) อ.ที่ปรึกษาหลัก : รศ. ดร.อภิชาติ อิ่มยิ้ม, อ.ที่ปรึกษาร่วม :
รศ. ดร.ณรงค์ ประไพรักษ์สิทธิ์

งานวิจัยนี้มุ่งเน้นการพัฒนาวิธีการวิเคราะห์สปีชีส์ของอาร์เซนิก ได้แก่ อาร์เซนิก(III) และอาร์เซนิก
(V) ในตัวอย่างทางสิ่งแวดล้อม ด้วยเทคนิคการแยกด้วยเฟสของแข็ง โดยใช้สำลีและลิแกนด์ที่มีซัลเฟอร์เป็น
องค์ประกอบ ได้แก่ แอมโมเนียมไพโรริดีนไดไทโอคาร์บาเมต, แอล-ซิสทีอีน และ ไดเอทิลไดไทโอคาร์บามิกแอซิด และ
วิเคราะห์ปริมาณของสารหนูทั้ง 2 ชนิด ด้วยเทคนิคอินดักทีฟลีคัพเปิลพลาสมาออฟติคัลอิมิสชันสเปกโทรเมตรี โดยศึกษาภาวะ
ที่เหมาะสมของการแยกสารหนู ได้แก่ ชนิดของลิแกนด์ที่มีซัลเฟอร์เป็นองค์ประกอบที่เลือกใช้, pH, ความเข้มข้นของลิแกนด์,
ปริมาณสำลี, อัตราการไหล และชนิดของตัวชะที่เหมาะสม จากนั้นจึงได้ทำการทดสอบกับตัวอย่างทางสิ่งแวดล้อม จากการ
ทดลองพบว่าที่ pH 2, ความเข้มข้นของแอมโมเนียมไพโรริดีนไดไทโอคาร์บาเมตที่ 0.1% และปริมาณสำลี 0.5 กรัม อาร์
เซนิก(III) สามารถถูกดูดซับไว้บนสำลีได้เกินกว่า 90% และอาร์เซนิก(V) ไม่ถูกดูดซับเอาไว้ จากนั้นจึงทดสอบการชะ
อาร์เซนิก(III) ออกจากคอลัมน์โดยใช้ตัวชะคือ สาระลายผสม 4 M HNO₃, 4 M HCl และ 0.5 M H₂O₂
อัตราส่วน 1 : 1 : 1 ปริมาตร 5 มิลลิลิตร สามารถชะอาร์เซนิก(III) ได้เปอร์เซ็นต์การคืนกลับที่ยอมรับได้ (>80%)
วิธีการนี้ถูกนำไปทดสอบกับสารละลายผสมอาร์เซนิก(III) และอาร์เซนิก(V) ความเข้มข้น 10 – 1000 ไมโครกรัมต่อ
ลิตร และตัวอย่างทางสิ่งแวดล้อม ผลการทดสอบสามารถแยกอาร์เซนิกทั้งสองสปีชีส์ได้อย่างสมบูรณ์ มีเปอร์เซ็นต์การคืนกลับ
อยู่ที่ 83 - 118 % และค่าส่วนเบี่ยงเบนมาตรฐานที่ยอมรับได้

สาขาวิชา	เคมี	ลายมือชื่อนิสิต
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KEYWORD: arsenic, speciation, solid phase extraction, ammonium pyrrolidinedithiocarbarmate

Kavee Triteeyaprasert : SPECIATION OF ARSENIC USING SULFUR CONTAINING LIGAND AND COTTON WOOL BY ICP-OES. Advisor: Assoc. Prof. APICHAT IMYIM, Ph.D. Co-advisor: Assoc. Prof. NARONG PRAPHAIRAKSIT, Ph.D.

This research aimed to develop a method for speciation of arsenic species including As(III) and As(V) in environmental samples. Cotton wool and sulfur containing ligands including ammonium pyrrolidinedithiocarbarmate (APDC), L–cysteine and diethyldithiocarbamic acid were used in a solid phase extraction and determination of arsenic by using inductively coupled plasma optical emission spectrometry. The separation parameters were studied including pH, ligand concentration, cotton amount, type of eluents and flow rate. It was found that at pH 2, 0.1% APDC concentration and 0.5 g of cotton, As(III) could form complex with APDC (As(III) – APDC) and was separated from As(V) by using cotton column. The adsorption percentage was around 90%. Then As(III) was eluted by using 5 mL of 4 M HNO_3, 4 M HCl and 0.5 M H_2O_2 at a ratio of 1:1:1 as eluent. The proposed method was then used to perform a speciation analysis of arsenic in solutions containing As(III) and As(V) in the range of 10 – 1000 μg L^{-1}. The results showed good recoveries of both arsenic species at 83 - 118% with acceptable relative standard deviation (%RSD). The proposed method was applied for arsenic speciation in environmental water samples. The results showed good recoveries and %RSD.

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Field of Study:	Chemistry	Student's Signature	....
Academic Year:	2018	Advisor's Signature	....
		Co-advisor's Signature	....

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CHAPTER I

INTRODUCTION

Global industrialization has continually led to increasing use of metals and metalloids around the world. Arsenic is one of the metalloids being used in various industries. Arsenic can be released into environment through many processes such as volcanic eruption, mining, usage of pesticides, herbicides and wood preservatives. Human can recieve arsenic by drinking contaminated water, using contaminated water in food preparation, irrigation of food crops, eating contaminated food and smoking tobacco. Exposure to arsenic even at low concentration can cause a variety of adverse health effects [1]. The maximum permissible concentration of arsenic in drinking water is 50 μg L^{-1} and the recommended value by EPA and WHO is 10 μg L^{-1} [2]. Conventional analytical methods which allow determining arsenic level in samples can only measure its total concentration. However, the toxicity of arsenic mainly depends on its chemical form such as inorganic compound and organic compound. Thus, accurate and sensitive methods for speciation of arsenic are required for obtaining important information on its toxicity.

Determination of arsenic in environment samples such as water is very important for evaluating its contamination level in environment as well as human exposure. Inductively coupled plasma optical emission spectrometry (ICP – OES) is a useful spectrometric method for the direct determination of total arsenic level. However, appropriate separation and/or preconcentration methods, such as solvent extraction, ion exchange, chromatography and solid phase extraction, are typically required to obtain the separation of arsenic species prior to its determination.

Chromatographic techniques combined with spectroscopic techniques commonly provide excellent speciation capability and sensitivity but high instrumentation cost and highly trained professionals are required. Alternatively, solid phase extraction is an effective method for the separation and preconcentration of trace metal ions. Many sorbents were employed for these purposes.

Cotton fiber is one of the materials that can be used as a sorbent for analytical purpose. Cotton fiber is a cheap and easy to use material. However, the cotton fiber alone has limited affinity towards metal ions. Therefore, chelating agents play important role to improve the adsorbtivity of this material. Sulfur containing ligands are chelating agent that has been widely used for the separation and preconcentration of arsenic ions because of its selectivity to interact with arsenic ion.

In this work we aim to combine the advantages of cotton wool and sulfur containing ligand to the preconcentration and speciation analysis of inorganic arsenic species, i.e. As(III) and As(V) in aqueous solutions and environment samples using ICP – OES.

1.1 Objectives

1. To develop a method for the speciation of inorganic arsenic (As(III) and As(V)) using a cotton wool modified with sulfur containing ligand, followed by determination by ICP – OES.

2. To apply the developed method for the arsenic speciation in real samples.

1.2 Scope of this work

This work was focused on developing a method for the speciation of inorganic As species in aqueous solution using sulfur containing ligand attached on cotton wool followed by determination by ICP – OES.

Three types of sulfur containing ligands were used for complexation with arsenic and then adsorbed onto cotton fiber to carry out the arsenic speciation. The parameters affecting speciation of arsenic e. g. pH, ligand concentration and flow rate were optimized. The method was later validated by speciation of arsenic in prepared solution. The recovery and relative standard deviation were used to evaluate accuracy and precision of the method. Finally, the developed method was used for the speciation analysis of As(III) and As(V) in real samples.

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CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Arsenic

Arsenic (As) is a metalloid and ubiquitous element in the environment. It is well known as an element of both environmental and health concerns due to its toxicity. It is released to environment through natural processes mainly from volcanic eruption or human activities such as mining, usage of pesticides, herbicides and wood preservatives. Arsenic is present in the environment in four oxidation states: +5, +3, 0 and -3, and can be classified into two categories: organic and inorganic compounds. Some important compounds of arsenic are shown in Figure 1 [3]. The toxicity mostly depends on the chemical forms of arsenic, i.e. inorganic trivalent arsenic (As(III)) that is more toxic than the pentavalent one, (As(V)) and inorganic arsenic species are more toxic than their organic species [4]. Forms of arsenic in environment depend on the physical, chemical and biological processes such as oxidation and reduction processes, adsorption/desorption, precipitation and microbiological processes.

2.2 Determination of arsenic

There are a number of factors that influence the selection of arsenic determination technique, for example, type of sample, concentration level, contamination of sample, equipment, number of samples, experience in instrumentation and limit of detection (LOD). The selection of these methods plays a key role in obtaining a good accuracy and precision of data. The commonly used techniques for arsenic determination are graphite furnace atomic absorption spectrometry (GF – AAS), hydride generation atomic absorption spectrometry (HG – AAS), inductively coupled plasma optical emission spectrometry (ICP – OES) and inductively coupled plasma mass spectrometry (ICP – MS).

AAS is a spectroanalytical technique for elemental determination based on the adsorption of electromagnetic radiation (EMR) by free atoms. The most common atomizers used for arsenic determination are graphite furnace (GF – AAS) which use electricity and hydride generation (HG – AAS) which is based on the generation of volatile hydride compound of arsenic [5].

ICP – OES has also been used for routine multi element analysis by monitoring emission spectral of the elements of interest using plasma as excitation source [6]. On the other hand, ICP – MS is a popular technique that can determine elements based on the measurment of their mass to charge ratios using a mass spectrometer.
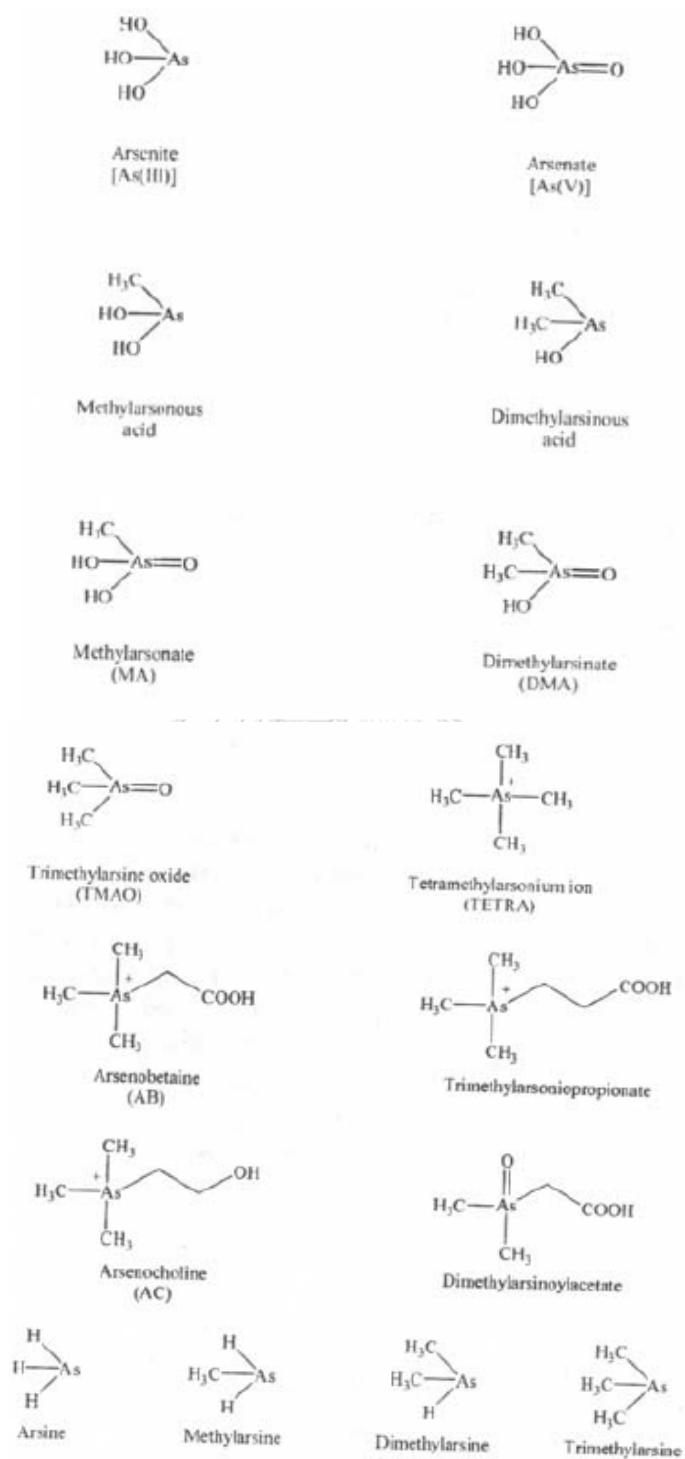
Figure 1. Some important compounds and their respective chemicals structures [3].

The typical detection limits (DL) of these techniques are shown in Table 1.

Table 1 Typical detection limits (DL) of arsenic analysis by various techniques [[5] (μg L^{-1})

Techniques	GF – AAS	HG – AAS	ICP – OES	ICP – MS
DL	0.05	0.03	2	0.0006

The above DL's are based on a 98% confidence level 3 (3 standard deviations). All detection limits are given in μg mL^{-1} and were determined using standards in dilute aqueous solution.

As mentioned above, all of these methods can only determine total arsenic concentration with no regards on its chemical forms. The speciation of arsenic species cannot be obtained using any of these techniques alone and thus, additional tools such as separation technique have to be employed to make speciation possible.

2.3 Arsenic speciation

In recent years, various methodologies have been developed for speciation of arsenic in samples. The majority of which is based on chromatography techniques that use phase column to separate arsenic species in samples. Moreover, non – chromatography methods which include many techniques like liquid – liquid extraction, hydride generation techniques and solid phase extraction have been developed as well.

2.3.1 Chromatographic methods

Various chromatographic methods have been used for arsenic speciation analysis. These include liquid chromatography (LC), high performance liquid chromatography (HPLC) and ion chromatography (IC). These techniques are commonly coupled to the suitable and sensitive determination techniques such as ICP – MS or HG – AAS [7]. HPLC – ICP – MS is a widely used technique for arsenic speciation because it gives the advantages of both outstanding separation and superior sensitivity [8]. Methods using HPLC equipped with reversed phase column and IC equipped with ion exchange columns, coupled with ICP – MS, are widely used. The IC method is suitable for the separation of As(III), As(V), monomethyl arsenic acid (MMAA) and dimethyl arsenic acid (DMAA) or arsenosugars, but it is tough to separate large organoarsenic compounds [8]. Arsenics have various ionic characteristics, which are pH dependent. The anionic species such as H_3AsO_3 (As(III)), H_3AsO_4 (As(V)), DMAA and MMAA can be separated by using anion exchange HPLC. Cation exchange can be used to separate the arsenobetaine (AsB), arsenochlorine (AsC), tetramethylarsonium (TeMA) and trimethylarsine oxide (TMAO) [9]. Narukawa et al. [8] used HPLC – ICP – MS combined with reversed phase

octadecyl group packing column to separate and determine 8 species of arsenic, As(III), As(V), MMAA, DMAA, TMAO, TeMA, AsB and AsC. It was shown that five arsenic species including As(III), As(V), MMAA, DMAA and AsB were completely resolved with the use of 10 mmol L^{-1} sodium 1 – butanesulfonate, 4 mmol L^{-1} malonic acid, 4 mmol L^{-1} tetramethylammonium hydroxide, 5 mmol L^{-1} ammonium dihydrogenphosphate and 0.05% methanol as an eluent.

All of these techniques provide excellent speciation capability and sensitivity but costly instrumentation and highly trained professionals are inevitable.

2.3.2 Non – chromatographic methods

As costly instrumentation, extensive skill and lengthy analysis time are usually associated with chromatography – based speciation method, several attempts have been made to develop a simple, fast and cheap analytical method to accomplish such task.

HG – AAS can be used as a tool for arsenic speciation with its proven high sensitivity and selectivity for arsenic quantification [10]. The methodology is based on different behaviors of arsenic species under different atomization conditions. As(III) was determined by using a reductant such as sodium borohydride (NaBH$_4$) to form arsine (AsH$_3$), whereas the determination of total As was performed by pre – reduction of As(V) to As(III) with mixture of potassium iodide and ascorbic acid. The As(V) concentration was obtained from the difference between As(III) and total As [11].

Liquid – liquid extraction (LLE) is another often used separation technique, which is based on the different solubility of the analytes in the immiscible solvents. Normally, one of the solvents is water or an aqueous mixture and the other is a non - polar organic liquid. Kamada [12] demonstrated that As(III), upon complexation with ammonium pyrolidinedithiocarbamate (APDC) could be extracted from As(V) into methyl isobutyl ketone (MIBK) or nitrobenzene.

Solid phase extraction (SPE) is the technique based on interaction between two phases which are liquid phase (samples) and solid phase (adsorbent). The analytes were isolated from matrices according to their physical and chemical properties. SPE provides separation and preconcentration capability, cheap and low chemical consumption and environmental friendliness [13]. SPE used different As properties to isolate the As species such as As(V), present in oxyanion form, from As(III) by using anion exchange resin. Conventional sorbent such as ion exchange resin, mesoporous silica and glass, have been developed for inorganic arsenic speciation. The SPE method was developed for onsite speciation of inorganic arsenic [13].

2.4 Principle of SPE

The basic principle of SPE is similar to that of LLE. The separation is based on a partitioning of analytes between liquid phase (sample matrix) and solid phase (adsorbent) [14]. This technique allows the separation and preconcentration of analytes

from matrix sample by adsorption on an adsorbent. Normally, SPE consist of three to four steps as shown in Figure 2.
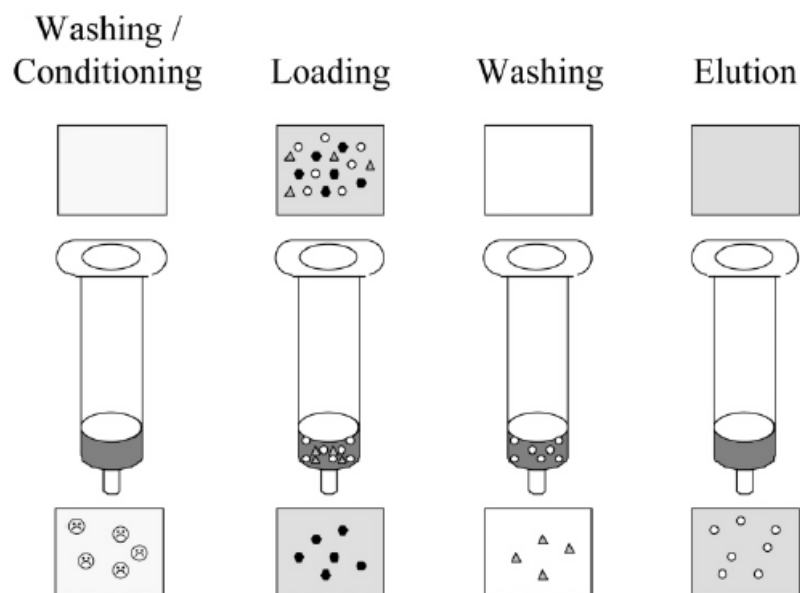
Figure 2. Schematic representation of processes involved in the SPE [14].

The first step is washing or conditioning step. In this step, the adsorbent should be washed using an appropriate solvent, followed by the same solvent as the sample. The proposed of this step is to wet the adsorbent and remove impurities contained in the sorbing material.

The next step is the loading of the sample. The sample solution was passed through the adsorbent. The loading parameters depend on the system used and the interaction between analytes and adsorbent.

The third step is washing step. The adsorbent is washed with an appropriate solvent. The solvent should not have interfered or eluted the analyte on the adsorbent at this point. This step is intended for the elimination of matrix components that have been retained by the solid sorbent.

The fourth step is the elution of the interested analyte by suitable eluent without removing adsorbed matrix components. The selection of eluent should be aware to not have any undesirable effect on the determination technique.

2.4.1 Retention of trace elements

The retention mechanism of trace elements mainly depends on the nature of those elements as well as the nature of adsorbent. Such mechanism may include adsorption, chelation, ion – paring and ion exchange.

2.4.1.1 Adsorption

Adsorption is a process in which elements or molecules are accumulated on an adsorbent. The adsorption of analytes can occur in 2 ways which are physical adsorption, such as Van der Waals forces and electrostatic forces and chemical adsorption, such as covalent bonds. This process depends on the reaction between analyte and adsorbent [15].

2.4.1.2 Chelation

Various functional group atoms are capable of chelating with trace elements. The atoms commonly used are nitrogen (N) present in amines, azo groups, amides and nitriles, oxygen (O) present in carboxylic, hydroxyl, phenolic or ether and sulfur (S) present in thiols, thiocarbamates and thioethers. The selection of the ligand towards trace elements depends on the nature of functional group. The inorganic cations may be classified into 3 groups [14]:

- Hard cations group

This group is preferred to react via electrostatic interactions. This group includes alkaline and alkaline - earth metals such as Ca(II), Mg(II) and Na(I) that form complexes with only hard ligands (O).

- Intermediate cations group

These cations have properties between hard and soft cations. This group includes Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Pb(II) and Mn(II). They tend to form a complex with both hard and soft ligands.

- Soft cations group

These cations possess a strong affinity for borderline (N) and soft (S) ligands and tend to form covalent bonds. As(III) was classified in this group.

For soft metals, the order of donor atom affinity is S > N > O. Complexing agents may be directly mixed with the sample for complexation with analytes, the chelates being retained on proper adsorbent. An alternative choice is introducing the functional group into the sorbent. Binding of metal ions to the chelate functionality is dependent on various factors such as charge and size of the analyte, character of metal ion, properties of the ligand, buffering conditions and nature of the solid support [14].

2.4.1.3 Ion – pairing

This mechanism is usually imposed by the non – polar adsorbent. Ion – pair reagent has both non – polar part and polar part, which non – polar parts interacts with the adsorbent and the polar part forms an ion - pair with the ionic species. Commonly, ion - pair reagents e.g. quaternary alkyltriethylamine, trimethylamine (TEA), and alkyl sulfonate.

2.4.1.4 Ion exchange

Ion - exchange sorbents can be divided in 2 groups which are cationic functional groups, which exchange positively charged ions or anionic functional groups which exchange negatively charged ones. Functional groups of ion – exchange are sulfonic acid for strong cation exchange and carboxylic acid group for weak cation exchange. Quaternary amines are functional groups for strong anion exchange, while primary, secondary and tertiary amines are for weak anion exchange. Strong ion exchange sites could work at any pH, while weak sites are only effective at pH values greater or less than the pK_a. Retention of analyte on ion - exchangers depends on the distribution ratio of the ion on the adsorbent, the stability constants of the complexes, the kinetics and the presence of interference ions. Ion exchanges are of limited use for speciation of trace elements due to the low selectivity and the retention of major ions.

2.4.2 Elution

The same kind of interactions usually occurs during the elution step. The eluent must be precisely picked to confirm higher affinity towards the target species. If the retention on adsorbent is due to chelation, the eluent may be contained chelating agent that could form stronger complex with analyte. Acid is commonly used as eluent due to the pH dependence of SPE allows the use of acids for elution of analyte. The acid will disrupt the complex and release the analyte from the adsorbent.

If the analyte is more highly adsorbed on the adsorbent than the interference compounds, a washing step by using a moderate elution strength eluent is advisable prior to the elution step [14].

2.5 Applications of SPE in the arsenic speciation

In recent years, many methodologies involving SPE have been developed for speciation of arsenic in samples. Various type of materials have been used as solid support in such SPE systems.

Anion exchange resin is a conventional sorbent which has been employed to separate As. It is well known that As(V) is present in oxyanion form ($H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}) that could interact with anion exchange resin while As(III) does not [7]. Based on this preferential interaction, a number of studies have been conducted to achieve the separation and preconcentration of As species.

Issa et al. [7, 16] studied the arsenic speciation by using three types of resin which include a strong base anion exchange resin (SBAE), hybrid (HY) resin iron (HY – Fe) and hybrid (HY) resin silver chloride (HY – AgCl). The selective separation of these arsenic species was presented in Figure 3.
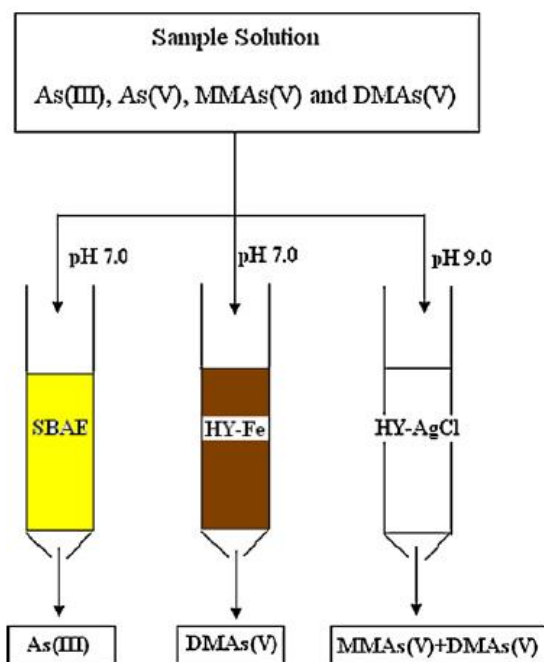
Figure 3. Schematic representation for selective separation of arsenic species in water using SBAE, HY - Fe and HY - AgCl resins [7].

It was found that the adsorption of different arsenic species depend on the pH value. The distribution of inorganic As (iAs) and organic As (oAs) species as a function of pH values are shown in Figure 4. At pH < 8.0, the neutral form of As(III) was not bonded with SBAE, thus As(III) can be separated from As(V) and oAs. Meanwhile, HY – Fe can adsorb As(III), As(V) and MMAs(V) with no affinity toward DMAs(V), allowing the direct determination of this particular species. All inorganic arsenic species are adsorbed by HY – AgCl resin, the determination of organic arsenic species was performed in the eluent. ICP – MS and HG – AAS were employed for the determination of the eluted As species.
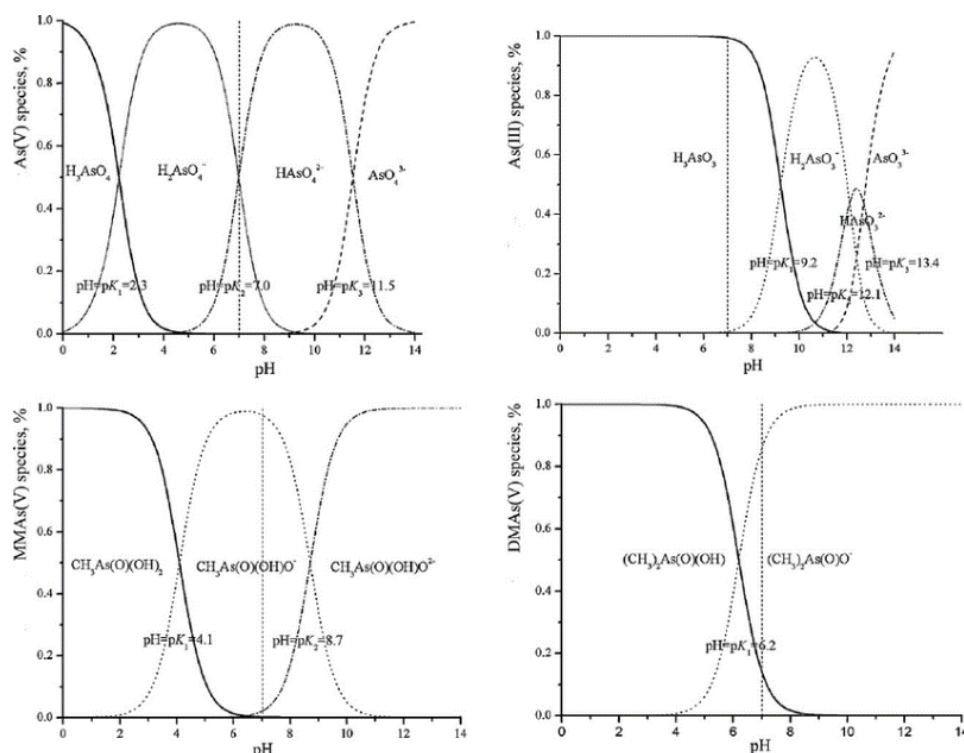
Figure 4. The distribution of iAs and oAs species
as a function of pH values [7].

Thongkhao and Imyim [17] developed a simple and selective method using two types of solid phase materials including a strong base anion exchange resin (SBAE) and iron – copper binary oxide coupled along with ICP – OES detection for the speciation of water – soluble arsenic (As(III), As(V) and DMA). Results indicated that As(V) could be adsorbed on SBAE at pH 11 while As(III) and DMA were not retained. For Fe – Cu binary oxide sorbent, the separation of DMA from As(III) and As(V) was attained at pH 11.

However, for As(III) that does not interact with anion exchange resin because it is present in neutral form (H_3AsO_3), functional materials have been employed to separate As(III) from other As species.

Jiang et al. [18] used APDC modified activated carbon (APDC – AC) as solid support for speciation of As(III). Under optimal condition, As(III) could be absorbed by APDC – AC while As(V) was not. The adsorption conditions optimized were pH, flow rate and desorption condition to obtain the maximum adsorption of As species. Results showed the maximum adsorption of As(III) on APDC – AC at pH 2 and a flow rate of 0.8 mL min^{-1}. Then 2 mL of 0.1 mol L^{-1} HNO$_3$ was employed for the elution of As(III) adsorbed in the column. The recovery As(III) was around 90%.

Chen et al. [19] prepared a carbon nanofibers (CNFs) microcolumn to separate As species. CNFs microcolumn was treated before use by passing 0.5 mol L^{-1} NH$_3$·H$_2$O and deionized water through the column, and pH was adjusted by using

buffer solution. A different As species sample solution was prepared with 1.0 mL of 5.0 mg mL^{-1} APDC and the pH value was adjusted with NH$_3$·H$_2$O and HNO$_3$. As(III) was separated from As(V) by using CNFs. The parameters involved in the separation and determination of As(III) and As(V) were evaluated. The optimal pH was 2.0 and 30 mL of 0.5 mol L^{-1} NH$_3$ was used as eluent.

Besides the previously described CNFs, other carbon sorbents were used for the separation and preconcentration of metals ions [20] as well such as graphitized carbons and fullerenes [21-25].

Many studies have shown that cellulosic materials can adsorb metal ions, especially with the introduction of functional groups therein. These studies were focused on the development of cellulosic materials as effective and cheap sorbents for the elimination of metal ions.

A modified thiol cotton fiber (TCF) was developed by Yu et al. [26-28] for the quantitative adsorption of trace heavy metals. TCF was prepared by impregnation of mercaptoacetic acid solution on fat – free cotton. The adsorption efficiency of TCF for these ions depends on the affinity of thiol group toward the ions and their complexing reactions in the solution. The method was also applied for determination of ultra-trace Au both in soluble and suspended phase in natural water, within the concentration range of 0.51 to 67.82 ng L^{-1}. The recovery of Au was 80 – 95%. Yu, Liu and Jin [29] also prepared TCF from thioglycollic acid for the determination of trace As(III), As(V), Sb(III), Sb(V), Se(IV), Se(VI), Te(IV) and Te(VI) in water. It was found that TCF efficiently adsorb only As(III), Sb(III), Se(IV) and Te(IV), making it a possible tool for speciation of these ions. Marin et al. [30] determined Se in 65 geological reference materials of different origins by GFAAS following its reduction to Se(IV) and isolation from matrix on thiol cotton fiber. They found the agreement between results from their method and published data satisfactory. The %RSD of the results varied from 2.6 – 17.7%. The detection limit was 0.02 µg g^{-1}.

There are other materials that have been modified with thiol ligand. For instance, Yang et al. [31] modified chitin nanofibers by using cysteine as an adsorbent materials for As(III) removal. Yu et al. [32] used APDC to form complex with Te(IV) under acidic condition. The Te(IV) complex was preferentialy retained on a non – polar Isolute silica – based octadecyl (C – 18) sorpbent containing solid – phase extraction cartridge. The method was applied for Te(IV) and Te(VI) speciation. The spiked recovery of Te(IV) at 86.0 – 108% and Te(VI) at 87.1 – 97.4%, were achieved.

Moghimi [33] prepared an alumina phase loaded with APDC based on chemical binding and physical adsorption approaches. Hg(II) was found to show the highest affinity towards extraction by these alumina phases. Qu et al. [34] prepared two kinds of adsorbents include chitosan-coated cotton fiber Schiff – base bond (SCCH and C – N single bond (RCCH) for adsorbtion of Au(III) ions from aqueous solution. It was demonstrated that the SCCH and RCCH fibers displayed strong affinity for gold in the solution and both exhibited 100% selectivity for the gold in the presence of Ni(II), Cd(II), Zn(II), Co(II), and Mn(II). Chai et al. [35] prepared thiol - functionalized

spent grain (TFSG) by functionalization of spent grain (SG) using thioglycollic acid in N,N - dimethylformamide (DMF) medium. TFSG demonstrated the adsorption capacity for Zn(II) was increased from 125.76 mg g^{-1} of SG to 227.37 mg g^{-1} of TFSG.

Amino groups were another type of ligand that had been used for metal speciation. Zang et al. [36, 37] prepared a sorbent by grafting amino – terminated hyperbranched polymer to cotton fibers and used it to adsorb heavy metal ions. The adsorption capacity obtained for Cu(II) and Pb(II) were up to 16.1 mg g^{-1} and 13.4 mg g^{-1} respectively.

This work was focused on developing a method for the speciation of inorganic As species in aqueous solution using 3 types of sulfur containing ligand including APDC, L – cysteine and diethyldithiocarbamic acid attached on cotton wool followed by determination by ICP – OES. The parameters affecting speciation of arsenic e.g. pH, ligand concentration and flow rate were studied. The method was validated by speciation of arsenic in sample solution and applied for arsenic speciation in real samples. Recovery and relative standard deviation were used to evaluate accuracy and precision of the method.
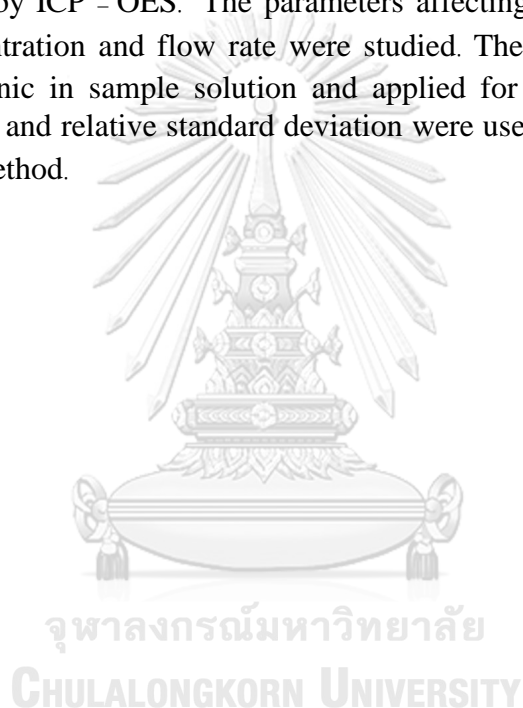
CHAPTER III

EXPERIMENTAL SECTION

3.1 Apparatus

3.1.1 Inductively coupled plasma optical emission spectrometer (ICP – OES)

ICP – OES model PQ 9000 elite (Analytik jena) was used to determine arsenic concentration. The operating conditions are listed in Table 2.

Table 2 ICP – OES conditions for the determination of As(III)

Operation parameters	
Wavelenght (As)	188.979
RF power (W)	1200
Plasma gas flow (L min^{-1})	12.0
Nebulizer gas flow (L min^{-1})	0.5
Viewing direction	Axial
Read time (s)	5.0
Sample uptake rate (mL min^{-1})	1.0
Repetition	3

3.1.2 pH Meter

A pH meter model Terminal 740 (WTW) was used for all pH measurements.

3.2 Reagents

All chemicals were ACS grade and were listed in Table 3.

Table 3 Chemical list

Chemicals	Supplier
Ammonium pyrrolidinedithiocarbamate	Sigma
L - cysteine	Sigma
Diethyldithiocarbamic acid	Sigma
Cotton wool	Ambulance
Hydrochloric acid, 37%	JT Baker
Hydrogenperoxide, 30%	Merck
Nitric acid, 65%	Merck
Single standard As(V) (1000 mg L^{-1})	Merck
Sodium arsenite	Kemaus
Sodium hydroxide	Mallinckrodt

3.3 Preparation of solutions

3.3.1 Arsenic stock solution

Stock solution of As(V) 1000 mg L^{-1} was purchased from Merck KGaA (Darmstadt, Germany).

As(III) stock solution 1000 mg L^{-1} was prepared by dissolving 0.1733 g of sodium arsenite in 3% HCl 100 ml. Then, As working standard solutions were prepared by stepwise dilution of As stock solutions to the required concentrations with de – ionized water.

3.3.2 Chelating agents

Sulfur containing ligand solutions were prepared daily by dissolving the designated amount of each ligand, including of APDC, L - cysteine and diethyldithiocarbamic acid in de – ionized water.

3.3.3 Arsenic sample solution

- As(III) sample solution

As(III) 1 mg L^{-1} solution was prepared by diluting 1000 mg L^{-1} As(III) stock solution to 1 mg L^{-1} and adjusted to the desired pH with 1 M HCl or 1 M NaOH.

- As(V) sample solution

As(V) 1 mg L^{-1} solution was prepared by diluting 1000 mg L^{-1} As(V) stock solution to 1 mg L^{-1} and adjusted to desired pH with 1 M HCl or 1 M NaOH.

- As(III) and As(V) mixture solution

As(III) and As(V) mixture 1 mg L^{-1} solution was prepared by mixing 0.05 mL of 1000 mg L^{-1} As(III) and As(V) stock solution in a 50 mL volumetric flask. The mixture was then adjusted to the desired pH with 1 M HCl or 1 M NaOH and made up with de – ionized water.

3.4 Preparation of the cotton wool

3.4.1 Cotton wool pre – treatment

The pre – treatment of cotton wool was adopted from Zang et al. [36]. Briefly, the cotton wool was scoured by steeping them in NaOH 2% wt, with a ratio of 1 : 50, at 95 °C for 90 minutes. After that the cotton wool was washed with de - ionized water several times to remove NaOH, and then dried in oven at 90 °C overnight. Finally, the treated cotton wool was packed into the medical syringe which was used as an extraction column.

3.4.2 APDC – impregnated column

An extraction column was prepared by packing 0.5 g of treated cotton wool into medical syringe. The tip of syringe was sealed with parafilm. Then 5 mL of 1% APDC solution was added into the syringe. The cotton wool was soaked for three days and the solution was removed through the tip after that.

3.5 Optimization of adsorption parameters

3.5.1 Effect of types of sulfur containing ligand on arsenic adsorption

Three types of sulfur containing ligand were investigated for arsenic speciation. Initially 1 mg L^{-1} of As(III) sample solution was adjusted to pH 2. Then 10 mL of this solution was mixed with 0.5 mL of 1% (w/v) sulfur containing ligand solutions including APDC, L - cysteine and dithiocabamic acid. The mixtures were shaken for 30 minutes at 150 rpm. The solutions were then allow to flow through 0.5 g cotton wool in syringe by means of gravity. The remaining solution on the cotton wool was displaced using the plunger and collected altogether. The As(III) concentrations in the solution were determined by ICP – OES. As(V) sample solution was processed in the same manner as As(III).

3.5.2 Comparison of solid phase extraction methods

This experiment compared two extraction methods which are Method I: mixing of APDC with arsenic solution prior to separation by cotton wool and Method II: impregnation of APDC onto cotton wool prior to arsenic adsorption. The efficiency of the two methods were compared by their percentages of arsenic adsorption.

3.5.2.1 Method I: mixing of APDC with arsenic solution prior to separation by cotton wool

This method used the extraction column from 3.4.1. The adsorption procedure was the same as described in section 3.5.1 using 1% APDC as sulfur containing ligand.

3.5.2.2 Method II: impregnation of APDC onto cotton wool prior to arsenic adsorption

The 1 mg L^{-1} As(III) sample solution was adjusted to pH 2. Then 10 mL of the solution was passed through the APDC – impregnated column obtained from section 3.4.2 by means of gravity. The retained solution was collected by using the plunger. The arsenic was determined by ICP – OES and As(V) was processed similarly to those of As(III).

3.5.3 Effect of pH on arsenic adsorption

The 10 mL of 1 mg L^{-1} As(III) model solution was adjusted to pH to 2, 3, 4, 5, and 6 with 1 M HCl and 1 M NaOH. Then each of the sample solution was mixed with 0.5 mL of 1% selected sulfur containing ligand solution. The adsorption procedure and As determination were the same as those described in 3.5.1

3.5.4 Effect of APDC concentration on arsenic adsorption

The effect of APDC concentration on arsenic adsorption was studied by adding 0.5 mL of APDC solution in the range of 0.01 – 1% w/v into the sample solution. The adsorption process was the same as those described 3.5.1.

3.5.5 Effect of the amount of cotton wool

The effect of the amount of cotton wool on arsenic adsorption was examined by using 1 mg L^{-1} As(III) sample solution and 1 mg L^{-1} As(V) sample solution. The solutions were conditioned by using the optimal pH and APDC concentration from 3.5.3 and 3.5.4. The amount of cotton wool used was varied in the range of 0.1 – 0.5 g.

3.5.6 Effect of adsorption flow rate

To evaluate the effect of flow rate on arsenic adsorption, 10 mL of 1 mg L^{-1} As(III) sample solution was adjusted to pH 2. Then 0.5 mL of 0.1% APDC was mixed with sample solution to form As(III) – APDC complex. The As(III) – APDC solution was passed through 0.5 g cotton wool column at the flow rate between 1 – 5 mL min^{-1} via peristaltic pump. After the solution came out of column, 1 mL of de – ionized water was added to the column to expel all the remaining As(III) – APDC solution out of the column and the whole solution was subjected for As determination.

3.6 Optimization of elution parameters

3.6.1 Types of eluents

As(III) – APDC solution was eluted by various eluents include 1 M HNO$_3$, 1 M HCl, 1 M NaOH, 1 M HNO$_3$ in 10% methanol, 1 M HCl in 10% methanol, 1 M HCl in 2% H$_2$O$_2$, 4 M HNO$_3$ and 0.5 M H$_2$O$_2$, 4 M HCl and 0.5 M H$_2$O$_2$ and 4 M HNO$_3$, 4 M HCl and 0.5 M H$_2$O$_2$. The efficiency of eluents was assessed by %recoveries of As(III) eluted by using 5 mL of each eluent by means of gravity. After the eluent was passed through the column, 4 mL of de – ionized water was added to the column and the retained solution in the cotton wool was displaced by the plunger and collected. The arsenic concentrations in the solution were then determined by ICP – OES.

3.6.2 Effect of elution flow rate

The effect of elution flow rate was investigated using the best eluent obtained from 3.6.1. As(III) was eluted by using 5 mL of eluent at the flow rate ranging from 1 – 5 mL min^{-1}. Then 4 mL of de – ionized water was added to column and the plunger was used to push the retained solution out of the column. The combined solution was determined for the arsenic concentration by ICP – OES.

3.7 Separation procedure

The optimized adsorption condition was used for arsenic speciation. The 10 mL of solution containing 1 mg L^{-1} As(III) and 1 mg L^{-1} As(V) at desired pH was initially mixed with 0.5 mL APDC. The mixture was shaken at 150 rpm for 30 minutes. The mixture was subsequently flown through 0.5 g cotton wool column via peristaltic pump at the flow rate of 5 mL min^{-1}. Then 1 mL of de – ionized water was added to the column. The As(V) was determined in the collected solution.

For As(III) determination, 5 mL of the selected eluent was added to the column at the flow rate of 1 mL min^{-1}. Finally, 4 mL of de – ionized water was added to column and the remaining solution in the column was collected using the plunger.

3.8 Method validation

In order to validate the developed method, the precision of the repeated measurements from this method was acquired as the relative standard deviation (%RSD). Recoveries were investigated by using the sample solution containing spiked As(III) and As(V).

3.8.1 Effect of sample concentration on arsenic speciation

The proposed method was applied for As(III) and As(V) speciation. The concentration of As(III) and As(V) mixed solution was varied in the range of 10 –

1000 µg L^{-1}. The solution was then treated in accordance with the procedure described in section 3.7. The As(III) and As(V) concentrations were determined using ICP - OES and the efficiency of the method was evaluated by arsenic recoveries and %RSD.

3.8.2 Application in real water samples

The validated method was applied to the determination of As(III) and As(V) in the real water samples. The collected samples were filtrated through 0. 45 µm membrane filter. Speciation procedure was the same as those described in section 3.7. The recoveries of spikes of the As(III) and As(V) were also studied.

CHAPTER IV

RESULTS AND DISCUSSION

In this chapter, the results are divided into 3 parts including (i) the optimization of adsorption parameters, (ii) the optimization of elution parameters and (iii) the method validation and application for arsenic speciation analysis in water samples.

4.1 Optimization of adsorption parameters

In this section, the key parameters that affect the adsorption efficiency of As(III) and As(V) on cotton wool were investigated as followed.

4.1.1 Effect of types of sulfur containing ligand on arsenic speciation

To evaluate a suitable sulfur containing ligand for arsenic speciation, APDC, L – cysteine and diethyldithiocarbamic acid were prepared at a concentration of 1% (w/v). Then 0.5 mL of each sulfur containing ligand solution was mixed with 10 mL of 1 mg L^{-1} As(III) or As(V). The solutions were passed through the untreated cotton wool column and the amount of arsenic in the solution was determined by ICP‑OES. The percentage of adsorption (%adsorption) of arsenic was calculated from the difference between the initial concentration (C_i) of arsenic and the concentration after passing through the cotton wool (C_f) as expressed by Equation 3.1.

$$\%\text{adsorption} = \frac{C_i - C_f}{C_i} \times 100 \quad \ldots\ldots\ldots\ldots\ldots(3.1)$$

The three types of sulfur containing ligand structure were shown in Figure 5.
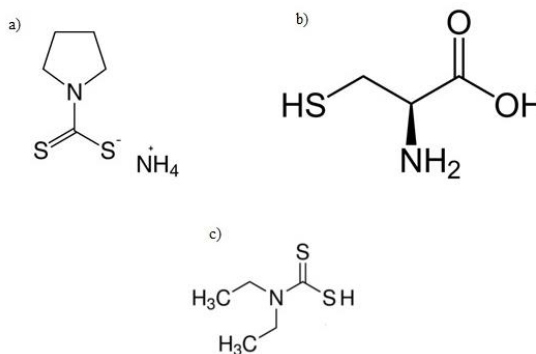
Figure 5. Structure of sulfur containing ligand. a) APDC; b) L‑cysteine;
c) diethyldithiocarbamic acid

Based on previous studies, the suitable pH range for adsorption of arsenic by using APDC as sulfur containing ligand is 1.0 – 3.0 [2, 10, 19, 28]. Thus, pH 2 was selected for evaluation of the As adsorption efficiency of each sulfur containing ligand. The results are shown in Figure 6. APDC displayed the highest adsorption efficiency of As on the cotton wool while L – cysteine and diethyldithiocarbamic acid did not produce satisfactory results. Also, it is clearly seen that, with the use of APDC, the adsorption of As(III) on the cotton wool was significantly higher than that of As(V). For the blank test using arsenic solution without ligand, the results showed that both As(III) and As(V) could not be retained on this cotton wool at pH 2.
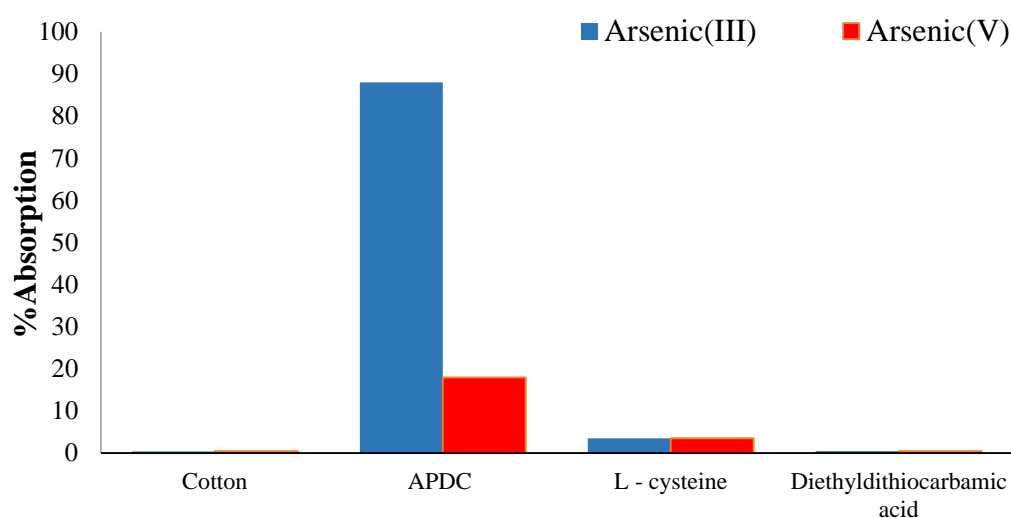
Figure 6. Adsorption percentages of As(III) and As(V) on cotton wool using different types of sulfur containing ligand.

As(III) is present as a neutral species in the form of arsenous acid (H_3AsO_3) at pH values lower than 8.0 and its successive acid dissociation constant (pK_a) are shown in Equation 3.2 - 3.4 [38].

$$H_3AsO_3 \rightleftharpoons H^+ + H_2AsO_3^- \qquad pK_{a1} = 9.23 \dots\dots\dots\dots(3.2)$$
$$H_2AsO^- \rightleftharpoons H^+ + HAsO_3^{2-} \qquad pK_{a2} = 12.10 \dots\dots\dots(3.3)$$
$$HAsO_3^{2-} \rightleftharpoons H^+ + AsO_3^{3-} \qquad pK_{a3} = 13.41 \dots\dots\dots(3.4)$$

For As(V), it exists in neutral water as monovalent or divalent ($H_2AsO_4^-$ and $HAsO_4^{2-}$). The pK_a of As(V) are shown in Equation 3.5 - 3.7 [38].

$$H_3AsO_4 \rightleftharpoons H^+ + H_2AsO_4^- \qquad pK_{a1} = 2.3 \dots\dots\dots\dots(3.5)$$
$$H_2AsO^- \rightleftharpoons H^+ + HAsO_4^{2-} \qquad pK_{a2} = 6.8 \dots\dots\dots\dots(3.6)$$
$$HAsO_4^{2-} \rightleftharpoons H^+ + AsO_4^{3-} \qquad pK_{a3} = 11.60 \dots\dots\dots(3.7)$$

As can be seen, under acidic condition as used herein, As(III) and As(V) are present in totally different species. This is the key point to optimize the speciation condition for As(III) and As(V). The neutral form of As(III) tends to form hydrophobic complex with APDC. On the other hand, As(V) could not be complexed with APDC because literally they are all negatively charged [18].

The chemical compositions of cotton wool may affect the adsorption of As(III) – APDC complex. Cotton fiber is a cellulose based materials, which is the most abundant biopolymer in nature. This material has characteristic properties such as excellent hydrophilicity, biocompatibility and biodegradability [34]. Cotton fibers are composed of mostly α – cellulose (88.0 – 96.5%). The other chemical compositions are non – cellulosic substance which include proteins (1.0 – 1.9%), waxes (0.4 – 1.2%), pectins (0.4 – 1.2%), inorganics (0.7 – 1.6%), and other substances (0.5 – 8.0%) [39]. The chemical compositions of cotton wool varied according to species, growing and maturity. Cotton wool alone is not likely to adsorb As(III) as there is no functional group on the material which could bind with As(III) or its compounds. The chemical structure of cotton is shown in Figure 7.
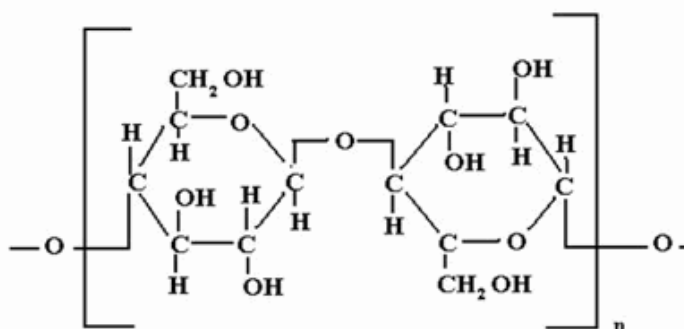
Figure 7. Chemical structure of cotton [39].

In APDC system, As(III) can be complexed with APDC and adsorbed on the cotton wool. From Kamada research [12], the optimal ratio between As(III) and APDC should be 1 : 3 which confirmed by continuous variation plots. The formations of As(III) - APDC complex is presented in Figure 8. The adsorption of the As(III) - APDC on the cotton can be attributed to the van der Waals attraction between neutral hydrophobic complex and hydrophobic moieties of the cotton i.e. protein and wax [31].
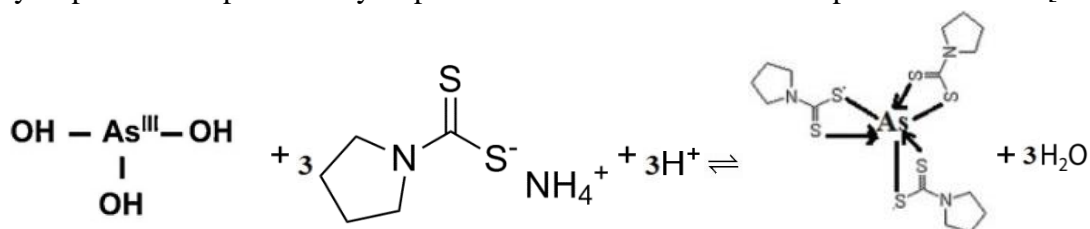
Figure 8. Schematic of As(III) – APDC complexation in acidic condition.

Incontrast, As(V) often present in oxyanion form, which has negative charge similar to APDC. So, As(V) could not interact with APDC due to this reason. The chemical forms of As(V) is presented in Figure 9.
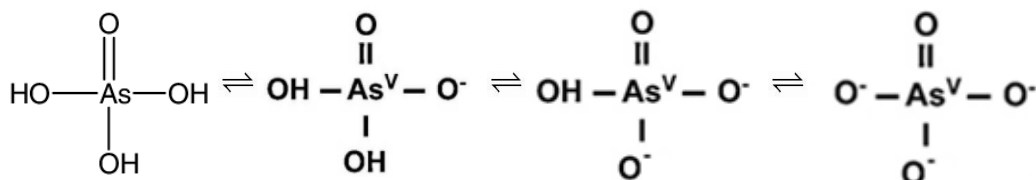
Figure 9. Chemical forms of inorganic As(V).

For L - cysteine system, the As(III) forms a 1 : 3 complex with and L – cysteine. The complex of As(III) – cysteine is shown in Figure 10.
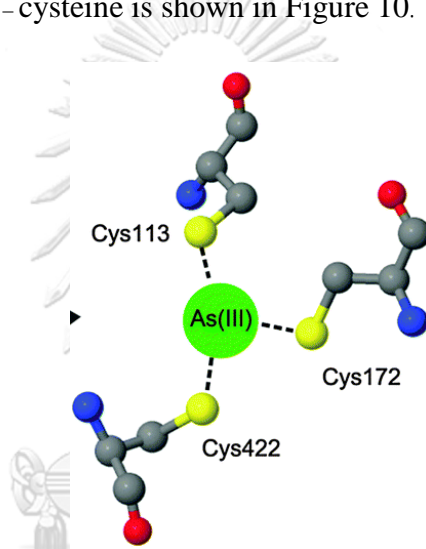
Figure 10. Schematic of As(III) – cysteine complex [40].

However, the % adsorption of As(III) and As(V) on the cotton wool by using L – cysteine as sulfur containing ligand was very low. The possible reason may be described from the reaction between As(III) and L – cysteine in Equation 3.8.

$$As(III) + 3(HS - cys) \rightleftharpoons As(S - cys)_3 + 3H^+ \ldots\ldots\ldots\ldots(3.8)$$
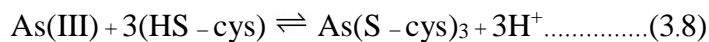
The H^+ from the reaction caused an increase of acidity of solution. In a strong acidic medium the H^+ competes with As(III) – cysteine complex for the binding with cotton wool [41]. Moreover, As(III) - cysteine complex consists of carboxyl group (-COOH) and amino group (-NH$_2$) which are hydrophilic and that increase the hydrophilicity of the molecule. Thus, As(III) – cysteine complex could be dissolved in de – ionized water and desorbed form the cotton wool column.

As for the diethyldithiocarbamic acid system, from Kamada studies [12], the reaction between As(III) and diethyldithiocarbamic acid could occur at pH 6. So, at pH 2, diethyldithiocarbamic acid could not form complex with As(III). Thus, the

adsorption efficiency is similar to those obatained when using only cotton wool. The structure of As(III) and diethyldithiocarbamic acid complex is shown in Figure 11.
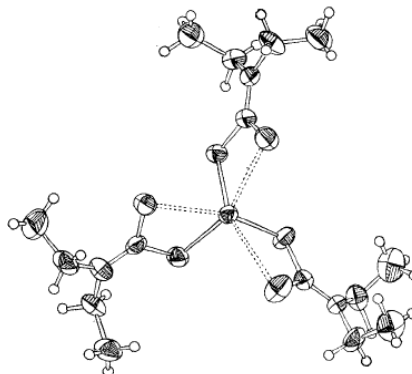
Figure 11. Structure of As(III) and diethyldithiocarbamic acid complex [42].

Based on these findings, APDC was selected as the model sulfur containing ligand for further experiments.

4.1.2 Comparison of solid phase extraction methods

As previously described, in method I, 10 mL of 1 mg L^{-1} arsenic solution at pH 2 was mixed with 0.5 mL 1% APDC solution. The mixture was shaken and then passed through the cotton column. For method II, APDC was impregnated by soaking cotton wool in 1% APDC solution to prepare an adsorption column. Then 10 mL of 1 mg L^{-1} arsenic solution at pH 2 was passed through the column. The results are shown in Figure 12. The adsorption efficiency of arsenic obtained from Method I was roughly 98% while Method II produce merely 55% adsorption efficiency. Typical contents of cotton wool, apart from cellulose, include protein, wax, and others, all of which might have contributed to the lower adsorption efficiency toward the analyte. Thus, the pre-treatment method (alkaline treatment) was employed for the elimination of those mentioned compositions. The alkaline treatment allows the removal of hydrophobic contents such as lignin, hemicellulose, wax, protein and oils from cotton wool surface [43, 44]. However, the adsorption efficiency of this pretreated material further decreased. It may be explained that the alkaline treatment could improve the hydrophilicity of the cotton wool [45] making it unfavorable for the adsorption of relatively hydrophobic As – APDC complex [18]. For Method II, arsenic could only interact with APDC on the cotton wool when the solution was passed through the column, thus the complexation of As(III) – APDC might be incomplete as a result of the short contact time. In addition, the attachment of APDC on cotton wool may have a negative impact to the As(III) adsorption as well because, in order to form such complex, APDC molecules should have proper orientation to bind with arsenic which is not the case here.
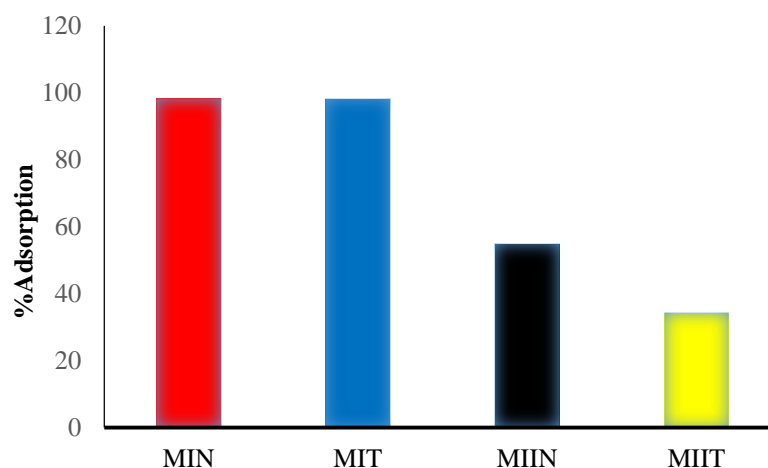
Figure 12. Adsorption efficiency between Method I and Method II.
MIN, non – treated cotton Method I; MIT, treated cotton Method I; MIIN, non – treated cotton Method II; MIIT, treated cotton Method II.

4.1.3 Effect of pH on arsenic adsorption

As suggested by a previous study [18], the pH value plays an important role with respect to the speciation of arsenic species using APDC. Hence, the effect of pH was examined in the pH range of 2 – 6. Figure 13 shows the pH dependence of adsorption efficiency of As(III) - APDC complex on the cotton wool. The results have indicated that As(III) - APDC complex was effectively adsorbed at pH 2 with decreaseing trend towards higher pHs, while only 20 - 30% of As(V) was adsorbed on the cotton wool throughout the whole pH range studied. This insignificant adsorption was probably due to the reduction of As(V) to As(III) by sulfur contents of APDC. The following reactions occur when a sulfhydryl group (RSH) reduces As(V) to As(III) [46]:

$$\text{As(V)} + \text{RSH} \rightarrow \text{RS} - \text{As(V)} + \text{H}_2\text{O}.................(3.9)$$

$$\text{RS} - \text{As(V)} + \text{RSH} \rightarrow \text{R(SS)}_{\text{OX}} + \text{As(III)}............(3.10)$$

As(III) exist as AsO_3^{3-} in solution, which means that its adsorption by cotton wool should be carried out at a certain acidity. As mentioned in the literature [27], AsO_3^{3-} could be adsorbed on thiol-cellulose (cell-SH) in acidic condition as expressed by the following equation.

$$3[\text{cell} - \text{SH}] + \text{AsO}_3^{3-} + 3\text{H}^+ \rightarrow [\text{cell} - \text{SH}]_3\text{As} + 3\text{H}_2\text{O}......(3.11)$$
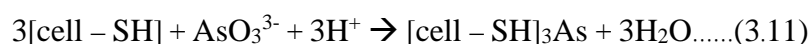
At pH 2, around 95% of As(III) – APDC complex could be adsorbed on cotton wool. This finding can probably be ascribed by the formation of hydrophobic complex between As(III) and APDC [18], and the hard/soft acid/base principle. As(III) is a soft acid due to its lower oxidation state as compared to As(V). Thus As(III) has affinity toward a soft base (APDC). In contrast, As(V) is a borderline acid and often prefer to bind with oxygens as arsenate compound [47]. The As(III) - APDC complex is unstable at high pH, thus the percentage of adsorption is unfavorable toward higher pH as experimentally demonstrated in Figure 13 [41]. The adsorption of As(III) – APDC complex can be ascribed by physisorption via van der Waals attraction for the neutral species [31]. Based on these results, pH 2 is selected for further experiments.

Figure 13. Effect of pH on the adsorption of As(III) and As(V) on the cotton wool. Condition: 1% w/v APDC.

4.1.4 Effect of APDC concentration on arsenic adsorption

As a portion of As(V) was presumably reduced and get adsorbed as As – APDC complex on the cotton wool which would lead to unsuccessful speciation, the concentration of APDC was therefore investigated in an effort to minimize this problem. The APDC concentration was varied in in the range of 0.01 – 1% w/v. The results are shown in Figure 14.
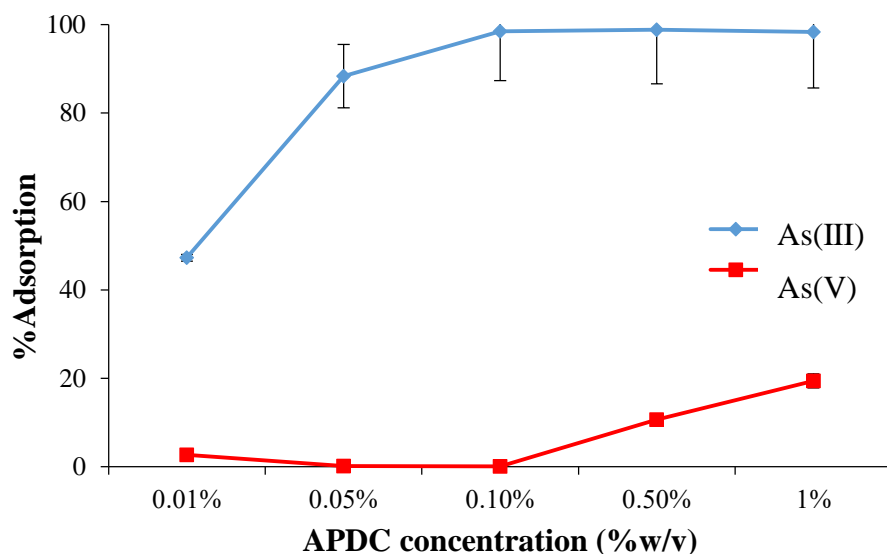
Figure 14. Effect of APDC concentration on arsenic adsorption.

It is apparent that the adsorption percentage of As(III) continually increase as the concentration of APDC increase and becomes somewhat steady from 0.1% upward wih approximately 98% of adsorption efficiency. On the other hand, As(V) was virtually not retained when the APDC concentration was below 0.1% but slightly increased to 20% as the APDC concentration was raised up to 1%. Such increase was belived to be due to the reduction of As(V) to As(III) when APDC was in excess and the subsequent APDC – complex formation. Therefore, 0.1% APDC was chosen as he optimal concentration for further experiments since this represented the condition where maximum As(III) adsorption could be obtained while the interference from the reduction of As(V) was minimized.

After that, the adsorption of As(III) and As(V) was evaluated again using 0.1% APDC with pH variation ranging from 1 to 6 to confirm whether the adsorption on the cotton wool was similar to those obtained when using 1%. The results were shown in Figure 15. The adsorption percentage of As(III) was still in the same range as using 1% APDC while As(V) could not be adsorbed on the cotton wool which indicated that the reduction from sulfur containing ligand might not occur. This result confirms that 0.1% APDC concentration is suitable for this method to allow the adsorbtion of As(III) on the cotton wool while As(V) is not retained. Thus, 0.1% APDC concentration was selected for complexation with As(III) in the subsequent experiments.
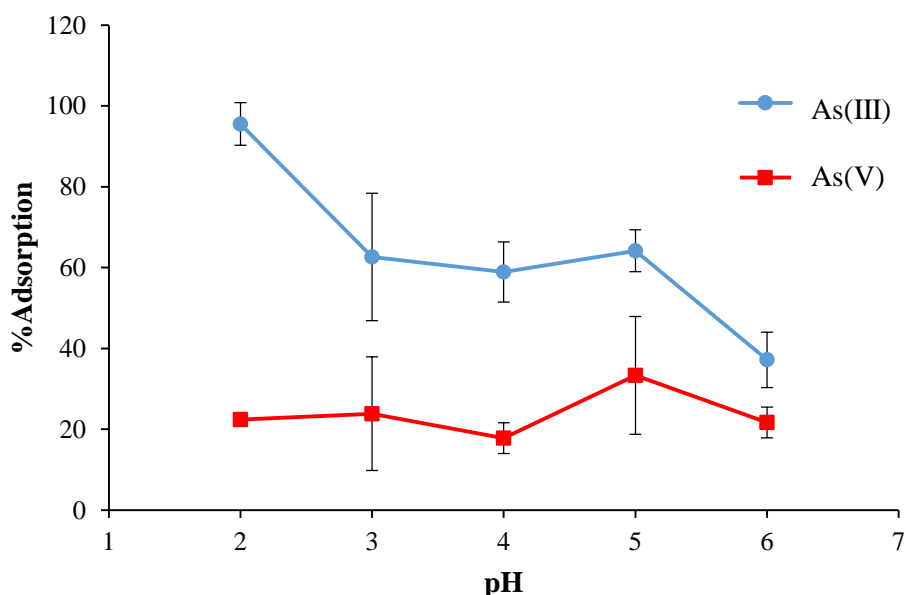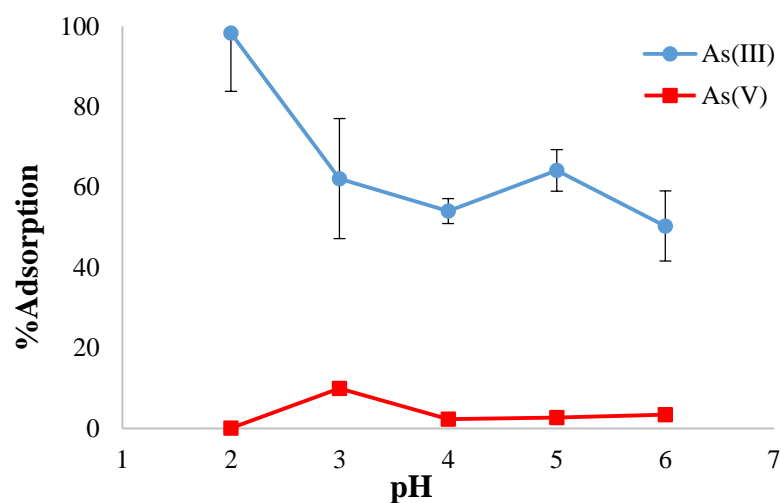
Figure 15. Effect of pH on the adsorption of As(III) and As(V) on the cotton wool.
Condition: 0.1% w/v APDC.

4.1.5 Effect of the amount of cotton wool

To evaluate the effect of the amount of cotton wool, the mass of cotton wool ranging from 0.1 - 0.5 g were evaluated. The result is shown in Figure 16. The adsorption percentages of As(III) are nearly constant throughout the conditions used. Even a little amount of cotton wool (0.1 g) could adsorb most As(III) in the solution. This efficient adsorption may be accredited to the high surface area of cotton which in turn increase the rate of adsorption [37]. Meanwhile, the As(V) still could not be retained on the cotton column regardless of its mass. However, 0.5 g of cotton was used for the preparation of extraction column in order to facilitate the packing into the syringe.
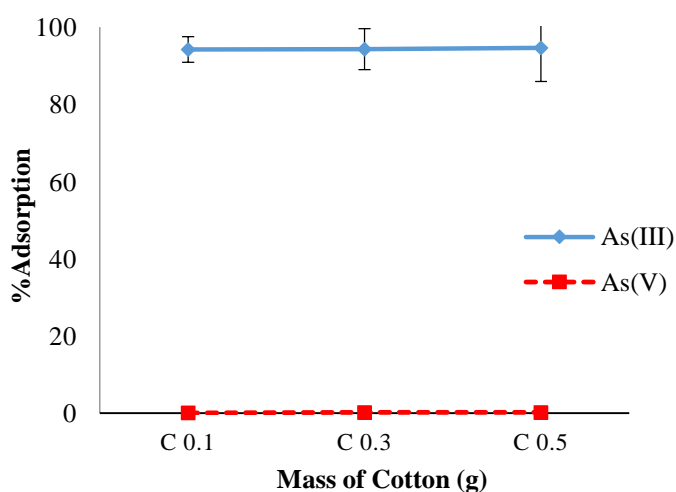
Figure 16. Effect of the amount of cotton wool on arsenic adsorption.

4.1.6 Effect of adsorption flow rate

The flow rate of sample solution is a very important parameter for quantitative retention of As(III) on the adsorbent and the length of complete analysis [19]. According to the previous experiments, the sample solution was passed through the column by means of gravity. For this experiment, the peristaltic pump was used and the flow was adjusted in the range of 1 – 5 mL min^{-1}. The result was shown in Table 4.

Table 4 The effect of flow rate on As(III) adsorption

Flow rate (mL min^{-1})	% adsorption	% RSD
1	99.1	6.10
3	98.3	12.5
5	99.5	6.64

n = 3

At flow rates of 1 - 5 mL min^{-1}, the adsorption percentages of As(III) on cotton wool were very similar. It was probably due to the high surface area of the cotton wool [37] that the adsorption of As(III) – APDC complex could be achieved relatively quickly. So, to complete the analysis in a shorter time, the flow rate of 5 mL min^{-1} was selected as the optimal adsorption flow rate.

4.2 Optimization of elution parameters

To effectively determine As(III) that was retained on the cotton wool, types of eluent and elution flow rate were evaluated to obtain the optimal eluting conditions for the determination by ICP - OES.

4.2.1 Types of eluent

In order to determine As(III) concentration, the analyte was eluted from the cotton column. The selection of eluent is based on the affinity between eluent and analyte. Normally, the analyte can be eluted by using a suitable acid, akali or complexing agent [27]. The effect of eluents on the elution of As(III) was studied by using various eluents. The recovery was used to evaluate the elution efficiency of eluents and calculated from the amount of As(III) in the initial solution (N_i) and the amount of As(III) eluted from the cotton wool (N_f) as Equation 3.2. The results are given in Table 5.

$$\%\text{Recovery} = \frac{N_f}{N_i} \times 100 \quad \ldots\ldots\ldots\ldots(3.11)$$

The first series of elution was mineral acids (1 M HNO_3 and 1 M HCl), which rely on the oxidization of As(III) to As(V) and the competition between As(III) – APDC complex and H^+ to bind with cotton wool in acidic medium [41]. It was found that the recovery of As(III) was very low for both eluents. These results may be caused by the oxidation of As(III) to As(V) that is a kinetically slow process [48].

The next eluent was 1 M NaOH, which was used to make the condition basic that could in turn create an unstable or unfavorable environment for As(III) – APDC complex (see Figure 13. Effect of pH on the adsorption of As(III) and As(V) on cotton wool). Nonetheless, the results showed an unacceptable recovery under this condition, one possible reason for this is that the contact time between NaOH and As(III) – APDC complex may be not enough for disrupting the As(III) and APDC bonding. In previous work by Doker [4] the desorption of As(III) – APDC complex by basic solution was achieved when a very low flow rate (0.2 mL min^{-1}) was employed resulting in longer operating time.

A combination of organic and inorganic reagents could be used for the elution of retained metal complex from the adsorbent [49]. In this research, methanol as organic reagent was employed to increase the elution efficiency of inorganic reagents. 1 M HNO_3 or 1 M HCl solutions were prepared in 10% methanol in de – ionized water. Then the mixture solutions were used for As(III) elution from the column. The recovery rose to 32.8 – 44.3% but it was still not quite satisfied. Moreover, methanol is not advisable for ICP-OES as the introduction of organic solvents can typically lead to a number of undesirable consequences, e.g. plasma instability, molecular spectral interferences, and carbon encrustation [50].

An oxidizing reagent, H_2O_2 was used next for improving the conversion of chemical form of As(III) during the elution step. 1 M HCl in 2% H_2O_2 produced a recovery of 44.3%. When the concentration of acids were increased to 4 M, the recovery was improved significantly to 80.6 – 85.1%. Finally, the mixture of 4 M HNO_3, 4 M HCl and 0.5 M H_2O_2 at a ratio of 1 : 1 : 1 was used and gave acceptable recovery at 95.5% with 1.95 %RSD. Thus 4 M HNO_3, 4 M HCl and 0.5 M H_2O_2 (1 : 1 : 1) was selected for the desorption of As(III) in further experiments.

Table 5 List of eluents that used for As(III) elution

Eluents	%Recovery	%RSD
1 M HNO_3	5.82	15.1
1 M HCl	7.53	42.8
1 M NaOH	8.82	1.22
1 M HNO_3 in 10% methanol	59.7	32.9
1 M HCl in 10% methanol	32.8	11.2
1 M HCl in 2% H_2O_2	44.3	23.5
4 M HNO_3 and 0.5 M H_2O_2	85.1	2.42
4 M HCl and 0.5 M H_2O_2	80.6	14.9
4 M HNO_3, 4 M HCl and 0.5 M H_2O_2	93.7	1.96

n = 3

To gain an insight into the elution of As – APDC complex, the mechanism of this elution process was investigated. The solution containing 50 µg L^{-1} As(III) and 50 µg L^{-1} As(V), was passed through the column and the eluate was analyzed to quantify sulfur content, a key indicative element of APDC, in the solution by using ICP – OES. The results were shown in Table 6.

Table 6 Emission of signal from sulfur content

Sample	Signal (counts/second)	%RSD
As 50 µg L^{-1} + APDC	283,688	4.05
Solution from adsorption process	25,639	16.8
Solution from elution process	14,064	9.65

Sulfur wavelength = 182.565 nm

The result indicated that the sample solution mixed with APDC gave a very high content of sulfur. After the adsorption, only small amount of sulfur was detected which meant that almost As(III) - APDC was adsorbed on the cotton column. In the elution step, a similar result was observed in that only insignificant sulfur signal was detected. This could imply that the elution mechanism might only be related to the oxidation of As(III) to As(V) by such oxidizing eluent (4 M HNO_3, 4 M HCl and 0.5 M H_2O_2) because the main parts of APDC still retained on the cotton column.

4.2.2 Effect of elution flow rate

The effect of elution flow rate was examined in the range of $1 - 5$ mL min^{-1} utilizing 5 mL of 4 M HNO$_3$, 4 M HCl and 0.5 M H$_2$O$_2$ (1 : 1 : 1) as eluent. The results were shown in Table 7 that the recovery percentage of the flow rate at 1 mL min^{-1} was 96.2% and this decreased when the flow rate was increased to 3 and 5 mL min^{-1}, respectively, probably due to the shorter contact time between the eluent solution and sample. Therefore, the elution flow rate of 1 mL min^{-1} was selected in this work.

Table 7 The dependence of As(III) recoveries on eluent flow rates

Flow rate (mL min^{-1})	%recovery	%RSD
1	96.2	3.33
3	79.2	3.02
5	83.0	3.34

n = 3

4.3 Method validation

The accuracy (%recovery) and precision (%RSD) of the method were examined in the following experiments for demonstration of the validity of the proposed method.

4.3.1 Effect of sample concentration

A series of mixed As(III) + As(V) solutions were prepared in the concentration range from $10 - 1000$ µg L^{-1} and then the speciation procedures were carried out as previously described. The accuracy and precision were determined. The accuracy was calculated from the recovery percentage of As(III) and As(V) and it should be in the range of $80 - 120\%$. Precision of the method was evaluated by using %RSD. The acceptable %RSD value should not be over 10%. The results were shown in Table 8.

Table 8 %recovery of As(III) and As(V) of mixed solution

Sample	As(III)				As(V)			
	As(III), µg L^{-1}		Recovery,	RSD,	As(V), µg L^{-1}		Recovery,	RSD,
	added	found	%	%	added	found	%	%
As10	10.0	9.68	96.8	6.84	10.0	11.0	110	2.94
As50	50.0	44.9	89.7	3.98	50.0	55.6	111	0.99
As100	100	84.0	84.0	1.54	100	112	112	1.16
As400	400	336	83.9	7.12	400	437	109	7.79
As800	800	667	83.3	6.67	800	813	102	0.49
As1000	1000	947	94.7	3.54	1000	1008	101	0.45

n = 3

As(III) and As(V) concentration are equal in each samples solution.

The numbers behind As in the sample column are refered to As concentrations.

       The results indicated that the present method was able to accurately determine both As(III) and As(V) in the mixed solution with acceptable %recovery and %RSD under a wide range of concentrations. The proposed method could separate As(III) and As(V) at 10 µg L^{-1} which met the USEPA standard for maximum concentration of arsenic in drinking water.

       Since the proposed method could be used for arsenic speciation at very low concentration (10 µg L^{-1}), the preconcentration step is unnecessary The method shows the good potential for preconcentration step, if the concentration is lower than the limit of detection.

4.3.3 Application to arsenic speciation in real water samples

       The developed method was next applied for the speciation of inorganic arsenic in real water samples. Water samples were collected from various sources as described in Table 9.

Table 9 Sample name and sources

Sample	Types	Source
Tap1	Tap water	Environmental research institute, Chulalongkorn University's laboratory
SW1	Surface water	Bueng Thap Raet, Krabu,
T1	Ground water	Kamphaeng Phet
C1		
TP5411	Water that used for push up crude oil from well	A petrochemical company in Thailand

       The accuracy of this method was assessed by spiking a required concentration of As(III) and As(V) into water samples and the results are given in Tables 11.

       The recoveries of As(III) and As(V) were in the range of 85 – 115%. This indicated a good performance and accuracy of As speciation in water samples and %RSDs were within the range of 0.33 – 6.66%, showing a good precision of the method.

       The results of water samples may be different from those obtain with the arsenic solutions. In natural waters, organic and inorganic compounds may form stable complex with arsenic. The behaviors of metals may diverge from the artificial solutions due to the presence of strong complexes that are tough to degrade, or is adsorbed on colloids. Hence, the speciation efficiency may vary remarkably [51]. On sample T5411, totoal As from the determination by ICP – OES is 184 μg L^{-1}, but the summation of As(III) and As(V) is about 145 μg L^{-1}. This can be assumed in the sample may contain other As species e.g. organic arsenic which were adsorbed by cotton wool and could not be eluted by selected eluent. It is conclusive that the other As species in sample can not disturb the As speciation by using the present method.

       However, the results are closely associated with the literature reported by Tian et al [41]. It has been reported that only As(III) can form complex with APDC while the other species can not. This can be translated into a potentially speciation of As(III) by adsorption onto a suitable solid support or transferring into liquid medium.

Table 10 Determination of As(III) and As(V) in water samples

Sample	Total As µg L⁻¹	As(III)				As(V)			
		Added, µg L⁻¹	Found, µg L⁻¹	Recovery, %	RSD, %	Added, µg L⁻¹	Found, µg L⁻¹	Recovery, %	RSD, %
Tap1	nd	0	nd	-	-	0	nd	-	-
		1000	976	97.6	1.97	1000	1010	101	0.40
SW1	nd	0	nd	-		0	nd	-	-
		100	97.3	97.3	2.56	100	103	103	0.82
T1	33.10	0	3.89	-	32.3	0	30.6	-	1.68
		10	12.2	85.6	3.37	10	40.5	99.5	2.30
		50	49.1	91.1	6.11	50	86.6	112	2.42
		1000	956	95.2	4.44	1000	1041	104	1.44
C1	nd	0	nd	-		0	nd	-	-
		1000	962	96.2	2.67	1000	1010	101	0.89
TP5411	184*	0**	136	-	-	0	8.64	-	0.33
		50**	194	118	-	50	65.4	113	6.66
		100	250	114	4.65	100	105	96.3	0.65

n = 3, nd = not detectable

*Dilution factor = 1000, ** n = 2

CHAPTER V

CONCLUSION

This work was focused on developing a method for the speciation of arsenic in environmental samples by using cotton wool as solid phase extraction and a sulfur containing ligand as chelating agent followed by the determination by ICP – OES.

First, the adsorption conditions for As(III) were optimized. As(III) and As(V) solution were mixed with sulfur containing ligand solutions including ammonium pyrrolidinedithiocabarmate (APDC), L – cysteine and diethyl dithiocarbamic acid to form complex before passing into cotton wool. APDC was found to be the most effective complexing agent that could form As(III) – APDC complex at pH 2 which in turn get adsorbed onto the cotton wool. Alternatively, the APDC was impregnated onto the cotton wool to make a separation column. The adsorption efficiency of the two separation methods were compared. It was found that the adsorption efficiency obtained from mixing of As(III) amd APDC is significantly greater than those of the APDC – impregnated column. The optimal adsorption conditions were pH 2, 0.1% APDC concentration, 0.5 g of cotton and flow rate of 5 mL min^{-1}. As(III) – APDC complex was adsorbed onto the cotton wool while As(V) literally had no affinity toward APDC and thus not retained on the cotton wool. The adsorption efficiency of As(III) obtained from the proposed method was greater than 98%.

The As(III) – APDC complex previously adsorbed on the cotton wool was then eluted by using various eluents based on oxidizing of As(III) to As(V) and released from the cotton wool column. The recovery of 96.2% was obtained from a mixture of 4 M HNO$_3$, 4 M HCl and 0.5 M H$_2$O$_2$ with a ratio of 1 : 1 : 1 at a flow rate of 1 mL min^{-1}.

Next, the optimized conditions were used for arsenic speciation in a set of mixed synthetic solutions. As(III) and As(V) concentrations were varied from 10 – 1000 µg L^{-1}, and the solutions were processed through the proposed method. For As(III), the recovery was 83.3 - 96.8% and %RSD was 0.63 – 7.12%. For As(V), the recovery was 101 – 112% and %RSD was 0.45 – 7.79%.

The developed method was subsequently applied to perform the speciation analysis of arsenic in water samples from various sources including natural waters and wastewater. The method accuracy and precision were evaluated by using %recovery of arsenic in samples and %RSD. It was demonstrated that the present method exhibit decent %recovery and %RSD within acceptable range for both As(III) and As(V) in various water samples.

Potential applications

The present method showed the potential for speciation of arsenic in drinking water with the required maximum contamination level not over 10 μg L^{-1} as well as the capability of performing the preconcentration of the samples.

Suggestion for future work

The present method can be applied to the speciation and determination of As(III) and As(V) in other kinds of environmental samples such as soil, plants and sludge. The effect of potential interference, e.g. organo arsenic in sample also should be investigated.

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