Determination of arsenic(V) in freshwaters by flow injection with luminol chemiluminescence detection

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A simple and rapid flow injection (FI) method is reported for the determination of arsenic(V) based on luminol chemiluminescence (CL) detection. The molybdoarsenic heteropoly acid formed by arsenic and ammonium molybdate in the presence of ammonium vanadate in acidic conditions generated chemiluminescence emission via the oxidation of luminol. The limit of detection was $0.15\,\mu g\,L^{-1}$, with a sample throughput $120\,h^{-1}$. A linear calibration graph was obtained over the range 0.15 to $7.5\,\mu g\,L^{-1}$ ($r^2 = 0.9989$; $n = 9$) with relative standard deviation ($n = 4$) in the range 0.8 to 2.5%. Interfering cations were removed by passing the sample through an in-line iminodiacetate chelating column and phosphate (at $0.6\,mg\,L^{-1}$) was removed off-line by magnesium-induced coprecipitation (MAGIC) method. The method was applied to freshwater samples and the results obtained were in reasonable agreement with the results obtained using HGAAS as the reference method.

Keywords: flow injection analysis; chemiluminescence; arsenate; heteropoly acid; freshwaters

1. Introduction

Biochemically, arsenic acts to coagulate proteins, forms complexes with coenzymes, and inhibits the production of adenosine triphosphate (ATP) in essential metabolic processes involving the utilisation of energy [1]. Arsenic is the twentieth most abundant element in the terrestrial crust [2] and is commonly found throughout the environment in a wide array of chemical species that vary in toxicity and mobility [3]. Arsenite and arsenate are the major species in groundwater and their distribution depends on geochemical factors. The combined concentrations could be as high as tens of $mg\,L^{-1}$ in areas where the water is in direct contact with arsenic-bearing sediment. Arsenic concentrations in surface and groundwaters generally range from 1 to $10\,\mu g\,L^{-1}$, while in fresh water, the typical concentration of arsenic ranges from 0.1 to $80\,\mu g\,L^{-1}$ with As(III) and As(V) as the major species but elevated levels from 0.1 to $5\,mg\,L^{-1}$ have been reported in ground waters [4,5]. The recommended maximum contaminant level (MCL) of arsenic in drinking water in the USA [6] is $10\,\mu g\,L^{-1}$ and in Australia [7] is $7\,\mu g\,L^{-1}$. In seawater, arsenic is the tenth most abundant element with an average value [8] of $2\,\mu g\,L^{-1}$.

Several papers have been reported on the speciation of arsenic in environmental and biological samples; with emphasis on such arsenic measurement methods as
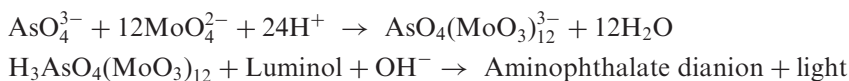
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spectrophotometric, electrochemical and atomic spectrometric [9,10]. Table 1, shows the comparison in terms of sample matrix, sensitivity and sampling frequency of several flow injection methods for the determination of arsenic [11–19]. Some of these methods are sensitive and accurate but involve relatively expensive and bulky instrumentation, and poor sample throughput.

Luminol CL reaction systems have been studied with a wide range of oxidants including permanganate, hypochlorite, iodine, hydrogen peroxide and cerium(IV) [20,21], and several of these systems have raised a great analytical potential for the determination of numerous analytes [22–25] based on flow injection analysis.

A number of FI-CL methods have been reported for the determination of arsenic using various CL reagents. An FI method with ion chromatographic separation using luminol-CL detection has been reported for the determination of As(V), Ge(IV), P(V) and Si(IV) with limits of detection 10, 50, 1.0 and $10 \, \mu g \, L^{-1}$, respectively [26]. A low capacity anion exchange column (IonPac AS4; $250 \, mm \times 0.5 \, mm$ i.d.) was used to separate the anions followed by post-column derivatization to form heteropoly acids in a long reaction coil ($10 \, m \times 0.5 \, mm$ i.d.) maintained at $80°C$. Another FI-CL procedure has been reported for the analysis of As(III) based on the oxidation of the analyte by acidic potassium permanganate in the presence of hexametaphosphate [27]. The limit of detection was $0.3 \, \mu g \, L^{-1}$ with a sample throughput of $150 \, h^{-1}$. The ions; sulfide, iodide and ferrous were found to cause serious interference because of reactions with potassium permanganate. A CL method has been reported for the speciation of As(III) and As(V) based on the increased CL emission with the addition of As(V) in a solution of lucigenin and hydrogen peroxide in an alkaline solution [28] and the limit of detection was $5.0 \times 10^{-3} \, \mu g \, g^{-1}$. The determination of As(III) by gas diffusion-FI, sequential injection analyser and gas flow procedures based on CL detection has been reported with limits of detection $0.6 \, \mu g \, L^{-1}$, $0.05 \, \mu g \, L^{-1}$ and $0.15 \, ng$, respectively [29–31].

This study reports a sensitive and rapid FI–CL method for the determination of arsenic in freshwater samples. The method is based on the oxidation of luminol by heteropolymolybdoarsenic acid in the presence of ammonium vanadate as shown below. Phosphate was removed by magnesium-induced coprecipitation (MAGIC) procedure [32]. A chelating resin mini-column was incorporated into the manifold to remove potential interferences from metal ions. Manifold parameters were optimised and the method was applied to freshwater samples collected from near to coal mines.

$$AsO_4^{3-} + 12MoO_4^{2-} + 24H^+ \rightarrow AsO_4(MoO_3)_{12}^{3-} + 12H_2O$$
$$H_3AsO_4(MoO_3)_{12} + Luminol + OH^- \rightarrow Aminophthalate \; dianion + light$$

2. Experimental

2.1 *Reagents and solutions*

All plastic ware used during the experiments and for storage of reagents and standards was precleaned with 20% HCl for 24 h, thoroughly rinsed with ultra high purity (UHP) deionised water ($18.2 \, M \, cm^{-1}$, Elgastat, Maxima, UK). All reagents were of analytical grade, supplied by Merck BDH, unless stated otherwise, and solutions were prepared in UHP water. Sodium arsenate (Na_2HAsO_4) stock solution (0.01 M) was prepared by

Table 1. Comparison among several flow injection methods for the determination of arsenic.

Detection technique	Matrix	Calibration range	Limit of detection	R^2 value	Sample rate (h^{-1})	Reference
SFIA-S	Natural waters	8×10^{-8}–2×10^{-4} M	NG	0.999	36	11
FIA-S	Standards	0.01–0.25 mmol L^{-1}	1 µmol L^{-1}	0.99994	N/G	12
FIA-S	Tap water	5–500 µg L^{-1}	1.2 µg L^{-1}	N/G	20	13
HG-GDFIA-EC	Contaminated soil	0.01–1.0 & 0.5–40 mg L^{-1}	0.01 mg L^{-1}	0.999	N/G	14
PFIA-S	Industrial effluents	2–15 mg L^{-1} & 25–1000 µg L^{-1}	15 µg L^{-1}	0.999 & 0.997	08	15
PFIA-HG-AFS	Dirty aqueous sample	pg–ng mL^{-1}	0.61 ng mL^{-1}	0.99	12	16
PFIA-HG-AFS	Industrial soil & CRMs	10–1000 ng mL^{-1} & 0.1–10 µg mL^{-1}	1 ng mL^{-1}	0.9995 & 0.9998	04	17
PFIA-S	Environmental waters	0.25–2000 µg L^{-1}	0.18 µg L^{-1}	0.999	07	18
MSFIA-HG-AFS	CRMs	0.1–3 µg L^{-1}	0.05 µg L^{-1}	0.994	10	19
FIA-CL	Freshwaters	0.375–7.5 µg L^{-1}	0.15 µg L^{-1}	0.9985	120	This work

Notes: N/G = not given; SFIA-S = sequential flow injection analysis spectrophotometry; FIA-S = flow injection analysis spectrophotometry; HG-GDFIA-EC = hydride generation-gas diffusion-flow injection analysis-electrochemical; PFIA-S = Pervaporation flow injection analysis spectrophotometry; MSFIA-HG-AFS = multi syringe flow injection analysis-hydride generation-atomic fluorescence spectrometry; CL = chemiluminescence.

dissolving the required amount of the compound in 100 mL of UHP water. Working standards were prepared by suitable dilution as required. Ammonium molybdate $((NH_4)_6Mo_7O_{24} \cdot 4H_2O)$ stock solution (0.01 M) was prepared by dissolving 1.24 g of ammonium molybdate in 100 mL of UHP water. A working solution (2.5×10^{-4} M) was prepared by diluting 10.0 ml of the stock in 100 mL of water containing H_2SO_4 (0.01 M). Ammonium vanadate (NH_4VO_3) stock solution (0.01 M) was prepared by dissolving the required amount of the compound in 100 mL of UHP water. From this, a working solution (7.5×10^{-4} M) was prepared in H_2SO_4 (0.01 M). Luminol (5-amino-2,3-dihydro-1,4-phthalazinedione, Aldrich) stock solution (0.01 M) was prepared by dissolving 0.178 g of luminol in 20 mL of NaOH solution (0.01 M) followed by sonication for 30 min, made up to 100 mL with water and stored at 4°C. A working luminol solution (5×10^{-5} M) was prepared by diluting 0.5 mL of the stock solution to 100 mL with borate buffer (0.05 M) and adjusting to pH 12 with sodium hydroxide solution (2.0 M). Stock solutions (1000 mg L^{-1}) of cations including Ca^{2+}, Mg^{2+}, Zn^{2+}, Fe^{2+}, Fe^{3+} Ni^{2+}, Co^{2+}, Mn^{2+} and Pb^{2+} were prepared in HNO_3 (0.01 M) and anions including Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-, NO_2^-, SiO_4^{4-} and PO_4^{3-} were prepared in UHP water. Various working solutions were prepared from these stock solutions for interference studies.

2.2 Chelating resin column

An acid washed Teflon tube (50 mm × 2.0 mm, i.d.) was packed with chelating resin (Chelex 100, sodium form, 50–100 mesh; Sigma), plugged with cleaned cotton wool at both ends and connected to the FI manifold with silicone tubing. The packed tube was washed with a stream of water for 30 min and incorporated in-line within the FI-CL system to remove possible interfering cations in water samples.

2.3 Instrumentation and procedures

The FI-CL manifold used for this work is shown in Figure 1. A peristaltic pump (four channels; Ismatec Reglo 100, Switzerland) was used to deliver the sample carrier and reagent solutions at a flow rate of 1.8 mL min^{-1}. A rotary injection valve (Rheodyne 5020, Anachem, Luton, UK) was used to inject As(V) standards (100 μL) into a UHP water
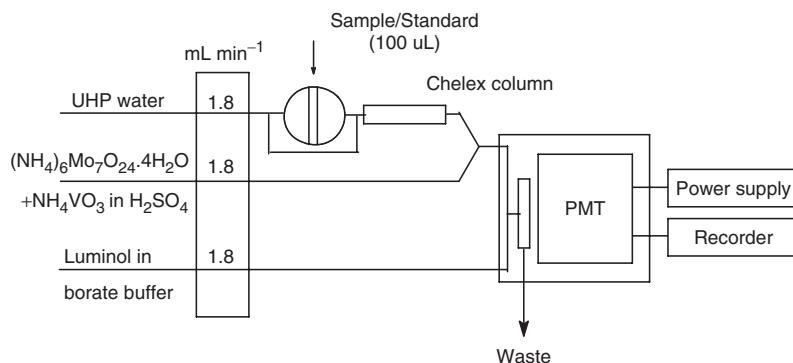

Figure 1. FI-CL manifold for the determination of As(V).

stream which was passed through a chelating resin column (50 mm × 2.0 mm i.d.) and merged with a stream of ammonium molybdate (2.5×10^{-4} M in 0.02 M H_2SO_4 containing NH_4VO_3 7.5×10^{-4} M). This stream was then merged at a T-piece with the CL reagent stream. The merged stream traveled 3.0 cm before passing through a quartz glass spiral flow cell (1.1 mm i.d., 130 µL, internal volume) placed directly in front of an end window photomultiplier tube (PMT, 9798QA, Electron Tubes, Ruislip, UK). The PMT, glass coil and T-piece were enclosed in a light tight housing. The PMT was attached to a 1 kV power supply (Electron Tubes, PM20SN, UK). The detector output was recorded using a chart recorder (Kipp & Zonen BD40, The Netherlands).

3. Results and discussion

3.1 *Optimisation of the FI manifold*

In order to establish optimal conditions for the lowest possible detection limit in a freshwater matrix, the effect of various parameters were investigated. These were the pH of the borate buffer (9.5–12.5), luminol, ammonium molybdate, ammonium vanadate and sulfuric acid concentrations, sample volume (30–240 µL), flow rate (0.5–2.5 mL min^{-1}) and PMT voltage (750–950 V). All of these studies were performed with a 7.5 µg L^{-1} As(V) standard solution and a detector (PMT) voltage of 900 ± 1.0 V.

The efficiency of luminol chemiluminescence is highly dependent on reaction pH and borate/NaOH buffer (0.05 M) typically gave a 20% higher response than NaOH alone, with an optimum pH of 12 (range studied pH 9.5–12.5) as shown in Figure 2a. The effect of luminol concentration in borate buffer over the range $1–75 \times 10^{-6}$ M (Figure 2b) showed increase in CL response and hence luminol (50×10^{-6} M) in borate buffer (0.05 M) at pH 12 was prepared 24 h before use for all subsequent studies. The influence of ammonium molybdate concentration on the formation of the molybdoarsenic heteropoly acid complex was studied over the range $5–17.5 \times 10^{-5}$ M and gave a maximum CL response at 12.5×10^{-5} M (Figure 2c). The effect of ammonium vanadate concentration added to ammonium molybdate and sulfuric acid mixture for complex formation was investigated. The maximum response was observed at 7.5×10^{-4} M as shown in Figure 2d (range studied $1–10 \times 10^{-4}$ M). Similarly, sulfuric acid gave a maximum response at 2×10^{-2} M (range studied $1–5 \times 10^{-2}$ M) as shown in Figure 2e. The optimum concentrations were used for all subsequent studies.

The effect of flow rate and sample volume on the CL response was investigated in terms of sensitivity, speed and reagent consumption and the results are shown in Table 2. CL reactions are transient in nature and CL intensity depends on merging of luminol carrier stream with ammonium molybdate (2.5×10^{-4} M in 0.02 M H_2SO_4 containing NH_4VO_3 7.5×10^{-4} M) stream at a T-piece and CL measurement in the reaction coil positioned in-front of PMT at a distance of 3.0 cm from the T-piece. The effect of flow rate was therefore investigated over the range 0.5–2.5 mL min^{-1}. A maximum CL intensity was obtained at a flow rate of 1.8 mL min^{-1}. At this flow rate a steady baseline was obtained with reproducibility of < 2.0% R.S.D. and was used subsequently for all three channels. Similarly, a sample injection volume of 100 µL for the arsenic–molybdate reaction gave almost the highest CL response providing maximum sample zone for reagents in the reaction coil. The optimum voltage required to operate PMT is 900 V. The effect of PMT voltage over the range 700–950 V was studied for
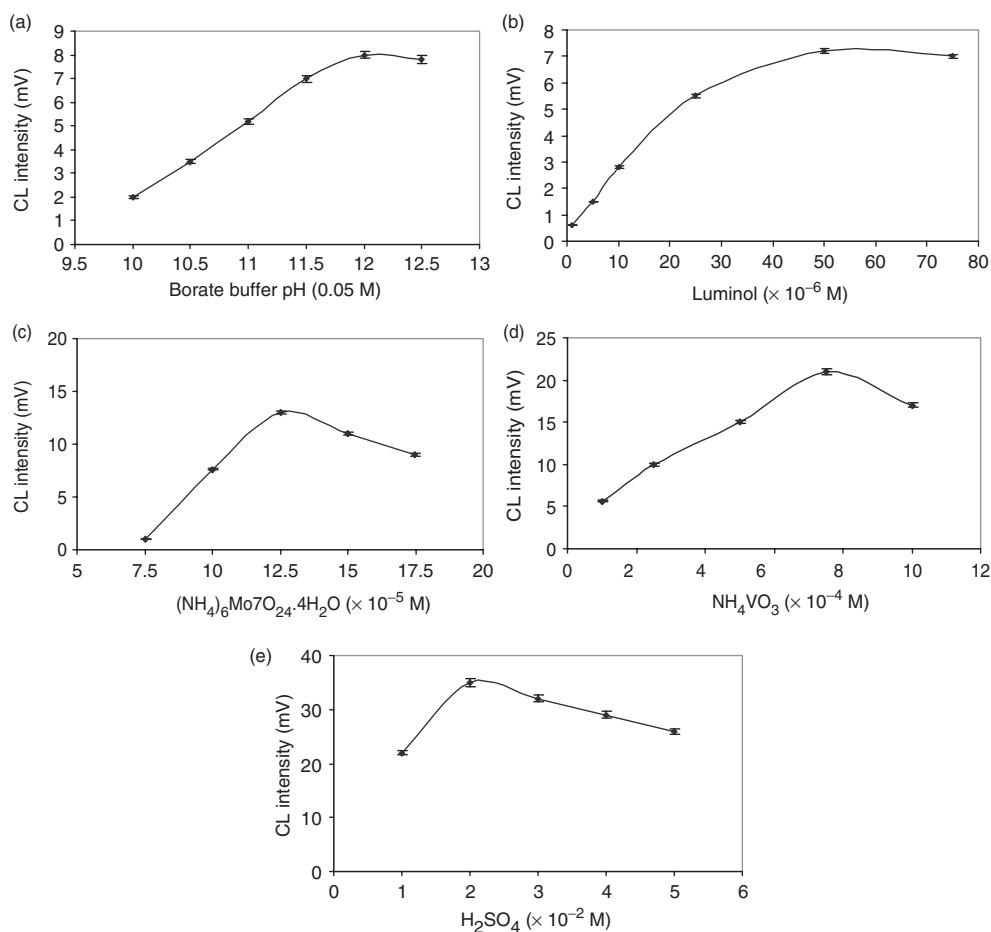
Figure 2. Variation of CL intensity with: (a) pH of borate buffer (0.05 M); and concentrations of (b) luminol; (c) ammonium molybdate; (d) ammonium vanadate and (e) sulfuric acid.

Table 2. Optimisation of variables for the determination of As(V) ($n = 4$).

Parameter	Range studied	Optimised values
Flow rate (mL min^{-1})	0.5–2.5	1.8
Injection volume (μL)	30–240	100
PMT Voltage (V)	750–950	900

maximum CL intensity. The CL output increased from 750 to 950 V. However, a voltage of 900 V was used to cope with the background signal.

3.2 *Analytical figures of merit*

A calibration graph of CL intensity versus concentration of As(V) over the range 0.15–7.5 μg L^{-1} was obtained using the optimum conditions given in Table 1 and Figure 2

Table 3. Calibration data for arsenic(V).

Arsenic(V) ($\mu g\,L^{-1}$)	Mean CL intensity (mV)	RSD (%) ($n=4$)
Blank (UHP water)	0.12	0.8
0.15	0.6	1.0
0.375	0.9	1.2
0.75	2.6	1.1
1.5	4.8	1.5
3.0	10.0	1.6
4.5	14.5	2.0
6.0	18.8	2.5
7.5	23.2	2.1
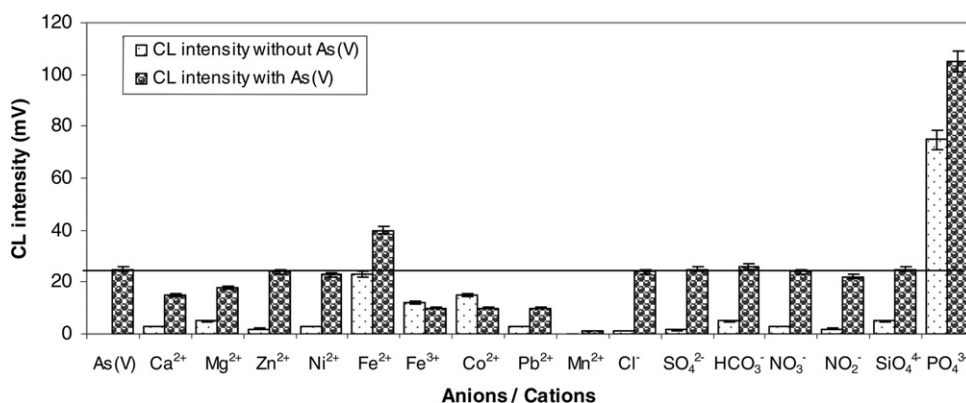
Figure 3. Effect of various cations (Ca^{2+}; $150\,mg\,L^{-1}$, Mg^{2+}; $30\,mg\,L^{-1}$, Zn^{2+} and Ni^{2+}; $1.0\,mg\,L^{-1}$, Fe^{2+}; $0.01\,mg\,L^{-1}$, Fe^{3+}; $0.1\,mg\,L^{-1}$, Co^{2+}; $0.01\,mg\,L^{-1}$; Pb^{2+}; $2.0\,mg\,L^{-1}$ and Mn^{2+} $0.1\,mg\,L^{-1}$) and anions (Cl^-; $250\,mg\,L^{-1}$, SO_4^{2-}; $300\,mg\,L^{-1}$, HCO_3^-; $20\,mg\,L^{-1}$, NO_3^-; $10\,mg\,L^{-1}$, NO_2^-; $0.1\,mg\,L^{-1}$, Si(IV); $1.0\,mg\,L^{-1}$ and PO_4^{3-}; $0.01\,mg\,L^{-1}$) on the blank signal (in the absence of As(V)) and on the determination of As(V) (at $7.5\,\mu g\,L^{-1}$). The solid line shows the response for As(V) in the absence of any interfering species.

($r^2 = 0.9989$; $n=9$) and the data are shown in Table 3. The regression equation was $y = 3.114x + 0.169$ [y = CL intensity (mV), x = concentration (M As(V)]. The R.S.D. was 0.8–2.5% ($n=4$) over the range studied and the sample throughput was $120\,h^{-1}$. A concentration of $0.15\,\mu g\,L^{-1}$ As(V) was clearly distinguishable from the blank and this represents a conservative practical estimate of detection limit with an improvement on spectrophotometric methods.

3.3 Interferences

The effect of major freshwater ions on the blank signal (in the absence of As(V) and on the determination of As(V) (at $7.5\,\mu g\,L^{-1}$) is shown in Figure 3. The effect of anions, Cl^-, SO_4^{2-}, HCO_3^- and NO_3^- had no significant effect. PO_4^{3-} ($0.01\,mg\,L^{-1}$) gave a significant blank signal due to the formation of the heteropolymolybdophosphoric acid [33]. Nitrite ($0.1\,mg\,L^{-1}$) had a suppressive effect on the luminol CL system and suppressed the As(V)

response but the concentration of nitrite in surface and ground waters is very low, generally $< 0.02\,mg\,NO_2^-\,L^{-1}$.

The effect of PO_4^{3-} interference on the determination of As(V) was investigated by using MAGIC method [32] with and without As(V) standard solution ($7.5\,\mu g\,L^{-1}$). Prior to analysis, $1 \times 10^{-7}\,M$ solution of highly purified $SnCl_2$ was added for the reduction of As(V) to As(III) containing PO_4^{3-} standard solutions over the range 0.1–$0.6\,mg\,L^{-1}$ ($25\,mL$ aliquot in triplicate) for $6\,h$ at room temperature. The precipitation process was initiated by the addition of $MgSO_4$ ($0.03\,M$) and NaOH ($0.06\,M$) to the mixture, forming white precipitate of brucite $[Mg(OH)_2]$. The precipitates were removed by centrifugation at $6000\,rpm$ for $20\,min$ at room temperature. The supernatants containing As(V) were treated with solid PbO_2 to oxidize As(III) to As(V) and then injected to the proposed FI-CL manifold. No CL response was observed when PO_4^{3-} standard solutions were treated without As(V). The CL response of treated PO_4^{3-} standards with As(V) were compared with untreated As(V) standard. Approximately 4–7% decrease in CL intensity was observed due to slow conversion process of As(III) to As(V). Blank solution was prepared using UHP water ($25\,mL$) containing $MgSO_4$ ($0.03\,M$) and NaOH ($0.06\,M$) solutions and treated as described. The supernatant was injected to FI-CL manifold and a blank CL signal of $0.12\,mV$ was obtained.

Cations, Ni^{2+}, Zn^{2+}, and Fe^{3+} had no significant effect. Co^{2+} ($0.01\,mg\,L^{-1}$) and Fe^{2+} ($0.01\,mg\,L^{-1}$) enhanced the CL signal due to their action as catalysts for luminol oxidation in the presence of molecular oxygen [34–36]. Ca^{2+}, Mg^{2+} ($100\,mg\,L^{-1}$) Cu^{2+} and Pb^{2+} ($1.0\,mg\,L^{-1}$) and Mn^{2+} ($0.01\,mg\,L^{-1}$) had suppressive effect on both the CL blank signal and on the As(V) response. However, free Cu^{2+} and Pb^{2+} concentrations in natural waters are typically low (1–$300\,\mu g\,L^{-1}$ in river water) [37] and would not interfere except in highly polluted waters. The effect of all of these cations was eliminated by the incorporation of an in-line iminodiacetate chelating resin micro-column. The lifetime of the micro-column was investigated by injecting separately freshwater samples (25 times) and Fe^{2+} standards ($1.0\,mg\,L^{-1}$) 20 times. There was no Fe^{2+} breakthrough and therefore the manifold can be used without interference from Fe^{2+} at environmentally relevant concentrations.

3.4 *Application to water samples*

The proposed method was applied to the determination of As(III & V) in freshwater samples collected at various distances from coal mines in acid washed (10%, v/v, HCl)

Table 4. FI-CL determination of As(III & V) in four water samples and comparison with HGAAS reference method.

Samples	pH	Conductivity (mS)	Proposed method ($\mu g\,As\,L^{-1}$)	Reference method* ($\mu g\,As\,L^{-1}$)
1	8.7	6.4	18.1 ± 1.1	20.6 ± 2.1
2	8.1	1.9	8.0 ± 2.1	10.1 ± 1.1
3	7.3	1.5	5.2 ± 2.3	7.1 ± 2.2
4	7.5	2.8	6.2 ± 2.0	8.5 ± 1.7

Notes: *HGAAS, Standard protocol, M-series Solaar, Thermo Electron Corporation. Uncertainties represent the 95% confidence interval for each sample ($n = 4$).

high density polyethylene bottles. After collection, samples were filtered through a cellulose membrane filter (cellulose acetate, pore size 0.45 µm, 47 mm diameter, Whatman, Maidstone, UK), kept refrigerated in the dark at 4°C and analysed within 12 h of sampling. The samples were treated according to the procedure described above. The results obtained for the four samples (range 8 ± 2.1 to $18.1 \pm 1.1 \,\mu g$ As L^{-1}) together with other physicochemical parameters including pH and conductivity and the results from HGAAS reference method are shown in Table 4. Overall, the results for the FI-CL method and the standard reference method were in reasonable agreement.

4. Conclusions

The proposed FI-CL method is simple, rapid ($120 \,h^{-1}$ sample throughput) with a limit of detection of $0.15 \,\mu g \,L^{-1}$ As(V) and comparatively sensitive to the methods reported in the literature. Common interfering cations present in freshwaters were removed by an in-line chelating resin micro-column. PO_4^{3-} was removed successfully by MAGIC method. The method was applied to freshwater samples collected near to coal mines and the results were in reasonable agreement with a reference method.

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