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Specific speciation of As(III) and As(V) in aqueous solution by a split microfluidic chemiluminescence system

N. Taokaenchan, R. Puntharod, T. Tangkuaram, P. Pookmanee, S. Phaisansuthichol, S. Sangsrichan and S. Satienperakul*

Department of Chemistry, Faculty of Science, Maejo University, Chiang Mai 50290, Thailand, e-mail: sakchais@mju.ac.th

The simultaneous determination of As(III) and As(V) in aqueous solution based on the acidic permanganate and luminol chemiluminescence (CL) detection systems have been applied to a split microfluidics flow injection (μFI) with dual-channel manifolds at rapid sampling rate. The μFI-CL system consisted of two halves of micro-conduit platforms, which ran on a simple device made from small pieces of the laser engraved polymethylmethacrylate (PMMA) and polydimethylsiloxane (PDMS). The specific CL reaction for As(III) was produced by the oxidation of acidic potassium permanganate in the presence of sodium hexametaphosphate media, while the CL reaction for As(V) was generated based on the oxidation of luminol with a vanadomolybdoarsenate heteropoly acid (AsVMo-HPA) complex in an alkaline solution. The μFI method involved the injection of the mixed standard solution into an acid carrier stream where it was then splitted and merged with the reagent solutions of each reaction systems on a spiral-designed microfluidic platform. The solution mixtures were passed through each spiral flow channel, where the CL intensity of both resulting reaction mixtures were measured with two photomultiplier tubes. Linear calibratons for As(III) and As(V) were established over the concentration ranges of 20-60 μg L^{-1}. The limits of detection (signal-to-noise ratio of 3) of As(III) and As(V) were found to be 4 μg L^{-1} and the limits of quantification (signal-to-noise ratio of 10) were found to be 10 μg L^{-1}, respectively. The proposed procedure was successfully applied for the determination of As(III) and As(V) in ground water samples.

Introduction

Arsenic is a naturally occurring element present in the environment in both organic and inorganic forms. Inorganic arsenic is considered to be the most toxic form of the element, and arsenic contamination of ground water is found in many countries throughout the world, including China, Bangladesh, Vietnam and Thailand. The presence of arsenic in natural water is of concern because of its toxicity and possible carcinogenic activity, and the biological effects of arsenic are significantly altered by its oxidation state as well as by its complexation with organic materials. Depending on the environment, inorganic arsenic can exist in two different oxidation states As(III) and As(V) in natural water, although As(V) is thermodynamically favored. Because of its ability to form complexes with certain co-enzymes, however, As(III) is more toxic to animal and plants than As(V).The USEPA reduces the maximum permissible level (MPL) of arsenic in drinking water from 50 to 10 μg L^{-1} [1]. Current arsenic detection always relies on large apparatus including atomic absorption spectrometry (AAS) [2], hydride generation atomic fluorescence spectrometry (HGAFS) [3-6], inductively coupled plasma atomic emission spectrometry (ICP-AES) [7-9] and inductively coupled plasma mass spectrometry (ICP-MS) [10-12]. The USEPA approved spectrometric methods are all based on atomic spectrometry which can readily provide detection limits in the sub-microgram per liter range, but the instrumentations are bulky, expensive, and require large amounts of pure gas in addition to the high cost of consumables. Hence, the alternative, portable and sensitive equipment is continually demanded for on-site measurement.

Microfluidic devices currently present unique advantages for sample handling, reagent mixing, separation, and detection. Microfluidic channel dimensions typically range from 1 to 1000 μm in width and height and require between 100 nL and 10 μL of sample and reagents. In addition to obvious advantages that are associated with smaller samples, reagent and waste volumes required which is ideal for handling costly and difficult-to-obtain samples and reagents. The materials used to construct microfluidic devices vary, depending on the application; however, the vast majorities are constructed of glass, silicon, polymers or even filter paper using photolithography to define hydrophobic micro-channels. One particular polymer that has recently been used extensively is poly (dimethylsiloxane), or PDMS since PDMS is a transparent, elastomeric polymer that can be fabricated rapidly by laser engraving with features having dimensions as small as 10 nm. The elastomeric nature of PDMS makes it a great sealant, since often the adhesion due to conformal surface contact with a smooth, flat surface is enough to seal meso- or even microchannels for low pressure applications [13, 14].

During the past decades, there have been word-wide efforts to develop miniaturized instrumentation for chemical analysis. However, the utilization of microfluidics in the attempts for the determination of arsenic has rarely appeared. One attempted had been reported by Matusiewicz *et al*.[15]. Only few reports exploited the use of chemiluminescence (CL) detection to determine inorganic arsenic spices and most of them were based on a flow injection (FI) system [16, 17].

In this present work, the integration of a microfluidic device with CL detection for the determination of As(III) and As(V) in aqueous samples is proposed. Since, CL provides high sensitivity and selectivity, while it is a simple and inexpensive optical instrumentation. The acidic permanganate and luminol chemiluminescence detections have been allocated for our system. The sandwich type microfluidics chip consisted of two halves of spiral conduit platforms where the CL reaction for As(V) was generated based on the oxidation of luminol with a vanadomolybdoarsenate heteropoly acid (AsVMo-HPA) complex in an alkaline solution. On the other hand the CL reaction for As(III) was produced by the oxidation of acidic potassium permanganate in the presence of a sodium hexametaphosphate media.

Experimental

Chemical and apparatus

All chemicals used are analytical reagent (AR) grade, and all standard and reagent solutions were prepared with deionized water. As(III) and As(V) stock solution (1,000 mg L^{-1}) were prepared by dissolving 0.1734 g of $NaAsO_2$ (Ajax, Australia) and 0.4160 g of $Na_2HAsO_4{\cdot}H_2O$ in 100 mL of deionized water, respectively. The As(III) and As(V) stock solutions were kept in a sealed container in a refrigerator at 4

°C when not in use. Standard solutions of As(III) and As(V) (4-60 µg L^{-1}) were made up by making appropriate dilution of As(III) and As(V) stock solution in 6.0 mM sulfuric acid solution. Potassium permanganate stock (1.0×10^{-2} M) was prepared by dissolving 0.1578 g of $KMnO_4$ (Ajax, Australia) in 100 mL deionized water. Rhodamine B solution (100 mg L^{-1}) was prepared by dissolving 0.01 g of $C_{28}H_{31}ClN_2O_3$ (Fluka, UK) in 100 mL deionized water. The stock solution of luminol (1.0×10^{-2} M) was prepared by dissolving 0.0886 g of luminol (Sigma-Aldrich, USA) in 50 mL of 0.1 M NaOH solution. Ammonium metavanadate solution (0.1 M) was prepared by dissolving 1.17 g of NH_4VO_3 (BDH, UK) in 0.02 M sulfuric acid solution. Ammonium molybdate solution (0.1M) was prepared by dissolving 12.40 g of $(NH_4)_6Mo_7O_{24}.4H_2O$ (BDH, UK) in 0.02 M sulfuric acid solution

The carrier stream solution (C) was a 6.0 mM of sulfuric acid. The reagent stream solution (R1) comprises of acidic potassium permanganate (1.5×10^{-4} M), and Rhodamine B (8 mg L^{-1}) was prepared by making appropriate dilution of the $KMnO_4$ stock solution and Rhodamine B solution in 0.70 % (m/v) sodium hexametaphosphate (Sigma-Aldrich, USA) diluents in 6.0 mM sulfuric acid solution. The mixed carrier solution (R2) of 0.70 % (m/v) sodium hexametaphosphate and formaldehyde (1.7 M) was prepared by making appropriate dilution a 32 mL of concentrate formaldehyde (BDH, UK) in 0.70 % (m/v) of sodium hexametaphosphate and 6.0 mM sulfuric acid solution in 250 mL volumetric flask. The heteropoly acid solution (R3) consisted of 8.0×10^{-4} M ammonium metavanadate, 7.0×10^{-3} M ammonium molybdate was prepared by making appropriate dilution of ammonium metavanadate solution and ammonium molybdate solution in 0.03 M sulfuric acid. The luminol solution (R4) was prepared by making appropriate dilution of luminol stock solution to the final concentration of 5.0×10^{-5} M in 0.10 M NaOH solution.

Design and fabrication of microfluidic device

The microchannel was designed by Adobe IIustrator 10 software and a designed-microchannel was illustrated in Figure 1(A). CO_2 laser was used for the engraving and cutting of a microchannel in the polymethyl methacrylate (PMMA) followed by the pattern. The flow conduit comprises the carrier and reagent stream inlets, a spiral coil of a 500 µm-wide and 200 µm-deep of all 52.0 cm-long channel with 2.5 cm diameter. The microchip consisted of two halves of similar CL micro-conduit platforms sandwiched with polydimethyl-siloxane (PDMS) middle sheet prepared by mixing of 10:1 prepolymer and curing agent (Sylgard 184, Dow Corning, Midland, USA). The prepolymer mixture was stirred thoroughly and degassed in a vacuum for 15 min, then poured onto the glass slide template and cured at 70 °C for 1 h. After curing, the PDMS replica was peeled from the template and cut to respectively sheet size. The completed set up microfluidic device was declared as sandwich type as illustrated in Figure 1(B) with aluminium foil sheet was put in the middle. After that the device was sealed by tightening the PMMA sandwich sheets with 6 screws.

Instrument set-up

The µFI -CL system used in all experiment is depicted in Figure 2. The experimental setup consisted of five peristaltic pumps with rate selector (Minipuls 3, Gilson, France), a sample injection vale (V-450, Upchurch Scientific, USA) and PTFE connection tubing (0.5 mm i.d., Agilent, USA). The CL signals were monitored in custom built flow-through luminometer, where a microfluidic device was mounted flush against two sensitive photomultiplier tubes (PMT, 9828SB and 9924SB, ET-enterprise, UK). The operational potential for both PMTs was provided by two high voltage power supplies (Thorn- EMI model PM20, Electron tubes Ltd., UK) at the voltage of 0.85 and 0.90 kV, respectively. The output signal of the PMTs, proportional to the CL intensity, were monitored continuously and displayed by a personal computer via a digital multimeter USB/RS-232 (UT60G, Hong Kong) interface with the voltage divider (C637BFN2, Electron Tubes, UK). The UNI-T® UT60G AC/DC software was used to determination of the peak maximum.

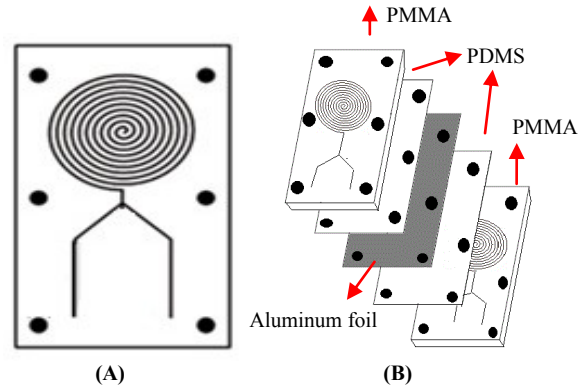

Figure 1 Illustration of the laser-engraved flow lines of the microfluidic platform (A); a sandwich type microfluidic device (B).

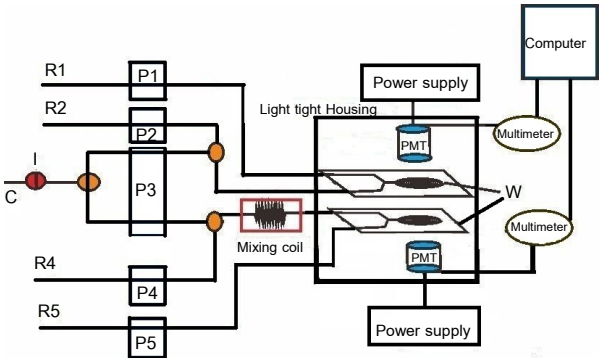

Figure 2 Manifold of a split microfluidics flow injection (µFI-CL) system for determination of As (III) and As (V)
R1 = acidic potassium permanganate, R2 = sodium hexametaphosphate/ formaldehyde, C = carrier stream (sulfuric acid), R3 = ammonium metavanadate/ammonium molybdate, R4 = luminol, W = waste, I = injection valve and PMT = photomultiplier tube

Preparation of samples

Seven ground water samples were collected from arsenic contaminated areas of Hang Chat district in Lampang province, Thailand, which is suffering from nearby mining and industrial waste landfill impacts. Water samples were collected in 1000 mL of clean PE containers, then the samples were treated by adding 2 mL of sulfuric acid and cooled at 4 °C until analysis. Samples were filtered through a 0.45 µm nylon filter to remove solid particles prior to analysis.

Analytical procedure

A 150 µL of mixed standard or sample solution was injected into 6.0 mM sulfuric acid carrier solution (C), which was propelled by peristaltic pump P3. The carrier solution was then equally split and merged with the CL carrier solutions for each reaction on both sides of spiral-designed microfluidic platforms. Peristaltic pumps (P1 and P2) were employed to control the carrier streams of sodium hexameta-phosphate/formaldehyde (R2) and reagent stream of acidic potassium permanganate (R1) at the equal flow rate of 5.50 mL min^{-1}, to symplify the flowing system. On the other hand,

the carrier stream flow rate for luminol chemiluminescence detection, ammonium metavanadate/ammonium molybdate (R3), was set at 0.50 mL min^{-1} while the luminol reagent stream solution was set at the flow rate of 2.5 mL min^{-1}. These instrument set-ups were allocated for As(III) and As(V) determination, respectively.

Once the combination mixtures of each reaction were passed through the microfluidic flow conduits, the CL intensity was instantly detected by two sensitivity PMT tubes put flush against each side of microfluidic chip. The output of the PMTs which is proportional to the CL intensity was monitored simultaneously and continuously. The signals of analytes were the maximum output corresponding to the peak maxima.

Experiments for the LC- ICP-MS method were performed with an Agilent 1100 series LC/diode array detector system including the following modules: Inductively coupled plasma–mass spectrometer (ICP-MS) Agilent 7500C series. The separation was carried out using an ODS column-CAPCELL Pack C18MG, 3.5 µm × 250 mm × 4.6 mm (Shiseido, Japan), thermostated at 25ºC. The mobile phase was 0.05% methanol, 10 mM sodium 1-butane sulfonate, 4 mM malonic acid, 4 mM tetramethylammonium hydroxide in deionized water adjusted to pH 3.0 with nitric acid and set at a flow rate of 0.75 mL min^{-1}. The quadrupole mass analyzer was monitored as follows: detection ion m/z = 75.0 a.m.u. with sampling rate of 1 Hz.

Results and Discussion

The previous reports by Taokaenchan *et al* [18] and Somaum *et al* [19] were used for preliminary studies. The integration of a microfluidic device with two specific CL reactions was proposed in a single microfluidics chip which ran on a simple device made from small pieces of polymethylmethacrylate (PMMA) and polydimethylsiloxane (PDMS). The chemiluminescence detection of As(III) and As(V) based on the acidic permanganate[20] and luminol [21] were employed for specific detections for each arsenic species.

Principle of the CL reaction

The CL reaction for As(V) was generated based on the oxidation of luminol with a vanadomolybdoarsenate heteropoly acid (AsVMo-HPA) complex in an alkaline solution as shown in the reaction formulas 1-3 [19-20]. The reaction rate could be improved by elevating the reaction temperature [21].

$$Mo(VI) + As(V) + H^{+} \longrightarrow [AsMo_{10}O_{37}]^{9-} \quad (1)$$

$$[AsMo_{10}O_{33}]^{9-} + Mo(VI) + V(V) \longrightarrow [AsVMo_{11}O_{40}]^{4-} \quad (2)$$

$$Luminol + [AsVMo_{11}O_{40}]^{4-} + OH^{-} \longrightarrow Aminophthalate + N_2 + \text{other products} + h\nu \quad (3)$$

The As(III) species have been successfully determined with chemiluminescence detection by using acidic permanganate reaction. Adcock *et al* [22] reviewed a possible CL mechanism of As(III) with acidic $KMnO_4$ which may be attributed to following reactions formulas (4-6) :

$$5\,H_3AsO_3 + 2MnO_4^{-} + 6\,H^{+} \longrightarrow 5H_3AsO_4 + 2Mn^{2+*} + 3\,H_2O \quad (4)$$

In the presence of certain fluorophore, the energy resulting from the redox reaction can be an effective transfer to fluorophore dye which in turn generates CL emission [11].

$$Mn^{2+*} + \text{fluorophore} \longrightarrow Mn^{2+} + \text{fluorophore}^{*} \quad (5)$$

$$\text{fluorophore}^{*} \longrightarrow \text{fluorophore} + h\nu \quad (6)$$

Optimization of the microflow parameters

To establish the optimum microflow conditions for the determination of As(III) and As(V), the effects of the key chemical and physical parameters on the CL signal were thoroughly investigated using an univariate approach. The µFI system's parameters optimized in this study were the: (i) PMT applied voltage; (ii) concentration of reagent solution for determination of As(III) consisting of concentration of mixture $KMnO_4$ and Rhodamine B in reagent stream; concentration of mixture sodium hexametaphosphate and formaldehyde in reagent stream, respectively; (iii) the concentration of reagent solution for determination of As(V) consists of concentration of mixed ammonium metavanadate and ammonium molybdate reagent stream, concentration of luminol in reagent stream, (iv) sample injection volume and (v) flow rates of each carrier and reagent streams for both CL detection system. A series of experiments were conducted to establish the optimum analytical conditions for the CL oxidation of As(III) by acidic $KMnO_4$ and AsVMo-HPA by luminol. All measurements were performed in triplicate.

(i) Effect of photomultiplier tube applied voltage

The effect of the photomultiplier tube (PMT) voltage was investigated in the range 700-1000 V for both PMTs. For these experiments, 100 µg L^{-1} of mixed standard solution of As(III) and As(V) were injected into µFI-CL system. The potential of the power supplies were increased stepwise and the CL signals were measured after the injection of mixed arsenic solution at each potential step. The noise from the background current fluctuation was also measured at each potential step. As expected, The CL intensities were increased when the applied voltage was increased stepwise. However, the background noise was also increased. It was found that the signal-to-noise (S/N) ratio reached a maximum value at 850 V for As(III) and 950 V for As(V), respectively. The results are illustrated in Fig 3.

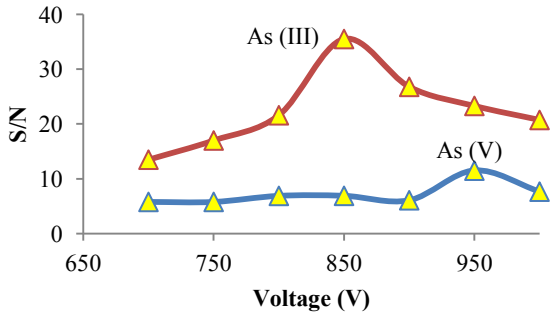

Figure 3. Effect of photomultiplier tube on the applied voltage.

(ii) Effect of carrier and CL reagent concentrations on the CL intensity for As (III) determination

The CL reagent stream solution (R1) was composed of sodium hexametaphosphate, $KMnO_4$ and Rhodamine B in sulfuric acid media, while the carrier stream solution (R2) comprised of acidic sodium hexametaphosphate and Rhodamine B. The effect of sodium hexametaphosphate concentration on both streams was studied over the concentration range from 0.4-0.9% (m/v) when the concentration of sulfuric acid was fixed at 5×10^{-3} M. The CL intensity increases when the concentration of sodium hexametaphosphate increases. At the concentration of 0.7 % (m/v) sodium hexametaphosphate, the highest signal was

observed; after this concentration the noise signal increase gradually made the S/N ratio decrease dramatically.

The concentration of $KMnO_4$ was studied similarly to the previous parameter by varying the concentration from 0.05-0.4 M, the result showed that the CL intensity reached maximum when the concentration of $KMnO_4$ was at 0.15×10^{-3} M.

Previous reports by Satienperakul *et al* [23] and Anastos *et al* [24] and reported that CL intensity from the reaction of acidic permanganate can be increased by adding formaldehyde and Rhodamine B. In this research, the addition of Rhodamine B (8 mg L^{-1}) into the $KMnO_4$ reagent solution resulted in the increase of CL intensity by two orders of magnitude. Beyond this concentration, the CL signal decreased gradually with increasing rhodamine B concentration. Besides, it was also noted that the addition of formaldehyde into sodium hexametaphosphate carrier solution significantly increased the CL intensity and reached maximum at the concentration of 1.7 M.

(iii) Effect of carrier and CL reagent concentrations on the CL intensity for As (V) determination

The research study by Fujiwara *et al* [25] on the determination of the As(V) was based on the heteropoly acid reaction with luminol. The best heteropoly acid reagent was mixed with the ammonium metavanadate and ammonium molybdate in sulfuric acid. In this work, the investigation for the suitable condition for the complexation of vanadomolybdoarsenate heteropoly acid in reagent stream was studied by optimizing the concentration of a mixed reagent.

The concentration of ammonium metavanadate, ammonium molybdate and sulfuric acid in the reagent stream (R3) were studied in range of $5.0\text{-}9.0\times10^{-4}$ M, $5.0\text{-}9.0\times10^{-3}$ M and $0.5\text{-}6.0\times10^{-2}$ M, respectively. The increase in the concentration of ammonium metavanadate, ammonium molybdate and sulfuric acid resulted in the steep increase up to 8.0×10^{-4} M, 7.0×10^{-3} M and 3.0×10^{-2} M, respectively, above which the background response increased, causing an unstable baseline in CL intensity. Therefore the concentration of ammonium metavanadate, ammonium molybdate and sulfuric acid were chosen and used for vanadomolybdoarsenate heteropoly acid (AsVMo-HPA) complex formation in this study.

The CL intensity of the vanadomolybdoarsenate heteropoly acid (AsVMo-HPA) with luminol in NaOH media (R4) does not only affect on the CL intensity, but also the linearity of the method. The effect of luminol concentration on CL intensity was examined over the range 1.25×10^{-5}-30.0×10^{-5} M in alkaline media of 0.1 M NaOH. The CL intensity rapidly increased when the concentration of luminol was increased up to 5.0×10^{-5} M, above which the CL intensity decreased. Therefore, a concentration of luminol was chosen and used subsequently in this work.

The efficiency of luminol CL is highly dependent on the concentration of NaOH. The concentration of NaOH was varied from 0.0125-0.25 M. The optimal NaOH concentration was at 0.10 M, and therefore, a NaOH concentration of 0.10 M was selected and used subsequently. In the complexation of vanadomolybdoarsenate heteropoly acid we found that the CL intensity could arise due to the increasing of temperature, hence, these solutions (R3, R4) and the reaction coil were kept in water bath at 80 °C during the operation.

(iv) Effect of reagent and carrier stream flow rate (total)

Flow rate is an important parameter in CL detection as the same time taken to transfer the excited product into the flow cell is critical for maximum collection of the emitted light. The effect of the flow rates of the four channels was simultaneously over the range 0.5-5.0 mL min^{-1} in term of the sensitivity, sample throughput and reagent consumtion. The CL intensity of mixed arsenic standard solution (100 µg L^{-1}) gave maximum intensity at total flow rate of 5.8 and 4.2 mL min^{-1} for the determination of As(III) in the upper half and As(V) in the bottom half, respectively.

(v) Effect of injection volume

Similarly, the influence of the sample volume on the CL intensity of the flow system, over the range of 20-250 µL, was investigated by injecting the mixed arsenic standard solution at 100 µg L^{-1}. It was found that the CL intensity was increased when the volume of sample volume increased up to 150 µL, and become almost constant. Thus, a volume of 150 µL was selected for economy of the sample comsumtion and speed of response for all remaining experiments. The summary of their optimal values is shown in Table 1.

Table 1 Optimization microfluidic system parameter.

Parameters	Optimal value	
	As(III)	As(V)
PMT applied voltage (V)	850	950
H_2SO_4 concentration (M), C	3.0×10^{-2}	
Injection volume (µL)	150	
Total flow rate (mL)	5.8	4.2
$KMnO_4$ concentration (M), R1	0.15×10^{-3}	-
Rhodamine B concentration (mg L^{1-}), R1	8.0	-
Sodium hexametaphosphate concentration (% m/v), R2	0.7	-
Formaldehyde concentration (M), R2	1.7	-
Ammonium metavanadate (M), R3	-	8.0×10^{-4}
Ammonium molybdate (M), R3	-	7.0×10^{-3}
Luminol (M), R4	-	5.0×10^{-5}
NaOH (M),R4	-	0.10

Analytical performances

Under the optimal condition the linear calibration curve observed from 20-60 µg L^{-1}, the linearity regression equation for As(III) was $CL_{intensity} = (0.050\pm0.007)C_{As(III)}$(µg L^{-1}) + (17.06±0.019), r^2= 0.996 and As(V) was $CL_{intensity} = (0.089\pm0.007)C_{As(V)}$(µg L^{-1}) + (3.874±0.019), r^2= 0.995, respectively. The limits of detection (S/N≥3) of As(III) and As(V) were found to be 4 µg L^{-1} and the limits of quantification (S/N≥10) were found to be 10 µg L^{-1}, respectively. A 100 µg L^{-1} of As(III) and As(V) gave the injection throughputs of 60 h^{-1}.

Interference studies

Interfering effects on common cations and anions such as Fe^{2+}, Zn^{2+}, Mg^{2+}, Mn^{2+}, Cu^{2+}, Fe^{3+}, F^-, Cl^-, NO_3^-, NO_2^-, SO_4^{2-} and PO_4^{3-} were investigated to study for interferences in the determination of 10 µg L^{-1} As(III) and As(V) using the proposed method. The tolerance limit was chosen as the amount of an error of ± 10 % in peak height. The maximum tolerance concentration for each coexisting anion and cation is illustrated in Table 2. F^-, Cl^-, NO_3^-, SO_4^{2-} and Mg^{2+} show no effect on the determination of high concentration levels of As (III) and As (V). Serious interferences came from Zn^{2+}, Mn^{2+}, Cu^{2+}, Fe^{3+} and PO_4^{3-} where they react with $KMnO_4$ and luminol in the reagent stream even at the same concentration.

Table 2 Maximum tolerance of co-existing anion and cation for the determination of 10 μg L^{-1} As(III) and As(V).

Tolerance (μg L^{-1})	Interference anion and cation
100,000	F^-, Cl^-, NO_3^-, SO_4^{2-}, Mg^{2+}
1,000	NO_2^-, Fe^{2+}
10	Zn^{2+}, Mn^{2+}, Cu^{2+}, Fe^{3+}, PO_4^{3-}

Application to real samples

The developed μFI-CL method was applied to determinate As(III) and As(V) in ground water samples. The water samples were collected from Hang Chat district, Lampang province, Thailand. The comparative results with those obtained from from LC-ICP-MS method are illustrated in Table 3. The $t_{calculated}$ values for As (III) were 0.63 and 1.21 for As(V), respectively. There are no significant differences between the result values from both methods at 95 % confidence ($t_{critical}$ 2.45).

The accuracy of the proposed method was obtained by spiking three amounts of As(III) and As(V) standards sample solutions. The recovery was in the range 93-98 % as shown in Table 4.

Table 3. Comparative results for the determination of As(III) and As(V) in ground water samples.

Sample	Amount found (μg L^{-1})			
	μFI-CL[a]		LC-ICP-MS [b]	
	As(III)	As(V)	As(III)	As(V)
LP01	ND	8.70±0.10	ND	6.80
LP02	ND	13.02±0.11	ND	14.86
LP03	125.81±0.71	22.01±0.42	124.01	19.49
LP04	57.07±0.60	11.04±0.07	57.63	11.07
LP05	ND	ND	ND	ND
LP06	ND	19.78±0.85	ND	18.59
LP07	ND	83.86±0.73	ND	83.00

* Standard deviation from three determinations.
** ND = not detected, ([a] LOD = 4 μg L^{-1}, [b] LOD = 1 μg L^{-1}).

Table 4. Recovery of the μFI-CL results by spiked samples.

Level (n=3)	Added(μg L^{-1})		Found(μg L^{-1})		Recovery	
	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
1	35	35	32.79 ±0.06	32.61 ±0.57	93.68 ±1.86	93.18 ±1.62
2	45	45	43.46 ±0.90	41.67 ±0.57	96.56 ±2.01	92.59 ±1.26
3	55	55	52.03 ±0.38	53.55 ±1.13	94.59 ±0.68	97.36 ±2.06

Conclusions

A simultaneous microfluidic device coupling with dual-channel chemiluminescence detections, employing acidic potassium permanganate oxidation for As(III) and oxidation of luminol with a vanadomolybdoarsenate heteropoly acid (AsVMo-HPA) complex in an alkaline solution for As(V) has been successfully developed. The method is simple and rapid with low detection limit which could be established to imply with the requirement for a maximum residue limit of 4 μg L^{-1} of arsenic in surface water sample. The proposed procedure was applied to the determination of As(III) and As(V) in contaminated ground water samples from Lampang Province, Thailand. Moreover, the μFI-CL appears more attractive since it does not require sophisticated instruments, no external source, just a simple optical system only which makes these coupling easily to be adapted for being portable equipment and readily be a great potential to be an on-site detection equipment.

Acknowledgements

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