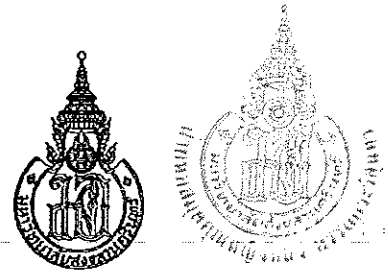

Determination of Inorganic Arsenic Species using Hydride Generation-Inductively Coupled Plasma-Optical Emission Spectrometry (HG-ICP-OES)

Duangrudee Muakthong

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science in Analytical Chemistry

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Major Program	Analytical Chemistry

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ชื่อวิทยานิพนธ์	การวิเคราะห์สารหนูอนินทรีย์โดยใช้เทคนิคไฮไดรด์เจนเนอเรชันควบคู่กับเทคนิคอินดักทีฟลีคอปเปิลพลาสมาออปติคอลอิมิสชันสเปกโตรเมทรี
ผู้เขียน	นางสาวดวงฤดี หมวกทอง
สาขาวิชา	เคมีวิเคราะห์
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บทคัดย่อ

เทคนิคไฮไดรด์เจนเนอเรชันควบคู่กับเทคนิคอินดักทีฟลีคอปเปิลพลาสมาออปติคอลอิมิสชันสเปคโตรเมทรีได้รับการพัฒนาเพื่อให้เหมาะสมกับการประยุกต์ในการวิเคราะห์เชิงปริมาณของสารหนูอนินทรีย์สามชนิด คือ Total As, As(III) และAs(V) ในตัวอย่างน้ำดื่มบรรจุขวด สภาวะที่เหมาะสมของเทคนิคอินดักทีฟลีคอปเปิลพลาสมาออปติคอลอีมีสชันสเปคโทรเมทรีที่ใช้ คือ ความยาวคลื่น 193.7 นาโนเมตร เวลาในการอินติเกรตพีก 5-10 วินาที ความถี่คลื่นวิทยุ 1.3 กิโลวัตต์ อัตราการไหลของแก๊สอาร์กอนที่ใช้เป็นพลาสมา 15 ลิตรต่อนาที และอัตราการไหลของแก๊สอาร์กอนที่ใช้เป็นอ๊อกซิลารี 0.2 ลิตรต่อนาที สำหรับสภาวะที่เหมาะสมของเทคนิคไฮไดรด์เจนเนอเรชันคือ อัตราการไหลของสารตัวอย่าง 1.2 มิลลิลิตรต่อนาที อัตราการไหลของตัวรีดิวซ์และกรดที่ใช้ 0.4 มิลลิลิตรต่อนาที และอัตราการไหลของแก๊สอาร์กอนที่ใช้เป็นตัวพา 0.3 มิลลิลิตรต่อนาที จากสภาวะที่เหมาะสมของระบบที่พัฒนาได้พบว่า สภาวะที่เหมาะสมในการวิเคราะห์ Total As คือ โซเดียมโบโรไฮไดรด์เป็นตัวรีดิวซ์ 0.4% (w/v) ในกรดไฮโดรคลอริก 2 โมลาร์ และโปแตสเซียมไอโอไดด์ 40% (w/v) เป็นเวลา 10 นาที สำหรับ As(III) สภาวะที่เหมาะสมคือ โซเดียมโบโรไฮไดร์ดเป็นตัวรีดิวซ์ 0.4% (w/v) ในกรดไฮโดรคลอริก 2 โมลาร์ โดย As(V) คำนวณจากผลต่างของ Total As และ As(III) จากสภาวะที่เหมาะสมดังกล่าวข้างต้น พบว่า ช่วงความเป็นเส้นตรงของสารหนูทั้งสามชนิดคือ 1-100 ไมโครกรัม ต่อลิตร ด้วยค่าสัมประสิทธิ์เชิงเส้น 0.9998 ขีดจำกัดต่ำสุดของการตรวจวัด(LOD) ของ Total As, As (III) และ As(V) เท่ากับ 0.38, 0.07 และ 0.37 ไมโครกรัมต่อลิตร ได้ศึกษาขีดจำกัดต่ำสุดในการวิเคราะห์เชิงปริมาณ(LOQ) ของ Total As, As (III) และ As(V) เท่ากับ 1.28, 0.24 และ 1.17 ไมโครกรัมต่อลิตร ให้ค่าการกลับคืนในช่วง 94.9-99.1% เมื่อนำเทคนิคนี้มาประยุกต์ใช้ในการวิเคราะห์หาปริมาณความเข้มข้นของสารหนูทั้งสามชนิดในตัวอย่างน้ำดื่มบรรจุขวด พบว่า ไม่มีการปนเปื้อนของสารหนู เมื่อศึกษาเปอร์เซ็นต์การได้กลับคืนของสารหนูทั้งสามชนิดในตัวอย่างน้ำดื่มบรรจุขวดพบว่า อยู่ในช่วง 79.3-111.6% นอกจากนี้เทคนิคดังกล่าวมีข้อดี คือ ใช้งานได้ง่ายและรวดเร็วในการวิเคราะห์ตัวอย่าง

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Abstract

The development of a hydride generation (HG)-inductively coupled plasma optical emission spectrometry (ICP-OES) technique was utilized for determination of inorganic As, including total As, As(III) and As(V) in drinking water sample. The ICP-OES and HG systems were optimized. The optimum conditions of ICP-OES were obtained at wavelength of 193.7 nm, integration time of 5-10 second, RF power of 1.3 kW, and the flow rates of plasma gas and auxiliary gas were 15 and 0.2 L min^{-1}, respectively. The optimum conditions of HG system were obtained at the sample flow rates of 1.2 mL min^{-1}, reductant and acid 0.4 mL min^{-1} and carrier gas 0.3 L min^{-1}, respectively. The conditions for total As and As(III) determination were optimized. The results showed that the conditions for total As were 0.4% (w/v) $NaBH_4$ in 2 mol L^{-1} HCl with 40% (w/v) KI within 10 min and for As(III) conditions were 0.4% (w/v) $NaBH_4$ as a reductant in 2 mol L^{-1} HCl. As(V) was calculated by the differential of total As and As(III). The results show that the linear dynamic range was 1-100 μg L^{-1} with a correlation coefficient of 0.9998. The limit of detection (LOD) of total As, As(III) and As(V) were 0.38, 0.07 and 0.37 μg L^{-1}, and the limit of quantitation (LOQ) of total As, As(III) and As(V) were 1.28, 0.24 and 1.17 μg L^{-1}, respectively with the 94.9-99.1% recovery of each As species. The developed method was applied to determine inorganic As species in drinking water samples. As was not detected. It was found that the percent recovery of samples water in the range 79.3-111.6. The advantages of this developed method were speed and ease of performance.

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Duangrudee Muakthong

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Chapter 1

Introduction

1.1 Introduction

Inorganic arsenic is known as one of the most hazardous elements widely distributed in the earth's crust. It has received increased attention in recent years because of its high toxicity, especially its carcinogenic properties (IARC, 1987 cited in Nriagu, 1994). Arsenic contamination of drinking water has been found to be the most frequent cause. Arsenic poisoning has occurred in Thailand (Arrykul, 1996 and William *et al.*, 1996) through consumption of contaminated well water.

Determination and speciation of arsenic contamination in environmental systems is necessary, mainly because the toxicity and bioavailability of this element is species dependent. In the environment, arsenic is found in combination with other elements. One form of arsenic combined with carbon and hydrogen is referred to as organic arsenic. Another form combined with oxygen, chlorine and sulfur is called inorganic arsenic (ATSDR, 2000).

Inorganic arsenic is considered to be the most toxic form and is found in groundwater, surface water, and foods (Yamauchi, 1994 cited in Nriagu, 1994). The toxicity and mobility of arsenic is dependent on the chemical forms in which it exists, the most toxic species being arsenite As(III) and arsenate (As(V) that represent the main forms in the environment (ATSDR, 2000). Several studies have shown that inorganic arsenic can increase the risk of lung cancer, skin cancer, bladder cancer, liver cancer, kidney cancer and prostate cancer. The World Health Organization (WHO), the Department of Health and Human Services (DHHS) and the Environmental Protection Agency (EPA) have determined that inorganic arsenic is a human carcinogen (IARC, 1987 cited in Nriagu, 1994). The American Conference of Governmental Industrial Hygienists (ACGIH) classifies inorganic arsenic forms as a confirmed human carcinogen; cancer category A1. The high

potential risk makes arsenic certainly one of the most intensively studied elements in speciation analysis (WHO, 2001; ATSDR, 2000). Thus the usefulness of speciation studies can be recognized. It is necessary to develop highly sensitive methods for determination of inorganic arsenic species in different matrixes. The most popular technique for the determination of inorganic arsenic species is hydride generation (HG).

In environmental samples, this hydride generation technique has been used combined with inductively coupled plasma optical emission spectrometry (ICP-OES), since 1978 (Thompson et al., 1978a). More recently USEPA has been developing this technique and has combined it with a continuous flow system (USEPA, 1990).

In a continuous flow system, the acidified sample, blank or standard is continuously flow and mixed with a stream of reductant, usually sodium borohydride, to produce the gaseous hydride of arsenic or arsine gas. Hydrogen gas is produces as a by-product. A flow of argon is added to this mixture and the hydride is "stripped" into the gas phase. A gas/liquid separator allows the gaseous, hydride-containing phase to enter the ICP for analysis, and allows the remaining liquids to be pumped to waste. Limits of detection can generally be improved by about two orders of magnitude over simple solution nebulization using hydride generation. The hydride generator is constructed of a simple and inexpensive continuous flow hydride generator for ICP-OES analysis (Davidowski, 1993).

Hydride generation combined with inductively coupled plasma optical emission spectrometry (HG-ICP-OES) has been conducted in this study with the aim to develop a method for determination of inorganic As species such as total As, As(III) and As(V). The experimental conditions of HG-ICP-OES system were optimized. Finally, this developed method was applied to the quantitative analysis of total As, As(III) and As(V) concentration in drinking water samples.

1.2 Literature review

1.2.1 Chemistry of arsenic (As)

Arsenic (As) is the third member in Group VA of the periodic table, and its atomic number and atomic mass are 33 and 74.9216 respectively. It has four oxidation state in nature: -3, 0, +3 and +5. The oxidation number +3 and +5 of arsenic species is commonly present in a variety of complex minerals and in dissolved salts in natural waters. Arsenic compounds in nature can be released to the environment by redox reduction processes (ATSDR, 2000).

Table 1 Common name, chemical structure, chemical formula, synonym and trade name of the arsenic, arsenite and arsenate species

Characteristic	Arsenic	Arsenite (As^{+3})	Arsenate (As^{+5})
Chemical structure	As	HO—As—OH | OH	O ‖ HO—As—OH | OH
Chemical formula	As	H_3AsO_3	H_3AsO_4
Synonym(s)	Arsenic black; colloidal arsenic; gray arsenic	Arsenious acid; arsenic oxide arsenious oxide; white arsenic;	Arsenic acid; orthoarsenic acid
Registered trade name	No data	Arsenolite®; Claudelite®	Dessican L-10®; Scorch®

(Source: ATSDR, 2000)

Arsenic trioxide (As_2O_3 or As_4O_6) is one of the primary intermediates used to make other forms of arsenic. Dissolved in water, it forms arsenious acid although the pure acid has not been isolated. Salts are called arsenites, and these forms represent the +3 oxidation state of arsenic, As(III). Arsenates (AsO_4^{3-}) are salts of arsenic acid, or more formerly orthoarsenic acid. This represents the +5 oxidation state of arsenic. Arsenite can be easily oxidized to arsenate, and arsenate can also be reduced to arsenite (ATSDR, 2000). The common name, chemical structure, chemical formula, synonym and trade name of the arsenic, and inorganic arsenic species of arsenite and arsenate species are shown in Table 1.

1.2.1.1 Physical and chemical properties

The physical and chemical properties of arsenic, arsenite and arsenate shown in Table 2

Table 2 Physical and chemical properties of arsenic, arsenite and arsenate species

Property	Arsenic	Arsenite (As^{+3})	Arsenate (As^{+5})
Molecular weight	74.92	131.92	150.95
Color	Gray	White	White
Odor	Odorless	Odorless	-
Physical state	Solid	Solid	Solid
Melting point	817°C at 28 atm	312.3°C	35.5°C
Boiling point	613°C at sublimes	465.5°C	160°C
Density d20	5.727 g/cm^3	3.738 g/cm^3	2.0-2.5 g/cm^3
Water(20°C)	Insoluble	37 g/L	3,020 g/L
Acid	Soluble in HNO_3	Soluble in HCl	-
Alcohol	-	Slightly soluble	Soluble
Vapor pressure	1 mm Hg (373°C)	66.1 mm Hg (312°C)	-
Valence states	0	+3	+5

(Source: ATSDR, 2000)

1.2.1.2 Application

The arsenic in used is estimated to in compound form, primarily of arsenate or arsenic trioxide. The major use for inorganic arsenic is in wood preservation. Inorganic arsenic compounds were used in medicine in the 1970s, primarily for treatment of leukemia, psoriasis, and asthma. It has been estimated that 70% of the world arsenic production is used in timber treatment as copper chrome arsenate, 20% in agricultural chemicals as arsenic-containing pesticides, and the remainder in glass, pharmaceuticals and non-ferrous alloys (USNRC, 1999).

1.2.1.3 Source and Potential Exposure

Inorganic arsenic is released to the environment from natural sources such as wind-blown dirt and volcanoes, release from industrial sources far exceed those from natural sources. Industrial sources of arsenic include nonferrous metal mining and smelting, pesticide application, coal combustion, wood combustion, and waste incineration. Thus, humans may be exposed to arsenic by eating food, drinking water, or breathing air. However, levels of inorganic arsenic, the form of most concern, are low. Levels of arsenic in various locations, weather conditions, industrial activity and urban air generally range from less than 1 to about 2,000 ng/m^3 and 20 to 30 ng/m^3 respectively. Of these, food is usually the largest source of arsenic. Fish and seafood contain the greatest amounts of arsenic, but this is mostly the organic form of arsenic that is less harmful. The level of inorganic arsenic intake from these sources is generally about 3.5 μg/day (ATSDR, 2000).

1.2.1.4 Health effects

Short-term (acute) poisoning with inorganic arsenic has been recognized since ancient times, and large oral dose (above 60,000 μg/L in food or water) can produce death, and swallowing lower levels (ranging from about 300 to 30,000 μg/L in food and water) may case stomach ache, nausea, vomiting and diarrhea. Other effects include decreased production of red and white blood cells which may cause fatigue, abnormal heart rhythm, blood-vessel damage resulting in

bruising, and impaired nerve function causing a "pins and needles" sensation in hands and feet.

Long-term (chronic) oral exposure to inorganic arsenic causes a pattern of skin changes. These include a darkening of the skin and the appearance of small "corn" or "warts" on the palms, soles, and torso. A small number of the corns may ultimately develop into skin cancer. Swallowing arsenic has been reports to increase the risk of cancer in the liver, bladder, kidneys, prostate and lungs. Several reported have classified inorganic arsenic as a known human carcinogen (ATSDR, 2000).

1.2.1.5 Maximum Contaminant Level (MCL) and Guidelines

The WHO guideline for arsenic in drinking water was provisionally reduced in 1993 from 50 μg/L to 10 μg/L. The new recommended value is based largely on analytical capability. If the standard basis for risk assessment applied to industrial chemicals were applied to arsenic, the maximum permissible concentration would be lower still. The USEPA limit was also reduced from 50 μg/L to 10 μg/L in January 2001 following prolonged debate over the most appropriate limit. The European Community's maximum admissible concentration (MAC) for As in drinking water is now also reduced to 10 μg/L. The Japanese limit for drinking water is 10 μg/L, and the interim maximum acceptable concentration for Canadian drinking water is 25 μg/L (Smedly and Kinniburgh, 2001).

1.2.1.6 Arsenic contamination in Thailand

In the September 1987, human health problems in Ron Phibun District (Figure 1) were exposed to the public when the first serious case of keratosis and hyperpigmentation was diagnosed on residents who suffered from arsenical skin cancer. A clinical survey during 1987-1988 the showed that more than 1000 people between the age 4 months and 85 years were affected (Chooprapawan, 1995). In 1992 a joint Thai-Japan clinical survey of blood taken from students was studied. Over 85% of students had high levels of arsenic in their blood, with a 22% incidence of skin lesions and hyperkeratosis (Paijitprapapon and Ramnarong, 1994). Many residents in the mining area suffered from the same problem; skin lesions and

hyperkeratosis that was related to consumption of contaminated surface and groundwater. Milintawisamai *et al.*, (1997 ; JICA, 2000) found arsenic at concentrations of up to 100 times more than is recommended by the World Health Organization (WHO) for potable water: 10 μg/L.

Analytical methods are of critical importance because the inorganic arsenic species occur at very low concentrations in the environment. The aim of the analytical methods that are available for detecting, measuring, and/or monitoring inorganic arsenic, its metabolites, and other biomarkers. So that we can define more clearly exposure and effects.

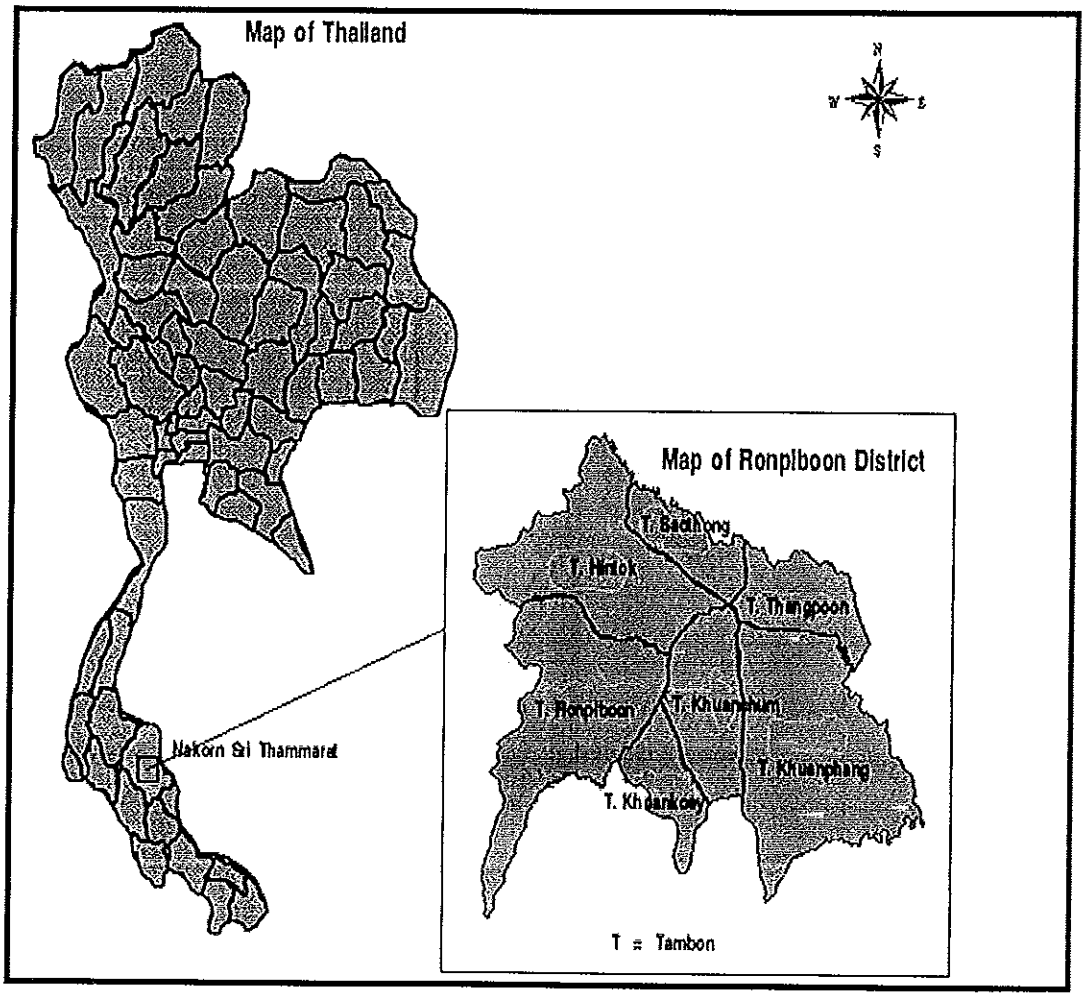

Figure 1 Map of Ron Phibun District, Showing the arsenic contamination (Source: Wiliam et al., 1996)

1.2.2 Inductively coupled plasma-optical emission spectrometry (ICP-OES)

An ICP source consists of a flowing stream of argon gas ionized by an applied radio frequency field typically oscillating at 40 MHz. This field is inductively coupled to the ionized gas by a water-cooled coil surrounding a quartz "torch" that supports and confines the plasma. A aerosol sample is generated in an appropriate nebulizer and spray chamber and is carried into the plasma through an injector tube located within the torch. The aerosol sample is injected directly into the ICP, subjecting the constituent atoms to temperatures of about 6000 to 8000 °K. Because this results in almost complete dissociation of molecules, significant reduction in chemical interferences is achieved. The high temperature of the plasma excites atoms producing an ionic emission spectra. The ICP provides an optically "thin" source that is not subject to self-absorption except at very high concentrations. Thus linear dynamic ranges of four to six orders of magnitude are observed for many elements (B. Boss and J. Fredeen, 1997).

The widely used analytical method for the determination of trace elements, ICP-OES marked its fortieth anniversary in 2004. This method is based on OES coupled with an ICP source. The ICP source, as described by Green field *et al.* and Wendt and Fessel (Greenfield *et al.*, 1964 Fessel, 1969) has a range of attractive properties for analytical optical emission spectrometry. Many advantages including low detection limits, good precision, fast sample throughput and short integration time, a wide linear calibration, negligible interference effects resulting from condensed-phase chemical reactions in the high-temperature discharge.

During inductively coupled plasma-optical atomic emission spectrometry, the sample is usually transported into the instrument as a stream of liquid sample. Inside the instrument, the liquid is converted into an aerosol through a process known as nebulization. The aerosol sample is then transported to the plasma where it is desolvated, vaporized, atomized, and excited and or ionized by plasma. The excited atoms and ions emit their characteristic radiation which is collected by a device that converts this data into concentration information for the analyst. A representation of the layout of a typical ICP-OES instrument is shown in Figure 2.

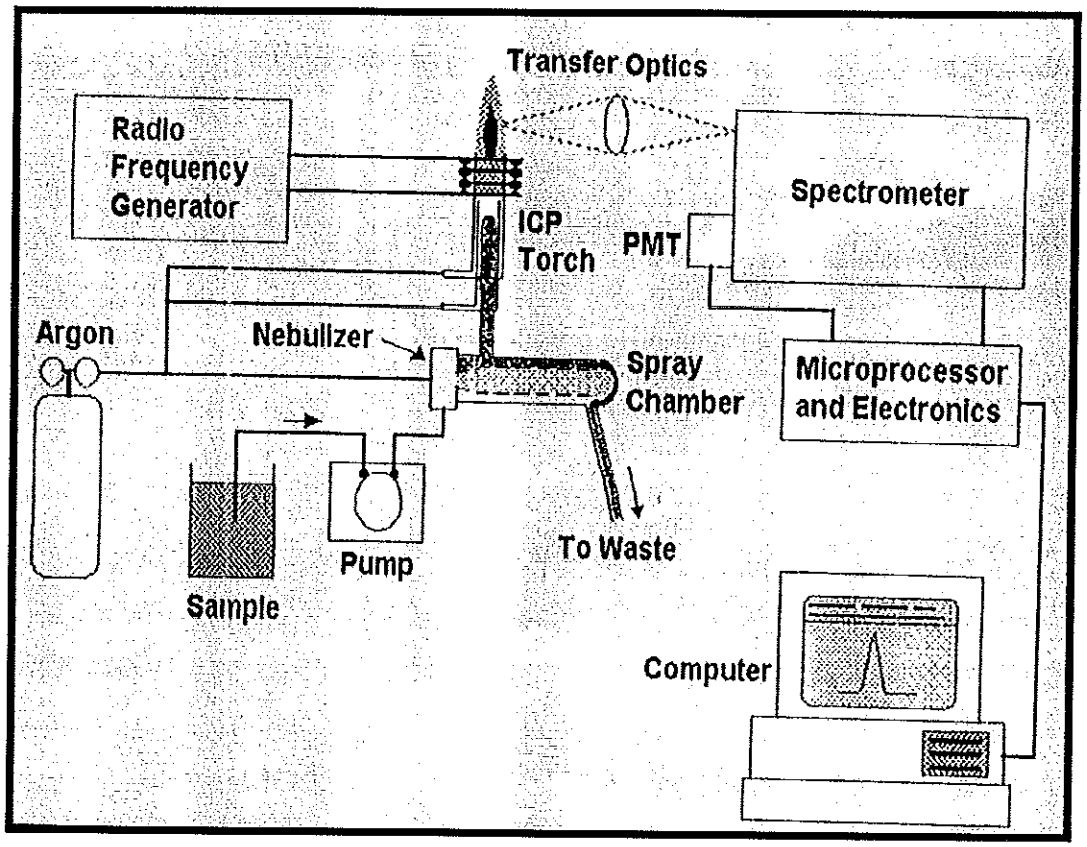

Figure 2 Major components and layout of a typical ICP-OES instrument (Source: Boss *et al.*, 1997)

The detection limits using ICP-OES with conventional aqueous-solution pneumatic nebulization techniques are not enough for inorganic arsenic analysis and moreover, have troublesome spectra interferences from the real samples. Then, the most widely used alternative sample introduction technique is hydride generation into the plasma. This increases the sensitivity considerably increased, and in addition achieves a useful separation from the sample matrix.

1.2.3 Continuous flow hydride generation method (HG)

The used of hydride generation for ICP-OES has been widely reported (Ding and Sturgeon, 1997; Muller, 1999; Do *et a.l*, 2000; and Gettar *et a.l*, 2000).

The continuous flow hydride generator, introduced recently, offers the advantages of simplicity in operation, excellent reproducibility, low detection limits, and high sample volume throughput for inorganic arsenic analysis. This method is applicable to determination of arsenic by conversion to arsine gas by sodium borohydride reduction and transported into a plasma of ICP-OES for analysis (Figure 3).

Arsenite, As(III) oxidation state is instantaneously converted by sodium borohydride in acid solution to arsine. The arsine is purged continuously by argon into a plasma of ICP-OES and converted to gas-phase atom. Arsenate, As(V) oxidation state of arsenic is reduced relatively slowly by sodium borohydride to As(III), which is then instantaneously converted to arsine. The arsine atoms emission peaks commonly are decreased by one-fourth to one-third for As(V) when compared to As(III). Determination of total arsenic requires that all inorganic arsenic compounds be in the As(III) state. Organic and inorganic forms of arsenic are first oxidized to As(V) by acid digestion. The As(V) then is quantitatively reduced to As(III) with sodium or potassium iodide before reaction with sodium borohydride.

The hydride generation technique is utilized for separation of the analyte arsenic from the matrix by conversion to its volatile hydride called arsine (AsH_3). This technique offers a route to the trace analysis of several important arsenic species that have specific problems when analyzed by conventional methods. Conventional methods of ICP-AES for arsenic determination is poor due to problems

associated with concentration by the sample matrix. HG-ICP-OES is an alternative method for arsenic analysis because of its sensitivity. (Tian *et al.*, 1998).

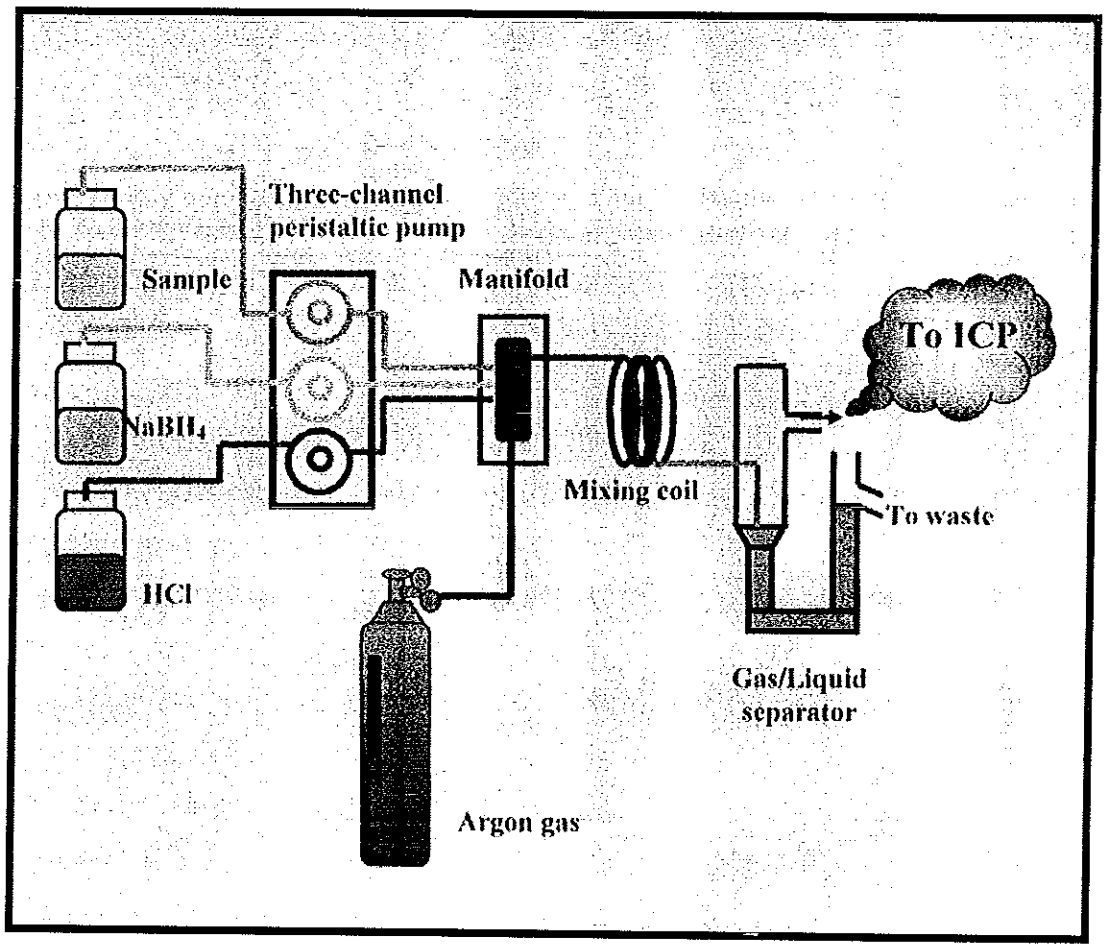

Figure 3 Schematic design and flow path of hydride generation system coupled online to ICP-OES
(Source: Davidowski, 1993)

1.2.4 Determination of inorganic arsenic

In 2000, Gettar *et al.* reported the determination of inorganic arsenic and organic arsenic species in water by ion chromatography separation, coupled on-line to post-column generation of the gaseous hydrides by reaction with $NaBH_4$ in an acid medium. Detection and measurement were performed by ICP spectrometry operating in the atomic emission mode. Arsenic emission was monitoring at 193.7 nm. Linear calibration curves were obtained in the 0.05-2 $\mu g\ mL^{-1}$ range of As(III)

and As(V). Results of the analyses of natural samples, such as river and ground water spiked with the studies, indicated that the analyte recoveries might be dependent on the sample composition. In addition, Muller *et al.*, (2000) develop method for determination of inorganic arsenic(III) in ground water using hydride generation coupled to ICP-AES (HG-ICP-AES) under variable sodium borohydride ($NaBH_4$) concentrations. The As(III) species shows significantly higher signal intensities at low $NaBH_4$ concentrations than the As(V) species. The $NaBH_4$ concentration used for the determination of As(III) cause very little considerable interference of As(V). The interference of As(V) during the As(III) measurements were very small, the interference were smaller than 2%. An amount of As(III) higher than 10% of the total arsenic amount could be determined. The linearity of calibration reaches from 2 $\mu g\ L^{-1}$ up to 1000 $\mu g\ L^{-1}$ with the detection limit routinely of about 1 $\mu g\ L^{-1}$ for each species. The advantages of the linear calibration range and a higher sensitivity are major advantages of this method. Additional merits of the developed method are easy handling and high sampling rates.

On the other hand, Barra *et al.*, (2000) developed atomic fluorescence method the for determination of inorganic arsenic in soils after microwave-assisted distillation. After reduction of As(V) to its As(III) with potassium iodide, inorganic arsenic was distilled as $AsCl_3$ and this was finally determined by atomic fluorescence spectrometry after hydride generation with $NaBH_4$ in HCl medium. The methodology developed has a detection limit of 0.015 $\mu g\ L^{-1}$, which corresponds to a concentration of 0.006 $\mu g\ g^{-1}$, and a relative standard deviation of 3% at 8.7 $\mu g\ g^{-1}$ of arsenic. The recovery percentages of As(III) and As(V) were 103±4 and 106±4%, respectively. Addition, Shraim *et al.* (2000) develop by used perchloric acid in the reduction medium for speciation of arsenic by hydride generation atomic absorption spectrometry. In these methods perchloric acid as a reduction medium, L-cysteine was used as a pre-reducing agent for a certain contact time between its addition and analysis, and $NaBH_4$ was used as a reducing agent. The methods developed for the determination of inorganic arsenic species in environmental water samples were as follows. As(III): 5 M acid and 0.08% $NaBH_4$ in the absence of L-cysteine. Total inorganic arsenic [As(III)+As(V)]: 8 M acid and 0.6% $NaBH_4$. As(V): by difference. Detection limits of added As spikes for all analyses were found to be between 0.5-0.7

μg L^{-1} and with recoveries of 90-112%. In 2000, Do *et al.* developed the HG-ICP-AES for determination of arsenic in the eluate from a high-performance liquid chromatography (HPLC) system. Arsenite; As(III) and arsenate; As(V) present in urine samples of patients treated intravenously with As(III), were analyzed separately by HPLC-HG-ICP-AES using a non-polar C_{18} column. This analytical method allowed the sensitivity determination of the arsenic species in the submicrogram per liter range. The measured concentrations obtained were 385 μg mL^{-1}. 1M HCl with 1% $NaBH_4$ was used in the HG system. The signal responses of arsenic with HG were at least ten time more intense compound to the ones obtained without HG.

Then, the develop method for determined of As(III) and total inorganic arsenic in water samples by using flow injection hydride generation atomic absorption spectrometry (FI-HG-AAS), by without pre-reduction of As(V). The flow system was operated in the merging zones configuration, where sample and $NaBH_4$ are simultaneously injected into two carrier streams. HCl and H_2O, respectively. The sample and reagent injected volumes were 250 μL with a flow rate of 3.6 mL min^{-1} for hydrochloric acid and de-ionised water. When the $NaBH_4$ concentration was maintained at 0.1%, it was possible to perform arsine selective generation from As(III) and on-line arsine generation with 3.0% $NaBH_4$ to obtain total arsenic concentration. As(V) was calculated as the difference between total As and As(III). With the proposed procedure detection limits of 0.3 ng mL^{-1} for As(III) and 0.5 ng mL^{-1} for As(V). were achieved. The relative standard deviations were 2.3% for 0.1 ng mL^{-1} As(III) and 2% for 0.1 ng mL^{-1} for As(V). The method was shown to be satisfactory for determination of trace arsenic in water samples. (Wrobel *et al.* 2002).

Moreover, inorganic and organic arsenic speciation have been detected in fish tissue using coupled high performance liquid chromatography-microwave digestion-hydride generation-atomic absorption spectrometry. Conditions for hydride generation were 3.5 M HCl, 1% $NaBH_4$, 90 mL min^{-1} was chosen for the carrier gas. Detection limits achieved were 0.3 and 1.1 ng with 95% recovery for all species (Villa-Lojo *et al.*, 2002).

Ferreira *et al.* (2002) develop method for determination of As(III) and arsenic(V) in natural waters by cathodic stripping voltammetry at a hanging mercury drop electrode. For determination of As(III) the quantification limit was 0.2 μg L^{-1}

for a deposition time of 40s, and the relative standard deviation (RSD) was calculated to be 6% (n=13) for a solution with 8 μg L^{-1} of As(III). For As (total), the quantification limit was 2 μg L^{-1} for a deposition time of 3 min, and the RSD was calculated to be 3% (n=10) for a solution with 8 μg L^{-1} of As(V). The method was validated by application of recovery and duplicate tests in measuring of As(III) and As (total) in natural spring and mineral waters. For As (total), the results from the literature were compared with the results obtained by optical emission spectrometry with ICP coupled to hydride generation (OES-ICP-HG) and good correlation was observed.

In addition, Goessler and Pavkov (2003) developed anion-and cation-exchange chromatography to separate arsenic compounds and determined them with inductively coupled plasma mass spectrometer as an arsenic-specific detector. As(III) was completely oxidized to As(V) at 100 °C. and other species required >280 °C. Nevertheless, accurate results are obtained with the hydride generation technique of incompletely mineralized samples when an appropriate calibration is performed.

1.3 Objectives

1.3.1 To modify and optimize methods for determination of inorganic arsenic species by using an online HG-ICP-OES technique.

1.3.2 To apply this method to real sample analysis such as drinking water samples.

Chapter 2

Experimental

2.1 Standards and chemicals

2.1.1 Arsenous acid standard (As(III), As_2O_3 99%, Aldrich, USA)

2.1.2 Arsenic(V) oxide hydrate standard (As(V), As_2O_5 99.99%, Aldrich, USA)

2.1.3 Hydrochloric acid (HCl 37%, AR grade, Merck , Germany)

2.1.4 Nitric acid (HNO_3 69%, AR grade, Merck, Germany)

2.1.5 Sodium borohydride ($NaBH_4$ 97%, AR grade, Fluka, Switzerland)

2.1.6 Sodium hydroxide (NaOH 99%, AR grade, Merck, Germany)

2.1.7 Potassium iodide (KI 99%, AR grade, Merck, Germany)

2.1.8 Deionized water (From laboratory by Maxima, ELGA, England)

2.2 Instrumentation and apparatus

2.2.1 Inductively coupled plasma optical emission spectrometer (ICP-OES, Model Optima 4300 DV, Perkin-Elmer, USA)

2.2.2 Hydride generator (HGV-1, Shimadzu, Japan)

2.2.3 Argon gas (Ar 99.999%, Ultra High Pure grade, TIG, Thailand)

2.2.4 Nitrogen gas (N_2 99.99%, High Pure grade, TIG, Thailand)

2.2.5 Digital balance (Mettler AE 200, USA))

2.2.6 Microliter pipette and Tips (Eppendorf, Germany)

2.2.7 Volumetric cylinder 10, 50, 100 and 500 ml (Pyrex, USA)

2.2.8 Volumetric flask 25, 50, 100 and 500 ml (Pyrex, USA)

2.2.9 Beaker 25, 50, 100 and 250 ml (Pyrex, USA)

2.2.10 Polyethylene bottle 500 ml (Nalgene, England)

2.2.11 Polyethylene tank 5000 ml (Nalgene, England)

2.3 Methodology

A Perkin-Elmer Model 4300 DV inductively coupled plasma optical emission spectrometer with axial plasma view equipped with a Shimadzu Model HGV-1 continuous flow hydride generator was used in this experiment. The reagents and instrumental conditions used for this analysis are listed in Table 3. The instrumental conditions of hydride generation-inductively coupled plasma optical emission spectrometer (HG-ICP-OES) were optimized in order to yield an optimal signal/noise ratio. The investigation of this method consisted of: the standard and reagents preparation, instrumental set up, optimization of HG-ICP-OES conditions, linear dynamic range, detection limit, accuracy, and the finally this developed method will be applied to determine inorganic As species in drinking water samples.

2.3.1 Preparation of standard and reagent solutions

All chemical used in this experiments are analytical-reagent grade (AR grade). The working standard 100 μg L^{-1} of As(III) and 100 μg L^{-1} of As(V) were prepared daily with deionized (DI) water. In addition 4 mol L^{-1} HCl and 0.4% (w/v) of $NaBH_4$ in 0.6% (w/v) of NaOH for hydride generation and 10% KI were prepared for the studied inorganic As species.

2.3.1.1 Preparation of working As(III) and As(V) standard solutions

The stock standard solutions in concentrations of 1000 mg L^{-1} of As(III) and As(V) were prepared as follow: As(III) stock standard solution was prepared by weigh 0.1320 g of As_2O_3 and dissolved with 1 mol L^{-1} NaOH and then the pH adjusted with conc.HNO_3 and the volume made to 250 ml with DI water. As(V) stock standard solution was prepared by weigh 0.1654 g of As_2O_5 and then the volume made to 250 ml with DI water.

The standard working solutions 100 μg L^{-1} of As(III) and As(V) can be prepared by diluting the stock standard solutions above.

2.3.1.2 Preparation of $NaBH_4$ solution

The reductant solution of $NaBH_4$ 0.4 % (w/v) used was prepared by weigh 1.25 g of $NaBH_4$ and 1 g of NaOH then dissolving with DI water to a final volume of 250 ml. This reducing reagent solution was prepared fresh daily.

2.3.1.3 Preparation of HCl solution

The acid medium solution of 4 mol L^{-1} of HCl was prepared by pipette 83.33 mL of conc.HCl into 250 ml volumetric flask and made up the volume with deionized water.

2.3.1.4 Preparation of KI solution

The pre-reductant solution of 10% (w/v) KI used was prepared as follows: by weigh 10 g of KI dissolving with deionized water then made up the made volume to 100 ml. This KI solution was prepared fresh daily.

2.3.2 Instrumental setup

The HG-ICP-OES system set up is shown in Figure 4.

2.3.2.1 Hydride generation system

The continuous hydride generation system consisted of: a three-channel peristaltic pump (4300DV ICP-OES instrumental) with three pump tubing (Trgon, 6.5 mm i.d. for sample and Tygon, 3.5 mm i.d. for $NaBH_4$ and HCl) a mixing coil and gas-liquid separator were used.

The hydride generation conditions used were optimized. For the first study the flow rates of sample selected was 3.6 mL min^{-1}, HCl and $NaBH_4$ both 1.2 mL min^{-1}. Arsenic in the sample was reduced to arsine or hydride gas by using the reductant in an acid medium. The three solutions were pumped with a three channel peristaltic pump into the manifold. After mixing the solutions were transported with argon carrier gas into the mixing coil, and passed to the gas/liquid separator for separating arsine gas into the hydride connector of the

ICP-OES system for analysis. The details and description of the hydride generation system and conditions are shown in Table 3.

2.3.2.2 ICP-OES system

A Perkin-Elmer Model 4300 DV inductively coupled plasma optical emission spectrometer with radial plasma view equipped with a Shimadzu Model HGV-1 continuous flow hydride generator was used in this experiment. The detailed descriptions of the ICP-OES instrument system and conditions are shown in Table 3. The data of arsenic emission signals were relayed to a printer. The data acquisition was realized with specific software, Winlab32. The integration peaks were achieved by area measurement.

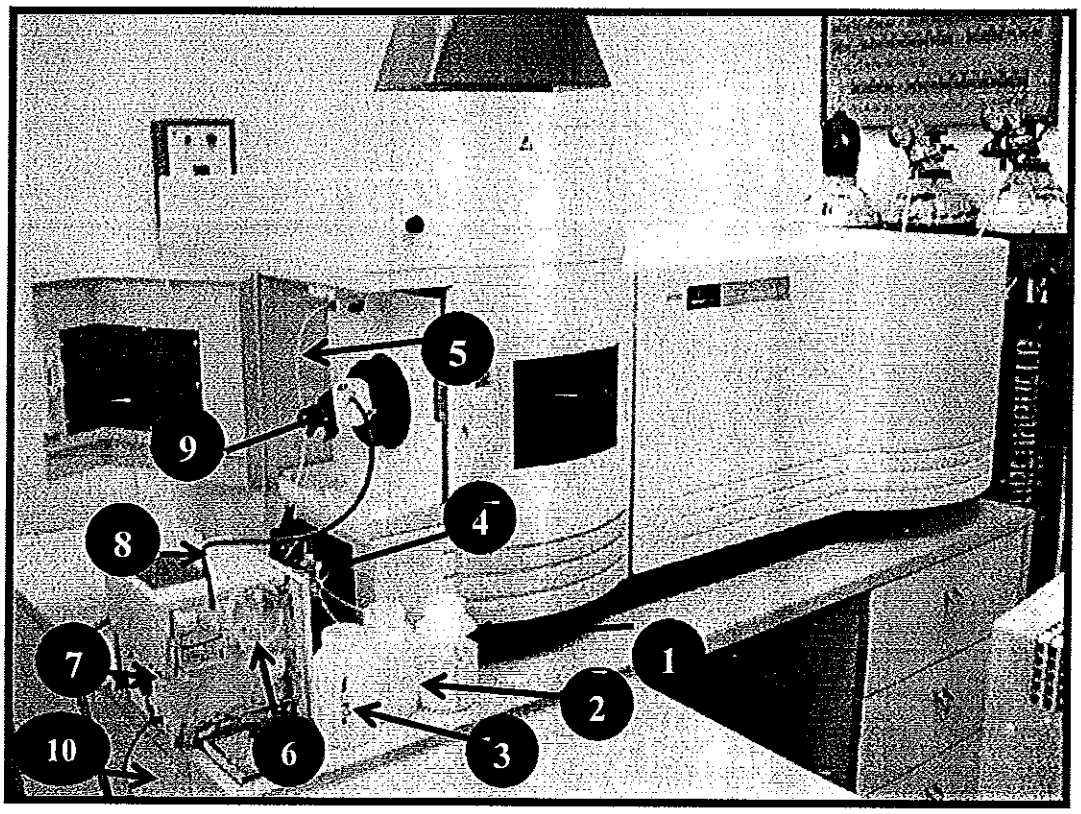

Figure 4 Instrumental setup of HG-ICP-OES system was used in these experiments consisted of; 1. Sample, 2. HCl, 3. $NaBH_4$ 4. Peristaltic pump,5. Ar carrier gas, 6. Mixing coil, 7. Gas/liquid separator, 8. Hydride gas, 9. Hydride connector, and 10. Waste.

Table 3 Experimental conditions for the HG-ICP-OES

Inductively coupled plasma optical emission spectrometer condition	
Wavelength [1]	193.7 nm
Measurements integration time[2]	
Maximum	10 second
Minimum	5 second
RF power[3]	1.4 kW.
Argon gas flow rates	
Nebulizer (Carrier gas) [4]	0.8 L min^{-1}
Plasma[5]	15 L min^{-1}
Auxiliary[6]	0.5 L min^{-1}
Generator	40 MHz
Delay time	30 second
Replicates	5
Plasma viewing	axial
Hydride generation condition	
Pumping rate[7]	0.8 mL min^{-1}
Sample flow rate[8]	3.6 mL min^{-1}
$NaBH_4$ and HCl flow rate [9]	1.2 mL min^{-1}
$NaBH_4$ Concentration[10]	0.4 % (w/v)
HCl Concentration[11]	4 mol L^{-1}

[1-11] These parameters were changed or optimized during this study

2.3.3 Optimization of the HG-ICP-OES conditions for arsenic analysis

The optimum conditions of continuous flow hydride combined with an inductively coupled plasma optical emission spectrometer system used in this study are shown in Table 3. The optimum conditions of the ICP-OES system used were based on the following parameters; wavelength, integration time, RF power, plasma argon gas flow rate, auxiliary argon gas flow rate. The optimum conditions of the continuous flow HG system used in this studied were; $NaBH_4$ and HCl concentration, Ar carrier gas flow rate, pumping rate, sample flow rate, $NaBH_4$ and HCl flow rate, and KI concentration and time.

2.3.3.1 Wavelength

The optimum wavelengths of the As(III) emission signal was studied at various wavelengths of 189.0, 193.7, 197.3 and 288.8 nm as following of ICP-OES manual, with a 100 $\mu g\ L^{-1}$ As(III) standard solution. The standard solution was analyzed by the HG-ICP-OES system under the conditions in Table 3. The optimum wavelength was selected as the one with the highest emission intensity.

2.3.3.2 Integration time

The optimization of integration time was investigated by using the same standard solution in 2.3.3.1. The standard solution was analyzed by the HG-ICP-OES system under the conditions in Table 3 with wavelength as found from 2.3.3.1. The integration time was studied by varying the time in the range of 1-5, 5-10, 10-20 and 20-50 seconds. The highest detectable emission intensity selected was the optimum of the integration time observed.

2.3.3.3 RF power

The optimization of RF power was performed by using the same standard solution in 2.3.3.1. The standard solution was analyzed by the HG-ICP-OES system under the conditions in Table 3 and value of the results from 2.3.3.1-2.3.3.2. The RF power was tested at 1, 1.2, 1.3, 1.4 and 1.5 kW, and then the optimum of the RF power was selected as the highest emission intensity obtained.

2.3.3.4 Plasma gas flow rate

The optimization of the flow rate of the plasma gas was studied by varying flows of 15, 16, 17, 18, 19 and 20 L min^{-1}. Other parameters were set as the conditions described in Table 3 and from the results of experiments 2.3.3.1-2.3.3.3. The optimum plasma gas flow rate was selected as the one giving the highest emission intensity.

2.3.3.5 Carrier gas flow rate

The carrier gas flow rates was studied by varying flows from 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 L min^{-1}. The optimum of carrier gas flow rate was obtained from are giving the highest emission intensity. The same parameters were set as the conditions given in Table 3 and from the results of 2.3.3.1-2.3.3.4.

2.3.3.6 Auxiliary gas flow rate

The previous parameters were set according to conditions given follows in Table 3 and from the results from 2.3.3.1-2.3.3.5. The optimization of the flow rate of the auxiliary gas was studied by varying the gas flow rate from 0.10 0.2, 0.3, 0.4, 0.5 and 0.6 L min^{-1}. The optimum flow rate of the auxiliary gas was selected by considering the best emission signal of As(III).

2.3.3.7 $NaBH_4$ concentration

The emission signal of the As(III) standard was studied using various $NaBH_4$ concentrations of 0.1, 0.2, 0.3, 0.4, 0.8 and 1% (w/v). The described conditions in Table 3 and the results from 2.3.3.1-2.3.3.6. The optimum concentration of $NaBH_4$ was selected that with the highest emission intensity.

2.3.3.8 HCl concentration

The optimium concentration of HCl was studied by varying the concentration from 0.5 to 4 mol L^{-1}. The highest detectable emission signal was selected as the optimum for the HCl concentration. The set parameters those obtained from the result of 2.3.3.1-2.3.3.7.

2.3.3.9 Pumping rate

The emission signal of the As(III) standard was studied using various pumping rates of 0.3, 0.5, 0.8, 1 and 1.5 mL min^{-1}. The HG-ICP-OES system was used under conditions given in Table 3 and from the results of 2.3.3.1-2.3.3.8. The highest detectable emission signal was selected as the optimum pumping rate.

2.3.3.10 Sample flow rate

The optimization of the flow rate of the sample was varied from 0.6, 1.2, 3.6, 4 and 6 mL min^{-1} using the same parameters as described in Table 3 and from the results from 2.3.3.1-2.3.3.9. The highest emission intensity was selected as the optimum sample flow rate.

2.3.3.11 $NaBH_4$ and HCl flow rate

The optimization of the flow rate of $NaBH_4$ and HCl was studied using flow rates of 0.2 to 2 mL min^{-1} the same conditions as described in Table 3 and plus the results from 2.3.3.1-2.3.3.10. The highest detectable emission signal was selected as the optimum for the $NaBH_4$ and HCl flow rates.

2.3.3.12 KI concentration

The determination of total As concentration was performed after a complete reduction of As(V) to As(III) with KI. The emission signal of total As with mixed standards of 4 μg L^{-1} As(III) and 4 μg L^{-1} As(V) standard was studied using various KI concentrations of 5, 10, 20, 40 and 60%. The same parameters were set as the conditions obtained as follows in Table 3 and from the results of 2.3.3.1-2.3.3.12. The best emission signal obtained was selected as the optimum concentration of KI.

2.3.3.13 KI time

The optimum time to reduce As(V) to As(III) was studied using various KI times of 5, 10, 20, and 30 min. The same parameters were in

Table 3 and from the results of 2.3.3.1-2.3.3.12. The highest emission signal found was selected as the optimum time of KI.

2.3.4 Linear dynamic range

The dynamic range can be specified as the concentration range or analytical signal range over which the analytical curve is linear or the calibration slope is constant. It is usually defined at the lower end by the detection limit and at the upper end by an analyte concentration where the analytical signal deviates a specific relative amount (e.g., 5%) from the extrapolated linear portion of the curve or where the slope deviates a specific relative amount from the slope in the linear portion. Non linearity can be inherent in the technique or due to the matrix of the standards, non ideal instrumental performance, instrumental distortion, or incorrect utilization of the instrument. A linear calibration curve is usually preferred because it is easier to detect an abnormality and because it is easier to work with mathematically. A large dynamic range is preferred because a wide range of analyte concentrations can be used without sample dilution. A nonlinear calibration curve can be used as long as enough standards are measured to establish the calibration function (Ingle and Crouch, 1988)

The linearity of the calibration curve was established using three series of total As, As(III) and As(V) standard solutions with concentrations of 1, 5, 10, 25, 50, 75 and 100 $\mu g\ L^{-1}$. The linear dynamic range was obtained by plotting the detector response (emission intensity-Y axis) *versus* the concentration (X-axis). Each slope of the calibration curve were evaluated as a linear equation.

2.3.5 Limit of detection and limit of quantitation

The limit of detection (LOD) was defined as the smallest concentration which could be measured with a specified degree of certainty (IUPAC Definition) and is defined arbitrarily as $3S_B$ (Currie, 1999 and Taylor, 1987).

The lower level where measurements become quantitatively meaningful has been called the limit of quantitation (LOQ) (IUPAC Definition) and is defined arbitrarily as $LOQ = 10S_B$ (Currie, 1999 and Taylor, 1987). In this work, the LOD and LOQ were studied. The limit of detection and limit of quantitation

were established by using series of total As and As(III) standard solutions with concentrations of 1, 5, 10, 25, 50, 75 and 100 μg L^{-1} and 10 replications deionized water as a blank. The calibration curve was plotted and the mean value of the blank responses (X_B) and the standard deviation (S_B) were calculated. Each slope of the calibration curve were evaluated as a linear equation.

The probability that the smallest discernible analytical signal (X_L) can be measured is

$$X_L = X_B + kS_B \qquad (1)$$

Where k is a numerical factor chosen in accordance with the confidence level desired. C_L, the limit of the detection concentration, is a function of X_L, *i.e.*

$$C_L = (X_L - X_B) / m \qquad (2)$$

Where m is the analytical sensitivity. Because the average blank reading, X_B, is not always 0, the signal must be corrected with the background, By substituting Equation 1 in to Equation 2.

$$C_L = kS_B / m$$

Where C_L = Limit of detection concentration value (IUPAC Definition)

k = 3 allows a confidence level of 99.86%

S_B = the standard deviation of blank

m = the analytical sensitivity

2.3.6 Accuracy

The accuracy indicates how close the measured analyte concentration in the sample is normally to the actual value and is expressed as the relative percent error. The accuracy depends on the analyte concentration, precision and interference effects.

The accuracy of this experiment was conducted by using recovery. The recovery is best evaluated by measurement of known composition and spikes or added to the sample. The recovery is often stated as the percentage measured with respect to what was added. Complete recovery (100%) is of course the ultimate goal (Taylor, 1987). The % recovery can be evaluate by spiking of 1, 5, 10, 25, 50, 75 and 100 μg L^{-1} of As(III) and As(V) in to a blank and samples respectively.

2.4 Samples analysis

This investigation shows that this technique can be applied to drinking water samples for inorganic As species. The drinking water samples were purchased from the supermarket and the detail of these are shown in Table 4 and Figure 5.

Table 4 Drinking water samples for total As, As(III) and As(V) analysis using HG-ICP-OES

Sample No.	Sampling date
1	23/09/05
2	23/09/05
3	23/09/05
4	23/09/05
5	23/09/05

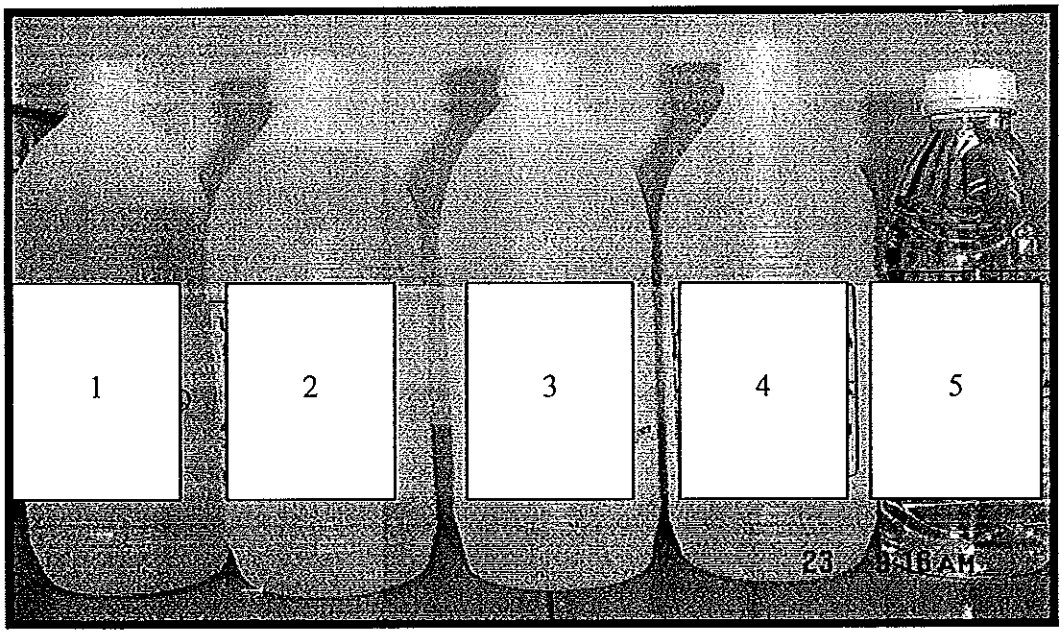

Figure 5 Drinking water samples used in these experiment

2.4.1 Determination of inorganic As in drinking water

Inorganic As in drinking water was determined by using the optimum conditions established in this study. Due to the very low concentration of arsenic in drinking water in this study the spiking technique must be applied to measure inorganic As. In addition, % recovery was also studied to check the accuracy of this method.

Chapter 3

Results and discussion

3.1 Optimization of the HG-ICP-OES conditions

Hydride generation combined with an inductively coupled plasma optical emission spectrometry (HG-ICP-OES) was used in these experiments. The instrumental set up is shown in Figure 4. The chemicals and instrumental conditions used experiment are listed in Table 3. The instrumental conditions were optimized in order to yield an optimal signal/noise ratio. The conditions for inorganic As determination were studied. The parameters tested and fixed were wavelength, integration time, RF power, argon gas flow rate of plasma, auxiliary and carrier, concentration and flow rate of sodium borohydride ($NaBH_4$), and acidity (HCl) and flow rate of sample solution. The other parameters are linearity, detection limits and accuracy of the calibration graph. The concentration of As(III) species that was used for optimizing the parameters was 100 $\mu g\ L^{-1}$.

To achieve optimum conditions, for the emission signal following parameters were optimized.

3.1.1 Wavelength

The emission intensity of the As(III) at four wavelengths were investigated 189.0, 193.7, 197.2 and 288.8 nm and shown in Table 5 and Figure 6. The most sensitive emission wavelength was obtained at 193.7 nm. The results was in agreement with those observed by authors (Gettar *et al.*, 2000 and Ng *et al.*, 1998). Therefore, 193.7 nm wavelength was selected to study the next experiment.

Table 5 The relative emission signal of As(III) at various four wavelengths

As(III) wavelength (nm)	Emission intensity* x 10^4 ± %RSD
189.0	1.11 ±2.04
193.7	1.50±1.50
197.2	0.95±2.52
288.8	0.87±2.64

**5 replications*

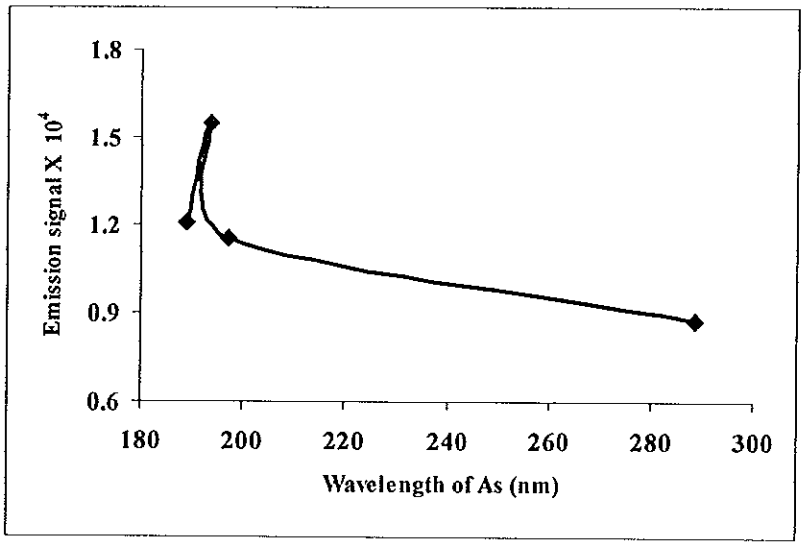

Figure 6 The relative emission signal of As(III) at various four wavelengths

3.1.2 Integration time

The integration times were varied in order to get a good integration peak. It was investigated by varying the time in the range of 1-5, 5-10, 10-20 and 20-50 seconds. The results are shown in Table 6 and Figure 7. The highest signal was obtained at 5-10 seconds. The signals were not significantly affected when compared with other integration times. This behavior was similar to that previously reported (Muller, 1999) Therefore, the integration time selected for further studies was 5-10 seconds.

Table 6 The relative emission signal of As(III) at various integration times

Integration time Min-Max.(Second)	Emission intensity* x 10^4 ± %RSD
1-5	2.84±1.24
5-10	2.98±0.62
10-20	2.83±1.12
20-50	2.82±0.85

**5 replications*

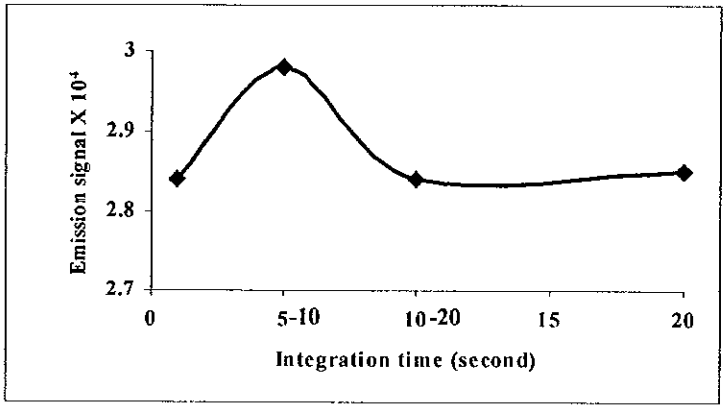

Figure 7 The relative emission signal of As(III) at various integration times

3.1.3 RF power

The radio frequency generator (RF) powers were studied in order to provide the best generation of the plasma discharge. The RF powers were investigated at 1, 1.1, 1.2, 1.3, 1.4 and 1.5 kW. The results are shown in Table 7 and Figure 8. High RF power levels can be used to increase the signal level up to about 1.5 kW. The results was in agreement previously reported (Klaue *et al.*, 1999). 1.3 kW gave the optimum signal. Because the emission signal for this power produced the least %RSD, so this power was selected for the next studies.

Table 7 The relative emission signal of As(III) at various RF powers

RF Power (kW)	Emission signal* x 10^4 ± %RSD
1	4.62±1.52
1.1	4.82±1.01
1.2	5.28±1.33
1.3	5.48±0.67
1.4	5.61±1.52
1.5	5.74±0.89

**5 replications*

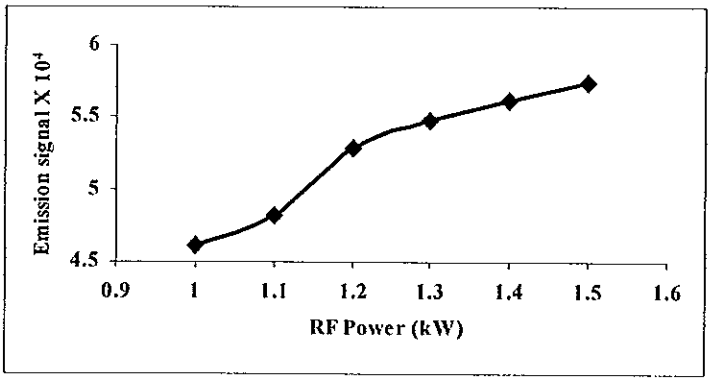

Figure 8 The relative emission signal of As(III) at various RF powers

3.1.4 Plasma gas flow rate

The plasma gas flow rates were studied by varying the range from 15 to 20 L min^{-1} with the carrier and auxiliary gas flow rates fixed. The minimum output plasma flow rate of the system is only 15 L min^{-1}. The results are shown in Table 8 and Figure 9. The emission signal decreased with an increase of the flow rate of plasma gas. The optimum emission signal was obtained at 15 L min^{-1} and then, this flow rate was selected for the next experiment.

Table 8 The relative emission signal of As(III) at various plasma gas flow rates

Plasma gas flow rate (L min^{-1})	Emission signal* x 10^4 ± %RSD
15	2.30±0.98
16	2.26±1.04
17	2.18±1.59
18	2.12±2.13
19	2.07±5.02
20	1.94±1.49

**5 replications*

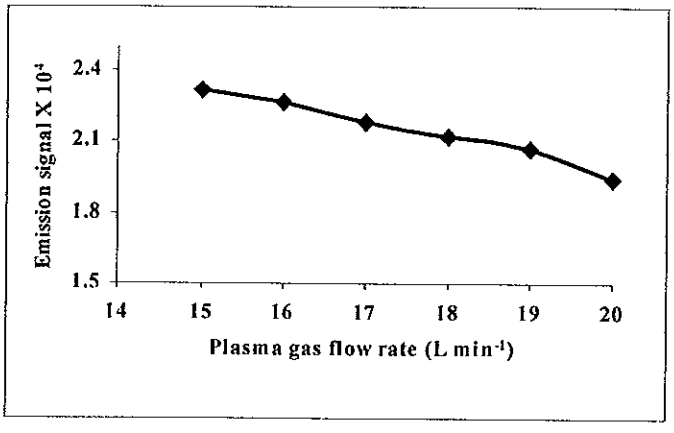

Figure 9 The relative emission signal of As(III) at various plasma gas flow rates

3.1.5 Carrier gas flow rate

Carrier gas can affect the efficiency of transference and extraction of AsH_3 from the gas-liquid separator. The carrier gas flow rate was assessed over the range of 0.1 to 0.6 L min^{-1}. The results are shown in Table 9 and Figure 10. A higher flow rate of carrier gas resulted in signal instability and decrease in sensitivity of the emission signal. This behaviour was similar to that previously reported (Gong *et al.*, 2001). The highest signal was obtained at 0.3 L min^{-1} of carrier gas. This flow rate was chosen for next experiment.

Table 9 The relative emission signal of As(III) at various carrier gas flow rates

Carrier gas flow rate (L min^{-1})	Emission signal* x 10^4 ± %RSD
0.1	2.73±1.95
0.2	4.26±1.27
0.3	4.91±0.95
0.4	4.12±1.36
0.5	3.13±1.97
0.6	2.40±2.26

**5 replications*

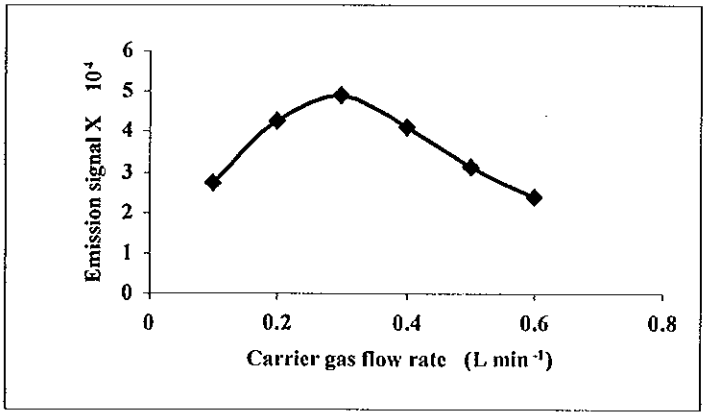

Figure 10 The relative emission signal of As(III) at various carrier gas flow rates

3.1.6 Auxiliary gas flow rate

The auxiliary gas flow rate was investigated from 0.1 to 0.6 L min^{-1}. The results are shown in Table 10 and Figure 11. The signal decreased as the flow rate of auxiliary gas was increased. A higher flow rate of auxiliary gas resulted in signal instability and a decrease in sensitivity. The signal was the highest at an auxiliary gas flow rate of 0.2 L min^{-1}. Therefore, a 0.2 L min^{-1} auxiliary gas flow rate was chosen for further experiments.

Table 10 The relative emission signal of As(III) at various auxiliary gas flow rates

Auxiliary gas flow rate (L min^{-1})	Emission signal* x 10^4 ± %RSD
0.1	5.34±1.58
0.2	5.91±1.05
0.3	5.23±2.40
0.4	5.35±2.03
0.5	5.43±2.06
0.6	5.48±2.43

**5 replications*

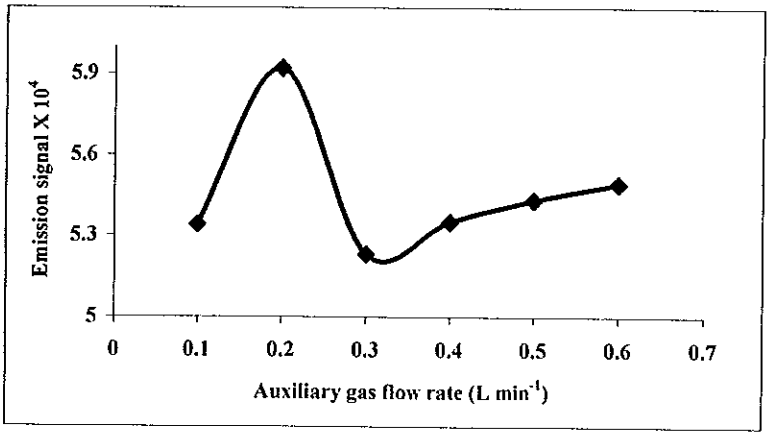

Figure 11 The relative emission signal of As(III) at various auxiliary gas flow rates

3.1.7 Pumping rates

The pumping rates were studied in order to obtain the optimum flow rate of the sample, HCl and $NaBH_4$ solutions. The results are shown in Table 11 and Figures 12-14. The emission signal increased with an increasing flow rate of sample as well as HCl and $NaBH_4$ flow rates. However, the signal was most suitable at a pumping rate of 0.5 mL min^{-1}, because of produced the lowest %RSD when compared with the other pumping rates. For the higher flow rates, the precision decreased and plasma is less stable. The flow rate of HCl and $NaBH_4$ were at least three time of sample flow rate, because of the tubing size not similar in this studied. It can be concluded that at this pumping flow rate the flow rate of the sample, HCl and $NaBH_4$ were 1.2, 0.4 and 0.4 mL min^{-1}. Therefore, this pumping flow rates were selected for the next experiments.

Table 11 The relative emission signal of As(III) at various pumping rates.

Pumping rate (mL min^{-1})	Sample flow rate (mL min^{-1})	HCl and $NaBH_4$ flow rate (mL min^{-1})	Emission signal* x 10^4 ± %RSD
0.3	0.6	0.2	2.17±1.95
0.5	1.2	0.4	3.66±1.07
0.8	3.6	1.2	4.01±2.97
1	4	1.6	4.32±2.55
1.5	6	2	5.03±2.97

**5 replications*

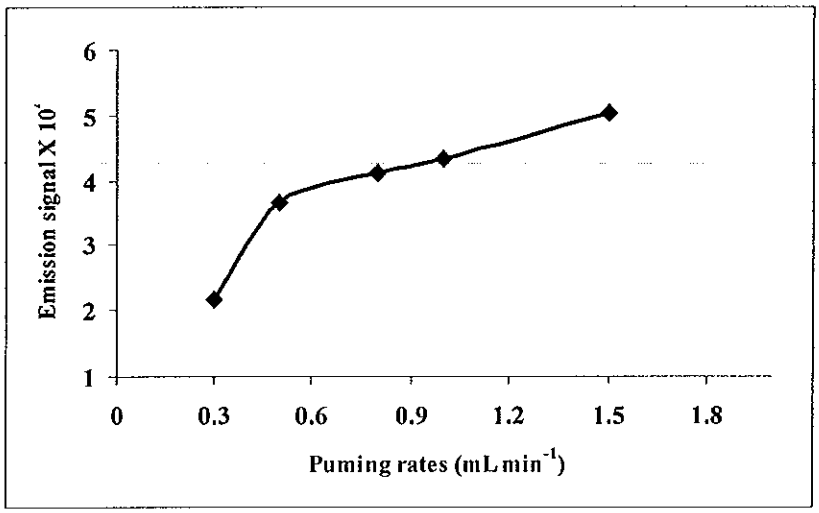

Figure 12 The relative emission signal of As(III) at various pumping rates

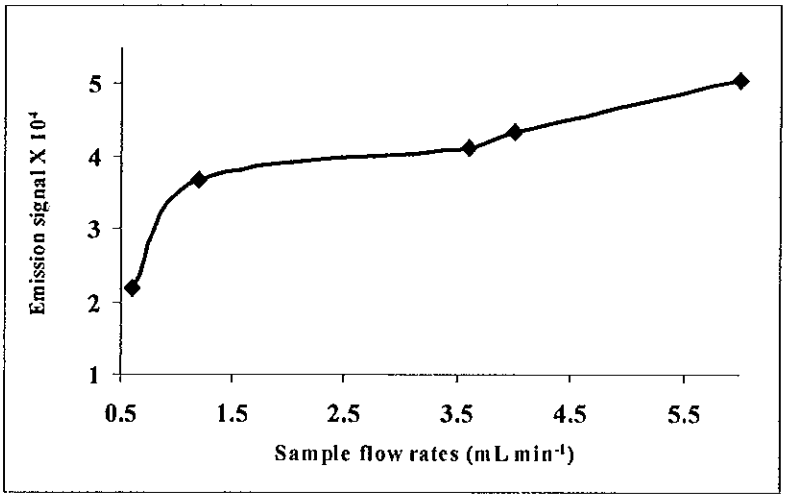

Figure 13 The relative emission signal of As(III) at various sample flow rates

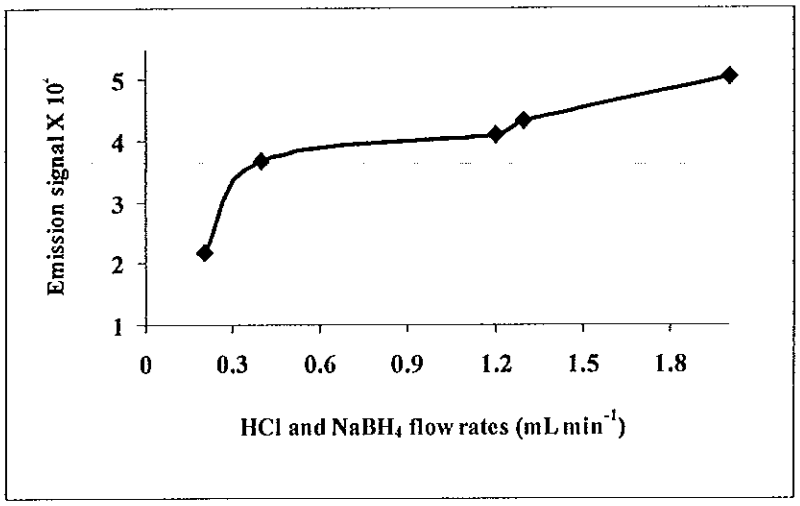

Figure 14 The relative emission signal of As(III) at various HCl and $NaBH_4$ flow rates

3.1.8 Hydrochloric acid concentration

The effect of HCl concentration used for generation of AsH_3 was investigated from 0.5 to 4 mol L^{-1} with the 0.4% (w/v) $NaBH_4$ concentration fixed. The results are expressed as emission signal *vs.* acid concentration in Table 12 and Figure 15. The emission signal rapidly increased when the HCl concentration with increased up to 2 mol L^{-1}, reaching maximum and constant value at concentration above 3 and 4 mol L^{-1}. This behaviour was similar to that previously reported. (Sigrist, 2004 and Thomson *et al.*, 1978).

The optimum concentration of HCl was 2.00 M. Because of produced the lowest %RSD. Therefore, this concentration of HCl was chosen for further experiment.

Table 12 The relative emission signal of As(III) at various HCl concentrations

HCl concentration (mol L^{-1})	Emission signal* x $10^4 \pm$ %RSD
0.5	1.04±1.56
1	2.23±1.21
1.5	2.58±1.05
2	2.79±1.01
3	2.90±1.17
4	3.05±1.09

**5 replications*

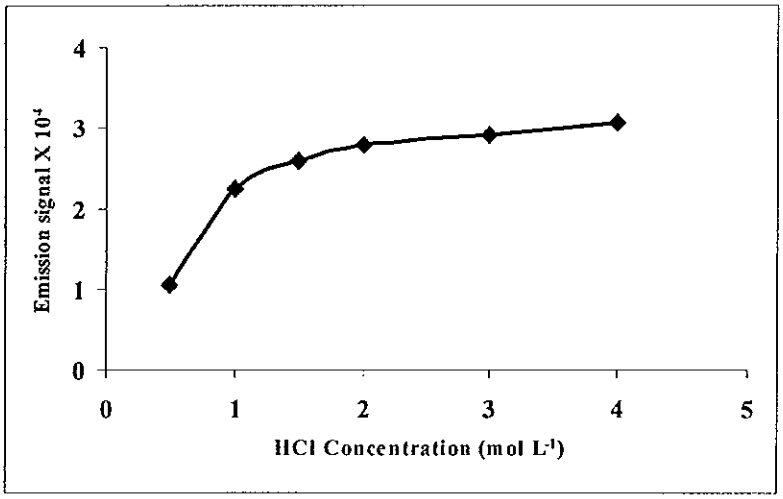

Figure 15 The relative emission signal of As(III) at various HCl concentrations

3.1.9 Reductant concentration

$NaBH_4$ was used as a reducing reagent to change arsenic to arsine gas. Therefore, the effect of $NaBH_4$ concentration was investigated at 0.1, 0.2, 0.4, 0.6, 0.8 and 1% (w/v). The results are shown in Table 13 and Figure 16. A higher signal rapidly increased when the $NaBH_4$ concentration increased up 0.1% to 0.4%, and constant value at concentration above 0.4-1%. Due to the high cost of high-purity $NaBH_4$, 0.4% was chosen as the working concentration for further experiment. The results was in agreement previously reported (Carrero *et al.*, 2001).

Table 13 The relative emission signal of As(III) at various $NaBH_4$ concentrations

$NaBH_4$ concentration (%)	Emission signal* x $10^4 \pm$ %RSD
0.1	1.51±1.23
0.2	2.31±1.20
0.3	2.97±1.59
0.4	3.46±1.96
0.8	3.57±2.45
1	3.50±3.00

**5 replications*

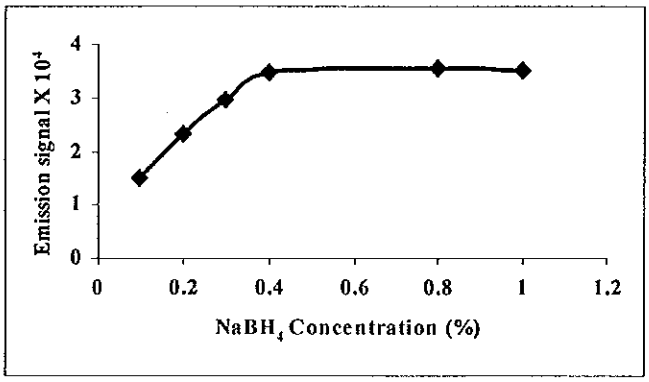

Figure 16 The relative emission signal of As(III) at various $NaBH_4$ concentrations

3.1.10 Pre-reductant concentration

The KI concentration used as a pre-reductant is one of most important parameters for reducing As(V) to As(III), by generation a more potent reducing agent than $NaBH_4$ (Aggett *et al.*, 1976 and Nielsen *et at.*, 1997). Table 14 and Figure 17 shows the response of various 5-60% (w/v) KI concentration. The optimum pre-reductant concentration was 40 % for 10 min, because of highest emission signal. Therefore, this concentration was selected for further experiments.

Table 14 The relative emission signal of As(III) at various KI concentrations

KI concentration (%)	Emission signal* x 10^3 ± %RSD
5	0.30±1.73
10	0.98±1.50
20	1.00±1.41
40	3.41±0.87
60	3.02±0.99

**5 replications*

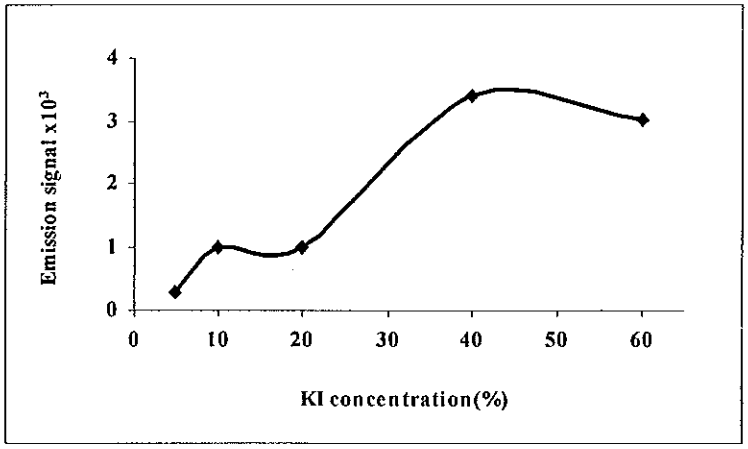

Figure 17 The relative emission signal of As(III) at various KI concentrations

3.1.11 Pre-reductant time

The reaction time for completing reduction of As(V) to As(III) was examined. Table 15 and Figure 18 show the response of the reduction time at 5 to 30 min. The optimum reduction time was 10 min and this time was used for the next experiments.

Table 15 The relative emission signal of As(III) with present for various KI times

KI time (min)	Emission signal* x 10^3 ± %RSD
5	2.30±0.73
10	3.41±0.50
20	2.07±1.01
30	1.53±1.87

**5 replications*

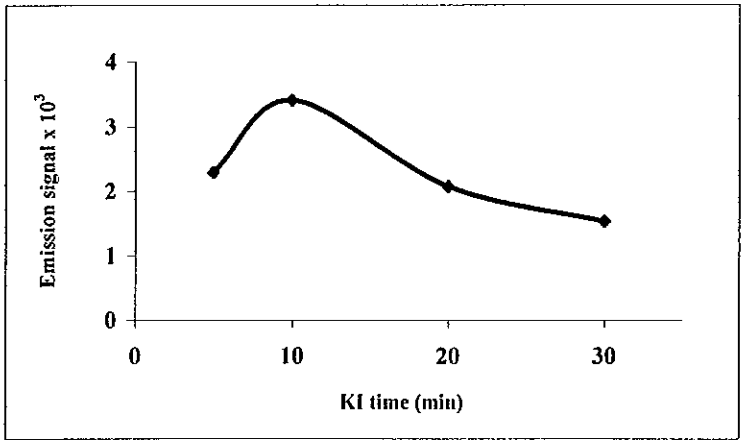

Figure 18 The relative emission signal of As(III) with present for various KI times

From this investigation the optimum conditions of the HG-ICP-OES for determination of inorganic As species are summarized in Table 16

Table 16 The optimum conditions of the HG-ICP-OES for determination of inorganic As species in this investigation.

Inductively coupled plasma optical emission spectrometer conditions	
Wavelength	193.7 nm
Measurements integration time	
Maximum	10 second
Minimum	5 second
RF power	1.3 kW.
Argon gas flow rates	
Nebulizer (Carrier gas)	0.3 L min^{-1}
Plasma	15 L min^{-1}
Auxiliary	0.2 L min^{-1}
Generator	40 MHz
Delay time	30 second
Replicates	5
Plasma viewing	axial
Hydride generation (HG) conditions	
Pumping rate	0.5 mL min^{-1}
Sample flow rate	1.2 mL min^{-1}
$NaBH_4$ and HCl flow rate	0.4 mL min^{-1}
$NaBH_4$ Concentration	0.4 % (w/v)
HCl Concentration	2 mol L^{-1}
KI Concentration	40 % (w/v)
Reduction time	10 min

3.2 Linear dynamic range

3.2.1 Linear dynamic range of total As

The emission signal response at various total As concentrations is shown in Table 17 and Figure 19 with a relative standard deviation (RSD) of less than 3% for five replicates. It was found that the optimum linear dynamic range of total As was 1-100 μg L^{-1} with a good correlation coefficient, R^2>0.9999.

Table 17 The relative emission signal response at various total As concentrations

Total As concentration (μg L^{-1})	Emission signal* x 10^3 ± %RSD
1	0.12±2.98
5	0.51±2.30
10	1.10±2.02
25	2.17±1.70
50	5.34±1.41
75	7.89±1.23
100	10.50±1.05

**5 replications*

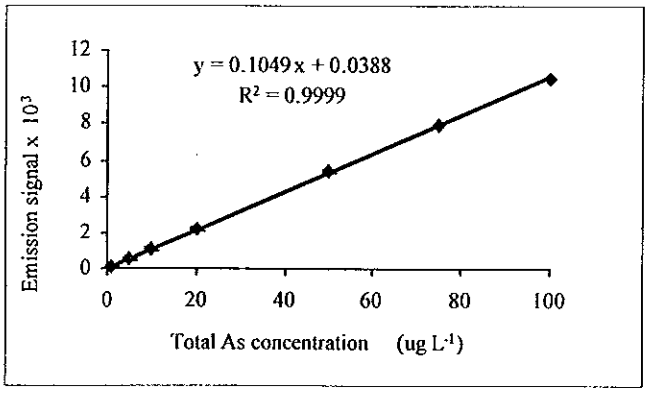

Figure 18 The calibration graph of total As concentration

3.2.2 Linear dynamic range of As(III)

Table 18 and Figure 20 show the emission signal at various As(III) concentrations giving a relative standard deviation (RSD) of less than 3% for five replicates. The results show a wide linear dynamic range of As(III) between 1-100 μg L^{-1} with a good correlation coefficient, R^2>0.9998.

Table 18 The relative emission signal at various As(III) concentrations

As(III) concentration (μg L^{-1})	Emission signal* x 10^3 ± %RSD
1	1.40±3.00
5	3.51±2.50
10	5.72±2.12
25	10.50±1.95
50	24.20±1.80
75	35.90±1.54
100	48.50±1.31

**5 replications*

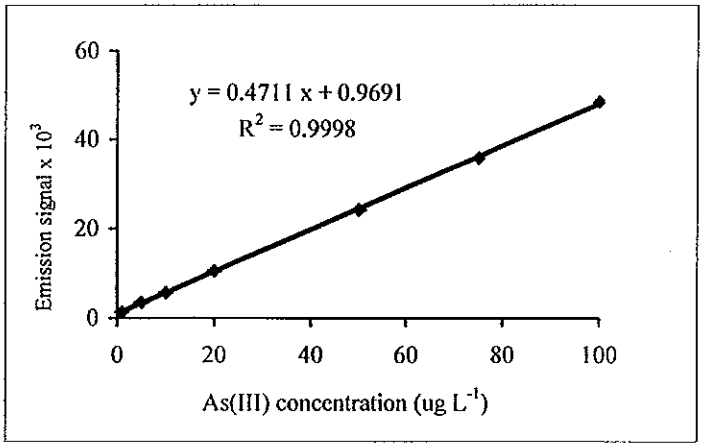

Figure 20 The calibration graph of As(III) concentrations

3.2.3 Linear dynamic range of As(V)

Table 19 and Figure 21 show the response at various As(V) concentrations with a relative standard deviation (RSD) of less than 3% for 5 replicates. The results show a wide linear dynamic range of As(V) between 1-100 μg L^{-1} with a good correlation coefficient, R^2>0.9998.

Table 19 The relative emission signal at various As(V) concentrations

As(V) concentration (μg L^{-1})	Emission signal* x 10^3 ± %RSD
1	0.19±3.00
5	0.50±2.61
10	0.99±2.10
25	1.95±1.90
50	5.80±1.61
75	7.96±1.60
100	10.50±1.25

**5 replications*

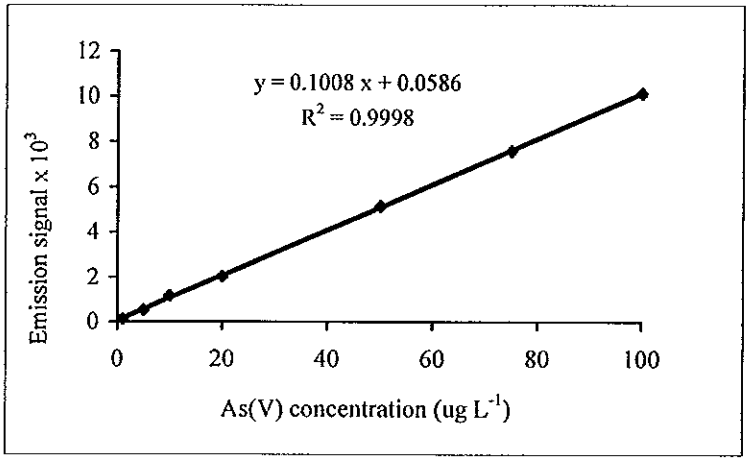

Figure 21 The calibration graph of As(V) concentrations

The linear dynamic range of three inorganic As species reaches from 1 up to 100 μg L^{-1} and covers the mostly common As concentrations in nature and also drinking water. The correlation coefficient, R^2 concerning calibration of these three inorganic As species are 0.9998-0.9999. This compares with 50 t0 200 μg L^{-1} (Gettar *et al.*, 2000) and 50 t0 100 μg L^{-1} (Wolnik *et al*, 1981).

3.3 Limit of detection and limit of quantification

The limit of detection (LOD) and limit of quantification (LOQ) of total As, As(III) and As(V) based on the calibration curve (seven standard solutions ranging from 1 to 100 μg L^{-1}, correlation coefficient R^2 = 0.9998) were tested. The limit of detection and limit of quantification were estimated from about 10 replicate peak area measurements as a concentration equivalent to three-times and ten-times (IUPAC Definition) the standard deviation of the background signal corresponding to each peak (Currie, 1999 and Taylor, 1987).

3.3.1 Limit of detection and limit of quantification total As

The total As concentrations of total As was 1 to 100 μg L^{-1} were tested with the HG-ICP-OES system. A calibration curve was then created by plotting peak area against total As concentrations. The responses are shown in Table 20, 21 and Figure 22.

Table 20 The total As concentration in blank (10 replicates)

Blank	Total As concentration in blank ($\mu g\ L^{-1}$)
1	0.020
2	0.061
3	0.063
4	0.050
5	0.064
6	0.057
7	0.045
8	0.059
9	0.046
10	0.040
Mean	0.050
SD	0.0134

Table 21 The relative emission signal at various total As concentrations

Total As concentration ($\mu g\ L^{-1}$)	Emission signal* x $10^3 \pm$ %RSD
1	0.11±2.98
5	0.52±2.30
10	1.09±2.02
25	2.20±1.70
50	5.31±1.41
75	7.80±1.23
100	10.55±1.05

**5 replications*

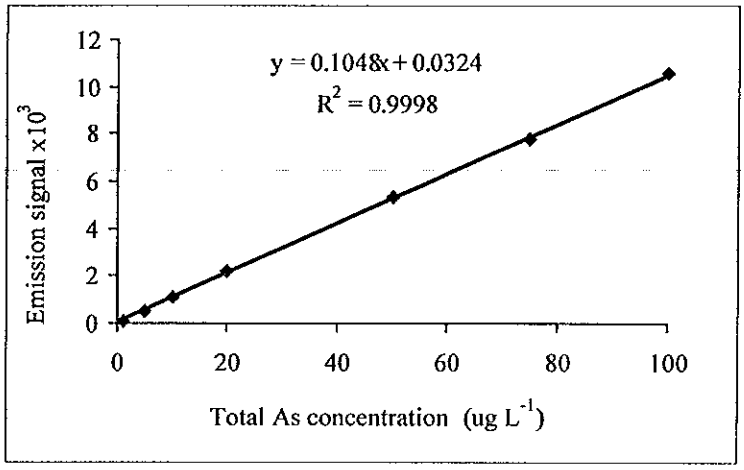

Figure 22 The calibration graph of total As concentrations

The limit of detection (3σ) for total As was calculated from the equation below:

$$C_L = kS_B / m$$

Where $k = 3$

$S_B = 0.0134$

$m = 0.0964$

$C_L = 3 \times 0.0134 / 0.1049$

$C_L = 0.38\ \mu g\ L^{-1}$

For, the limit of quantification (10σ) for total As was calculated from the equation below:

$$C_L = kS_B / m$$

Where $k = 10$

$S_B = 0.0134$

$m = 0.0964$

$C_L = 10 \times 0.0134 / 0.1049$

$C_L = 1.28\ \mu g\ L^{-1}$

Therefore, the limit of detection and limit of quantification method of total As gave a theoretical DOL of only 0.38 $\mu g\ L^{-1}$ and LOQ of 1.28 $\mu g\ L^{-1}$, respectively.

3.3.2 Limit of detection and limit of quantification As(III)

The As(III) concentrations of 1 to 100 μg L^{-1} were tested with the HG-ICP-OES system. The calibration curve was then created by plotting peak area against As(III) concentrations. The responses are shown in Table 22, 23 and Figure 23.

Table 22 The As(III) concentration in blank (10 replicates)

Blank	As(III) concentration in blank (μg L^{-1})
1	0.025
2	0.035
3	0.055
4	0.040
5	0.035
6	0.045
7	0.063
8	0.041
9	0.050
10	0.036
Mean	0.043
SD	0.0111

Table 23 The relative emission signal at various As(III) concentrations

As(III) concentration (μg L^{-1})	Emission signal* x 10^3 ± %RSD
1	1.41±3.00
5	3.50±2.50
10	5.72±2.12
25	10.50±1.95
50	24.20±1.80
75	35.90±1.54
100	48.48±1.31

**5 replications*

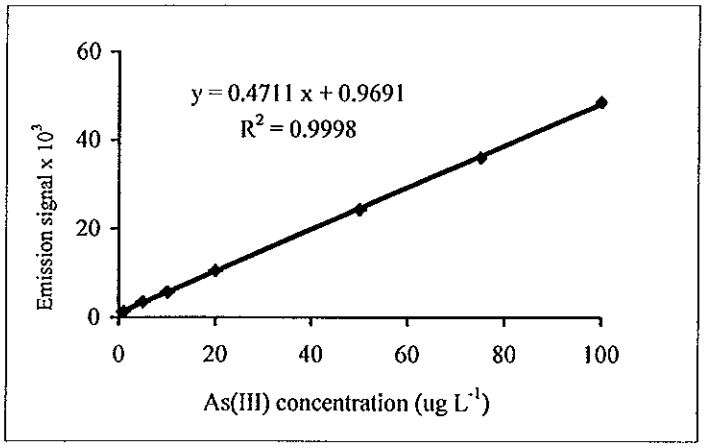

Figure 23 The calibration of As(III) concentrations

From the equation in 2.3.5, limit of detection of As(III), C_L was calculated as follow:

$$C_L = kS_B / m$$

Where $k = 3$

$S_B = 0.0111$

$m = 0.4711$

$C_L = 3 \times 0.0111 / 0.4711$

$C_L = 0.07\ \mu g\ L^{-1}$

For, the limit of quantification for As(III) was calculated from the equation below:

$$C_L = kS_B / m$$

Where $k = 10$

$S_B = 0.0111$

$m = 0.4711$

$C_L = 10 \times 0.0111 / 0.4711$

$C_L = 0.24\ \mu g\ L^{-1}$

Therefore, the limit of detection and limit of quantification method of As(III) gave a theoretical DOL of only 0.07 $\mu g\ L^{-1}$ and LOQ of 0.24 $\mu g\ L^{-1}$, respectively.

The summary of the limit of detection and limit of quantification of the total As and As(III) is shown in Table 24.

Table 24 The limit of detection and limit of quantification of total As and As(III) from this investigation

As species	Limit of detection ($\mu g\ L^{-1}$)	Limit of quantification ($\mu g\ L^{-1}$)
Total As	0.38	1.28
As(III)	0.07	0.24

The limit of detection and limit of quantification of As(III) is 0.07 and 0.24 μg L^{-1}, respectively. These compared with previous values of 1 and 10 μg L^{-1}, respectively. (Muller, 1998), and a limit of quantification of 36 μg L^{-1} (Do *et al.*, 2000). These results indicate that the scope of the method regarding its applications to real samples will be excellent for drinking water.

3.4 Accuracy

The accuracy of this method was carried out by studying % recovery. The % recovery of total As and As(III) was performed experimentally however it % recovery of As(V) concentration was obtained by calculating the of difference between total As and As(III).

3.4.1 % Recovery of total As

Total As concentrations of 4, 8, 16 and 24 μg L^{-1} were prepared in deionized water and tested in the HG-ICP-OES system. The calibration curve was then created by plotting peak area against total As concentrations as shown in Table 25 and Figure 24. With added total As amounts of 8 and 16 μg L^{-1}. The results of 7.59 and 15.69 μg L^{-1} were equal to 94.9 and 98.1% recovery, respectively as shown in Table 28.

Table 25 The relative emission signal at various total As concentrations

Total As concentration (μg L^{-1})	Emission signal* x 10^3 ± %RSD
4	0.41±3.00
8	0.81±2.91
16	1.58±2.45
24	2.34±2.09

**5 replications*

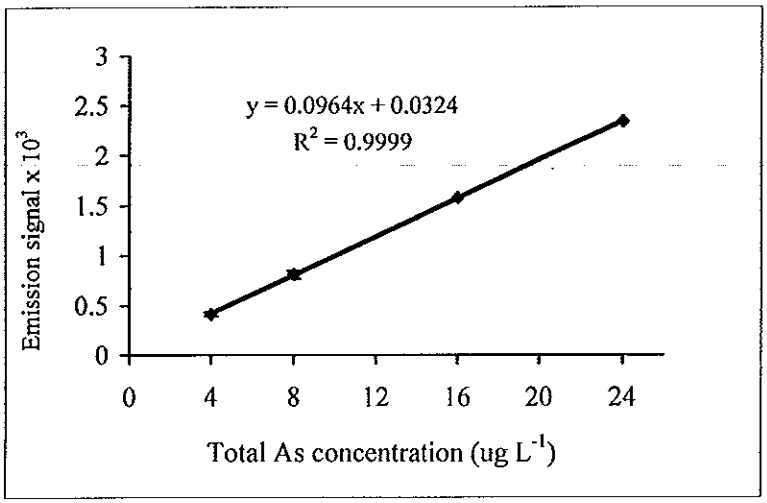

Figure 24 The calibration graph of total As concentrations

Table 26 % Recovery of total As

Added total As concentration ($\mu g\ L^{-1}$)	Found total As concentration ($\mu g\ L^{-1}$)	Recovery (%)
8	7.59	94.9
16	15.69	98.1

3.4.2 % Recovery of As(III)

As(III) concentrations of 4, 8, 16 and 24 $\mu g\ L^{-1}$ were prepared in deionized water and tested with the HG-ICP-OES system. The calibration curve was then created by plotting peak area against As(III) concentrations as shown in Table 27 and Figure 25. With added total As of 8 and 16 $\mu g\ L^{-1}$ value of 7.83 and 15.85 $\mu g\ L^{-1}$ were obtained equal to 97.9 and 99.1% recovery, respectively as shown in Table 28.

Table 27 The relative emission signal at various As(III) concentrations

As(III) concentration ($\mu g\ L^{-1}$)	Emission signal* x $10^3 \pm$ %RSD
4	1.79±3.00
8	4.15±2.96
16	8.58±2.12
24	13.41±1.40

**5 replications*

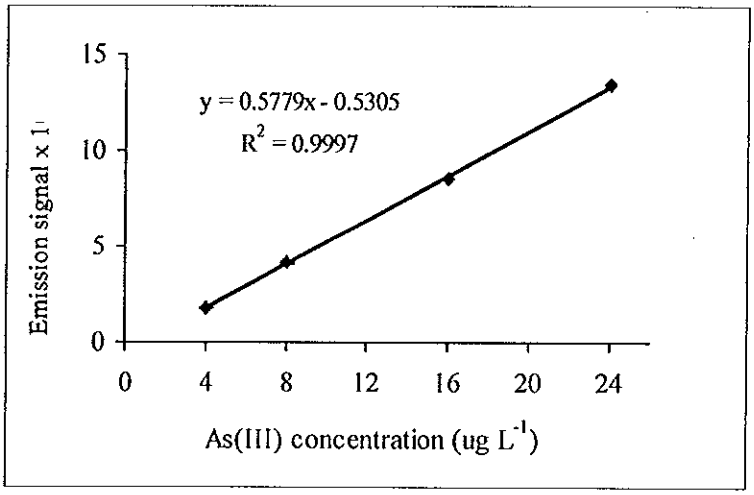

Figure 25 The calibration graph of As(III) concentrations

Table 28 % Recovery for As(III)

Added As(III) concentration ($\mu g\ L^{-1}$)	Found As(III) concentration ($\mu g\ L^{-1}$)	Recovery (%)
8	7.83	97.8
16	15.85	99.1

3.4.3 % Recovery of As(V)

The As(V) concentration was obtained by the difference between total As and As(III). From the calculation, it was found that the % recovery of As(V) was 96.9 and 98.3%, respectively as shown in Table 29.

Table 29 % Recovery of As(V)

Added total As ($\mu g\ L^{-1}$)	Found total As ($\mu g\ L^{-1}$)	Found As(III) ($\mu g\ L^{-1}$)	Found As(V) ($\mu g\ L^{-1}$)	Recovery (%)
8	7.59	3.72	3.87	96.9
16	15.69	7.83	7.86	98.3

The summary of % recovery with added the total As As(III) and As(V) concentration of 8 and 16 $\mu g\ L^{-1}$ into a blank is shown in Table 30.

Table 30 The % recovery of total As, As(III) and As(V) concentration of 8 and 16 $\mu g\ L^{-1}$ into a blank from this investigation

As species	Recovery of added 8 $\mu g\ L^{-1}$ As species into a blank (%)	Recovery of added 16 $\mu g\ L^{-1}$ As species into a blank (%)
Total As	94.9	98.1
As(III)	97.8	99.1
As(V)	96.9	98.3

The accuracy of three As species are found in the range of 94.9-99.1% recovery. The obtained results show that this method can be successfully applied to selective these three As species determination in such as natural and also drinking water samples.

3.5 Sample analysis

Drinking water samples was selected to study real samples for inorganic As determination. The five samples of drinking water were purchased from a supermarket in Had Yai, Songkhla. The quantitative analysis of total As, As(III) and As(V) was evaluated by using the calibration graph and spiking technique to check the accuracy of this method for drinking water samples.

3.5.1 Quantitative analysis of total As in drinking water

The calibration curve method was used to determine total As concentration in drinking water samples with the optimum conditions previously described in Table 16. This method is not suitable for very low concentration of total As due to the concentration of As in drinking water being below the detection limit of this investigation method as shown in Table 31.

Table 31 Total As concentration of drinking water samples determined by calibration curve method using HG-ICP-OES system with optimum conditions

Sample No.	Total As concentration ($\mu g\ L^{-1}$)
1	*n.d.*
2	*n.d.*
3	*n.d.*
4	*n.d.*
5	*n.d.*

n.d. = not-detectable

Further analysis was carried out with a calibration curve of total As at concentrations of 4, 8 and 12 $\mu g\ L^{-1}$ and then spiking at 8 and 16 $\mu g\ L^{-1}$ of total As into the drinking water samples to evaluate % recovery. The result is shown in Table 32-33.

Table 32 % Recovery of total As with spiked 8 μg L^{-1} in drinking water samples

Sample No.	Found total As conc. of spiked at 8 μg L^{-1} (μg L^{-1})	Recovery of total As at 8 μg L^{-1} (%)
1	7.50	93.8
2	7.13	89.1
3	7.36	92.0
4	6.97	87.2
5	6.90	86.3

**5 replications*

Table 33 % Recovery of total As with spiked 16 μg L^{-1} in drinking water samples

Sample No.	Found total As conc. of spiked at 16 μg L^{-1} (μg L^{-1})	Recovery of total As at 16 μg L^{-1} (%)
1	16.14	100.9
2	15.42	96.3
3	15.14	94.6
4	15.07	94.2
5	14.83	92.7

**5 replications*

The % recovery of 8 and 16 μg L^{-1} total As were in the range of 86.3-93.8 and 92.7-100.9% respectively.

3.5.2 Quantitative analysis of As(III) in drinking water

The calibration curve method was used to determine As(III) concentration in drinking water samples with the previous optimum conditions previously described in Table 16. This method is not suitable for very low

concentration of As(III) due to the concentration of As in drinking water being below the detection limit of this investigation method as shown in Table 34.

Table 34 As(III) concentration of drinking water samples determined by calibration curve method using HG-ICP-OES system with optimum conditions

Sample No.	As(III) concentration ($\mu g\ L^{-1}$)
1	*n.d.*
2	*n.d.*
3	*n.d.*
4	*n.d.*
5	*n.d.*

n.d. = not-detectable

Further analysis was carried out with the calibration curve of As(III) at concentration of 4, 8 and 12 $\mu g\ L^{-1}$ and then spiking 4, 8 and 12 $\mu g\ L^{-1}$ of As(III) into the drinking water samples to evaluate % recovery. The result is shown in Table 35-37.

Table 35 % Recovery of As(III) with spiked 4 $\mu g\ L^{-1}$ in drinking water samples

Sample No.	Found As(III) conc. of spiked at 4 $\mu g\ L^{-1}$ ($\mu g\ L^{-1}$)	Recovery of As(III) at 4 $\mu g\ L^{-1}$ (%)
1	3.73	93.2
2	3.59	89.7
3	3.93	98.2
4	3.80	95.0
5	3.61	90.1

**5 replications*

Table 36 % Recovery of As(III) with spiked 8 μg L^{-1} in drinking water samples

Sample No.	Found As(III) conc. of spiked at 8 μg L^{-1} (μg L^{-1})	Recovery of As(III) at 8 μg L^{-1} (%)
1	7.21	90.1
2	7.38	92.3
3	7.57	94.6
4	7.56	94.5
5	7.58	94.5

**5 replications*

Table 37 % Recovery of As(III) with spiked 12 μg L^{-1} in drinking water samples

Sample No.	Found As(III) conc. of spiked at 12 μg L^{-1} (μg L^{-1})	Recovery of As(III) at 12 μg L^{-1} (%)
1	11.00	91.7
2	11.01	91.8
3	11.17	93.01
4	11.06	92.2
5	10.95	91.3

**5 replications*

It was found that the % recovery of the 4, 8 and 12 μg L^{-1} spikes were in the range of 89.7-98.2, 90.1-94.6 and 91.3-93.1 % respectively.

3.6.3 Quantitative analysis of As(V)

The As(V) concentration was obtained by calculating total As –As(III). The result from Table 38 shows that the % recovery of 4 μg L^{-1} As(V) was in the range 79.4-94.3% and for 8 μg L^{-1} As(V) was in the range 90.7-111.6%.

Table 38 % Recovery of As(V) drinking water samples

Sample No.	Total As-As(III) (8-4 μg L^{-1}) =As(V) 4 μg L^{-1}*	Total As-As(III) (16-8 μg L^{-1}) =As(V) 8 μg L^{-1}*
1	7.50-3.73 = 3.77 (94.3%)	16.14-7.21 = 8.93 (111.6%)
2	7.13-3.59 = 3.54 (88.5%)	15.42-7.38 = 8.04 (100.5%)
3	7.36-3.92 = 3.44 (85.9%)	15.14-7.57 = 7.57 (94.6%)
4	6.97-3.80 = 3.17 (79.3%)	15.07-7.56 = 7.51 (93.9%)
5	6.90-3.61 = 3.29 (82.3%)	14.83-7.58 = 7.25 (90.6%)

**By calculating the total As-As(III) in Table 32-35, and 33-36, 5 replications*

The summary of three inorganic As concentrations of drinking water samples determined by standard curve method is shown in Table 39.

Table 39 Inorganic As concentrations of drinking water samples determined by standard curve method

Sample No.	Amount of As μg L^{-1}		
	Total As	As(III)	As(V)
1	*n.d.*	*n.d.*	*n.d.*
2	*n.d.*	*n.d.*	*n.d.*
3	*n.d.*	*n.d.*	*n.d.*
4	*n.d.*	*n.d.*	*n.d.*
5	*n.d.*	*n.d*	*n.d*

n.d. = not-detectable

The results was applied to determine inorganic As species in drinking water samples. As was not detected. Because the amounts of these As in drinking water samples is lower than the limit of detection of this technique, and lower than standard value in drinking water (WHO, 2003). It was found that % recovery of these As in five drinking water samples were 79.3-111.6, and then this method is high accuracy.

It can be concluded that the method established in this investigation is suitable for determination of inorganic As species because it is easy to manipulate, rapid and economic. However, this method is not applicable if the samples have very low concentrations (part per thousand billion, $\eta g\ L^{-1}$), so a preconcentration method must be applied to overcome this problem.

Chapter 4

Conclusion

The modify and optimize of an online hydride generation technique combined with an inductively coupled plasma optical emission spectrometer (HG-ICP-OES) was established for determination of inorganic As species in drinking water samples. It was found that the optimum conditions for inductively coupled plasma optical emission spectrometry in these experiments were a wavelength of 193.7 nm, integration time at a minimum of 5 up to a maximum of 10 seconds, RF power at 1.3 kW, plasma gas flow rate of 15 L min^{-1}, and auxiliary gas flow rate of 0.2 L min^{-1}.

Conventional hydride generation is a very expensive and a long time-consuming process. To overcome these disadvantages, a more economical, minimization of labor and faster continuous flow hydride generation combined with inductively coupled plasma optical emission spectrometry method has been developed.

In addition, a continuous flow hydride generation system was also developed in this experiments. Arsenic in the sample was reduced to arsine by using sodium borohydride as a reductant and hydrochloric as an acid medium. The three solutions were continuously pumped by using three-channels of a peristaltic pump of the inductively coupled plasma system into the manifold. After that the mixed solutions were transported with argon carrier gas into the mixing coil, and pass into the gas/liquid separator for separating arsine gas into the hydride connector of the inductively coupled plasma optical emission spectrometer for analysis. The hydride generation system conditions were optimized. The results showed that the optimum conditions were: a sample flow rate of 1.2 mL min^{-1}, reductant and acid of 0.4 mL min^{-1} and argon carrier gas of 0.3 L min^{-1}, respectively. The parameters affecting the hydride efficiency were studied. Then, the conditions of total As and As(III) determination were optimized. The results showed that the conditions for

total As determination were 0.4% (w/v) $NaBH_4$ in 2 mol L^{-1} of HCl with 10% (w/v) KI as a pre-reductant for 10 min and for As(III) conditions were 0.4% (w/v) $NaBH_4$ as a reductant in 2 mol L^{-1} of HCl. As(V) was calculated by the difference of total As and As(III).

This method could be used to analyze the inorganic As species including total As, As(III) and As(V) with high precision with RSD of less than 3% for five replicates. The results of the three inorganic As species have a linear dynamic range of 1-100 μg L^{-1} with correlation coefficient, R^2 are 0.9998-0.9999. This compares with 50 t0 200 μg L^{-1} and 50 t0 100 μg L^{-1}, respectively (Gettar *et al*, 2000 and Wolnik *et al*, 1981). It showed this method successfully used covers the most common As concentrations found in nature also drinking water.

The limit of detection (LOD) and limit of quantification (LOQ) of total As were 0.38 and 1.28 μg L^{-1}, As(III) were 0.07 and 0.24 μg L^{-1}, and As(V) were 0.37 and 1.17 μg L^{-1}, respectively. These compared with previous values of 1 and 10 μg L^{-1}, respectively (Muller, 1998) and a limit of quantification of 36 μg L^{-1} (Do *et al.*, 2000). LOD and LOQ are better than those obtained pervious reported. It showed this method is high sensitivity. The accuracy of three As species are found in the range of 94.9-99.1% recovery. It showed this method is high accuracy. The obtained results show that this method can be successfully applied to selective these three As species determination in such as natural and also drinking water samples.

The inorganic As species in drinking water samples obtained from a supermarket, in Had Yai, Songkhla were analysed. As was not detected of all inorganic As species. Because their concentrations were lower than the detection limit of this technique, and lower than 10 μg L^{-1} of standard value in drinking water (WHO, 2003). In addition the % recovery of inorganic As species added to drinking water at 4, 8 and 12 μg L^{-1} were in the range of 79.3-111.6%.

In conclusion, this HG-ICP-OES technique is a suitable technique which can be used to determine three inorganic As species in drinking water samples. Because its provided high sensitivity. In addition, its simple performance, easy to operate and rapid technique, with less than 30 seconds per sample.

References

Agency for Toxic Substances and Disease Registry (ATSDR). 2000. Toxicology Profile for Arsenic (draft) U. S. public health service, U. S. department health and human service, Altanta, GA. Also available at http://www.atsdr.cdc.gov/clist.html.

Aggett, J. and Aspell, A.C. 1976. The determination of arsenic(III) and total arsenic by atomic absorption spectrometry. *Analyst.* 101: 341-347.

Arrykul, S., Kooptarnon, K.and Witayarawat, W. 1996. "Contamination of Arsenic, Cadmium and Lead in Pakphanang River Basin, Nakhon Si Thammarat, Thailand". (31 Jan-2Feb). pp. 309-318. Changmai.

Barra, M.A., Luisa Cervera, M. De la Guardia, M and Erthal Santellli, R. 2000. Atomic fluorescence determination of inorganic arsenic in soils after microwave-assisted distillation. *Analytica Chimica Acta.* 407: 155-163.

Boss, C.B. and Fredeen, K.J. 1997 (Copyright). "Concepts, instrumentation and techniques in inductively coupled plasma atomic emission spectrometry". 2nd Edition. The Perkin-Elmer Corporation.

Carrero, P., Malave, A. and Burguera, J.L. 2001. Determination of various arsenic species by flow injection hydride generation atomic absorption spectrometry:differet reaction media on the generation of arsines. *Analytica Chimica Acta.* 438: 195-204.

Currie, L.A. 1999. Nomenclature in evaluation of analytical methods including determination and quantification capabilities (IUPAC Recommendation 1995). *Analytica Chimica Acta.* 391: 105-126.

Davidowski, L. 1997. A simple continuous flow hydride generator for ICP-OES. *ICP Application Study.* 67: 1-6.

Ding, W.W. and Sturgeon, R.E. 1997. Minimization of transition metal interferences with hydride generation techniques. *Anal Chem.* 69: 527-531.

Do, B., Alet, P., Pradeau, D., Poupon. J., Guilley-Gaillot, M., and Guyon, F. 2000. On-line reversed-phase liquid chromatography hydride generation emission spectrometry: speciation of arenic in urine of patients intravenously treated with As_2O_3. *Journal of Chromatography.* 740: 179-186.

Frerreira, M.A. and Barros, A.A. 2002. Determination of As(III) and As(V) in natural waters by cathodic stripping voltammetry at a hanging mercury drop electrode. *Analytica Chimica Acta.* 459: 151-159.

Gettar, R.T., Garavaglia, R.N., Gautier, E.A., and Batistoni, D.A. 2000. Determination of inorganic and organic anionic arsenic species in water by ion chromatography coupled to hydride generation-inductively coupled plasma emission specrtometry. *Journal of Chromatography A.* 884: 211-221.

Goessler, W. and Pavkov, M. 2003. Accuracy quantification and transformation of arsenic compounds during wet ashing with nitric acid and microwave assisted heating. *Analyst.* 128: 769-802.

Gong, Z., Chan, W.F., Wang, X. and Lee, F.S.C. 2001. Determintion of arsenic and antimony by microwave plasma atomic emission coupled with hydride generation and a PTFE membrane separator. *Analytica Chimica Acta.* 450: 207-214

Ingle, J. and Crouch, S. 1988. "Spectrochemical analysis". Prentice-Hall International. London, UK.

International Agency for Research on Cancer (IARC). 1987. *IARC Monograph on the Evaluation of Carcinogenic Rick of Chemical to Human. Suppl.7.* Overall Evaluations of Carcinogenicity, Updating of IARC Monographs, Vol. 1-42. World Health Organization, IARC, Lyon, France, pp.29-33, 57.

Japan International Cooperation Agency (JICA), The Kingdom of Thailand, and The Ministry of Science, Technology and Environment, 2000. Final Report (Summary) on the Environmental Planning Survey for Arsenic Contaminated Area of the Nakhon Si Thammarat Province in the Kingdom of Thailand. Misui Mineral Development Engineering Co., Ltd. And Kokusai Kogyo Co., Ltd.

Klaue, B. and Blum, J.D. 1999. Trace analysis of arsenic in drinking water by inductively coupled plasma mass spectrometry:high resolution versus hydride generation. *Anal. Chem.* 71:1408-1414.

Muller, J. 1999. Determination of inorganic arsenic(III) in groundwater using hydride generation coupled to ICP-AES (HG-ICP-AES) under variable sodium boro hydride ($NaBH_4$) concentrations. *Fresenius J Anal Chem.* 363: 572-576.

Nielsen, S. and Hansen, E.H. 1997. Determination of As(III) and As(V) by flow injection-hydride generation-atomic absorption spectrometry via on-line reduction of As(V) by KI. *Analytica Chimica Acta.* 343:5-7.

Ng, J.C., Johnson, D., Imray, P., Chriswell, B. and Moore, M.R. 1998. Speciation of arsenic metabolites in the urine of occupational workers and experimental rats using an optimized hydride cold-trapping method. *Analyst.* 123: 929-933.

Nriagu, J.O. 1994. "Arsenic in the environment. Part I: Cycling and Characterization". Wiley, New York.

Semenova, N.V., Bauza de Mirabo, F.M., Forteza, R. and Cerda, V. 2000. Sequential injection analysis system for total inorganic arsenic determination by hydride generation-atomic fluorescence spectrometry. *Analytica Chimica Acta.* 412: 169-175

Shraim, A., Chiswell, B., and Olszowy, H. 2000. Use of perchloric acid as a reaction medium for speciation of arsenic by hydride generation-atomic absorption spectrometry. *Analyst.* 125: 949-953.

Shraim, A., Hirano, S., and Yamauchi, H. 2001. Extraction and speciation of arsenic in hair using HPLC-ICPMS. *Analytical Science.* 17: 729-732.

Sigrist, M.E. and Beldomenico, H.R. 2004. Determination of inorganic arsenic species by flow injection hydride generation atomic absorption spectrometry with variable sodium tetrahydroborate concentrations. *Spectroshimica Acta Part B.* 9: 1041-1045.

Smedley, P.L. and Kinniburgh, D.G., 2001. Source and hehaviour of arsenic in natural waters. United Nations Synthesis Report on Arsenic in Drinking Water., Available http://www.who.int/water_sanitation_health/Arsenic UNRep1.html.

Taylor, J.K. 1987. "Quality assurance of chemical measurements". Lewis Publishers, Inc. Michigan, USA.

Thompson, M., Pahlavanpour, B., Walton, S.J., and Kirkbright, G.F. 1978. Simultaneous determination of trace concentrations of arsenic, antimony, bismuth, selenium and tellurium in aqueous solution by introduction of gaseous hydride into an inductively coupled plasma source for emission spectrometry. *Analyst.* 103: 703.

Tian, D.X., Zhuang, Z.X., Chen, B and Wang, X.R. 1998. Movable reduction bed hydride generator coupled with inductively coupled plasma optical emission

spectrometry for the determination of some hydride forming element. *Analyst.* 123: 627-632.

Villa-Lojo, M.C., Alonson-Rodriquez, E. Lopez-Mahia, O., Muniatequi-Lorenzo, S and Prada-Rodriquez, D. 2002. Couple high performance liquid chromatography-microwave dogestion-hydride generation-atomic absorption spectrometry for inorganic and organic arsenic speciation in fish tissue. *Talanta.* 57: 741-750.

Varma, A. 1991. "CRC Handbook of inductively coupled plasma optical emission spectrometry". Boca Raton, Fl: CRC Press.

William, M., Fordyce, F., Paijitprapapon, A., and Charoenchaisre, P. 1996. Arsenic contamination in surface drainage and groundwater in part of the southeast Asian tin belt, Nakhon Si Thammarat Province, Southern Thailand. *Environmental Geology.* 27: 16-33. http:www.psu.ac.th/epidemiology.

Wolnik, M.A. and Fricke, F.L. 1981. Sample introduction system for simultaneouse determination volatile elemental hydrides and other elements in foods by inductively coupled argon plasma emission spectrometry. *Analtical Chemisrty.* 53: 1030-1035.

World Health Organization. 2003. Guideline for Drinking Water Quality 2nd ed. WHO, Geneca.

Wrobel, K., Wrobel, K., Parker, B., Kannamkumarath, S.S., and Caruso, J.A. 2002. Determination of As(III), As(V), monomethylarsonic acid, dimethylarsinic acid and arsenobetaine by HPLC-ICP-MS: analysis of reference materials, fish tissues and urine. *Talanta.* 58: 899-907.

USEPA, 2001-a. Arsenic in Drinking water, Analytical Methods, Available at http://www.epa.gov/safewater/ars/ars7.html.

USNRC (United State National Research Council), 1999. Arsenic in Drinking Water. National Academy Press. Also available at http://www.nap.edu.

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Muakthong, D. and Wararatananurak, P. 2003. "Arsenic Speciation Analysis in Environmental Using On-line Continuous Flow Hydride Generation combined with Inductively Coupled Plasma Optical Emission Spectrometry (CFHG-ICPOES)". Poster presentation at the 29th Congress on Science and Technology of (20-22 October). Khonkan, Thailand.

Muakthong, D. and Wararatananurak, P. 2003. "Arsenic Speciation by Continuous Flow Hydride Generation-Inductively Coupled Plasma Optical Emission Spectrometry (CFHG-ICPOES)". Poster presentation at the 2nd PERCH Annual Scientific Conference. (11-14 May). Pattaya, Thailand.