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Pervaporation-flow injection determination of arsenic based on hydride generation and the molybdenum blue reaction

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Abstract

A pervaporation-flow injection system for the determination of As(III) by the molybdenum blue method is described. Samples containing As(V) were pretreated with KI and HCl prior to injection to reduce As(V) to As(III). As(III) samples were injected into a 0.5 M HNO_3 stream and then mixed with a stream containing 0.5% sodium borohydride. The arsine generated was transported in the pervaporation unit across a semi-permeable membrane into a 1.97×10^{-3} M I_3^- acceptor solution where it was oxidised to As(V). The acceptor stream was merged with a reagent stream containing 0.01% $SnCl_2$, 0.1% hydrazine sulfate and 0.5% ammonium molybdate thermostated at 70°C. The concentration of arsenomolybdenum blue was monitored photometrically at 840 nm. The calibration graph is characterised by two linear ranges between 2.0 and 15 mg l^{-1} and 25 and 1000 μg l^{-1}, a sampling frequency of 8 h^{-1} and a detection limit of 15 μg l^{-1}. The presence of phosphate, Ni(II), Cu(II), and Fe(II) which normally interfere with arsenic in the molybdenum blue reaction or with atomic absorption spectrometry does not affect the analytical determination in this new method at concentrations up to 1000 mg l^{-1}. The method was applied successfully to industrial effluents containing As in the concentration range from 15 to 250 μg l^{-1}. Very good agreement with hydride generation atomic absorption spectrometry was obtained.

Keywords: Pervaporation; Flow injection; Arsenic determination; Molybdenum blue method; Hydride generation

1. Introduction

The determination of arsenic and its compounds in environmental samples is of growing interest because of its high toxicity and abundance in the environment. Arsenic exists in natural systems in different chemical forms such as arsenite, arsenate, methylarsenic, dimethylarsenic and trimethylarsenic [1]. Arsenite and arsenate are the most common and toxic forms of arsenic in natural waters [1]. A number of analytical techniques exist to determine arsenic in environmental samples such as atomic absorption spectrometry (AAS) [2], HPLC-AAS [3], atomic emission spectrometry [4], flow injection-AAS (FI-AAS) [5,6], inductively coupled plasma-atomic emission spectrometry [7], amperometry [8,9], voltammetry [10], and spectrophotometry [11–22]. Some of the spectrophotometric methods for the determination of arsenic are based on colour reactions with silver diethyldithiocarbamate [11], silver salts [12–14] and molybdate to form molybdenum blue [15–22]. An FI spectrophotometric method for the determination

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of arsenic using the molybdenum blue reaction was developed by Linares et al. [23]. However, the interference of phosphate and silicate, which also form molybdenum blue complexes, seriously limits the applicability of this method. A better sensitivity and selectivity was achieved by utilising FI systems incorporating anion-exchange micro-columns [24–26].

A hydride generation gas-diffusion FI system with conductimetric detection was used by Farrell et al. for the determination of arsenic [27]. Though the interference of phosphate and silicate was avoided, volatile reducing agents present in the sample were detected conductimetrically. Further deterioration in the sensitivity of the method was caused by other sample constituents (e.g. particles and macromolecules) partially blocking the pores of the gas-diffusion membrane.

In the last decade, a technique called pervaporation-flow injection (PFI) has been successfully applied for the direct quantitative determination of volatile and semi-volatile analytes in 'dirty' samples, which can cause clogging of the gas-diffusion membrane [28]. The analytes evaporate into the headspace of the pervaporation module and diffuse through a gas-diffusion membrane into the acceptor stream where detection takes place. Since there is no direct contact between the sample and the membrane, deterioration in the membrane permeability due to pore blockage is avoided [29]. PFI has been used in the determination of a wide range of analytes such as mercury in solid samples [30], sulfide in kraft liquors [31], acetaldehyde in liquid, solid and semi-solid food samples [32], chemical oxygen demand and inorganic carbon in bleaching liquor [33], trimethylamine in fish samples [34], volatile organic compounds in solid samples [35], cyanide in the presence of sulfide [36], ammonia in the presence of surfactants [37] and phenol in suspensions [38].

On the basis of the above, it seems that PFI could allow the determination of arsenic by the molybdenum blue method in 'dirty' samples containing suspensions and emulsions as well as interferents such as phosphate and silicate. The aim of the present study is to develop such a method, optimise its main parameters and apply it to industrial samples.

2. Experimental

2.1. PFI system

The PFI system for arsenic determination, shown schematically in Fig. 1, consisted of two peristaltic pumps (Gilson Minipuls-2 and Minipuls-3, France), a rotary injection valve (Rheodyne 50, Rheodyne Inc., CA, USA), teflon tubing (0.5 mm i.d.), a debubbler, a home-made pervaporation unit, and a flow-through photometric detector (Shimadzu SPD-10AV, Japan) interfaced (PCL-818H, Advantech, Taiwan) to a PC (Pentium 166 MHz). The software written in MS Quick C 2.5 determined the peak maximum.

The pervaporation unit was similar to the one described earlier [37,38]. It consisted of two circular perspex blocks (61 mm diameter, 25 mm deep)

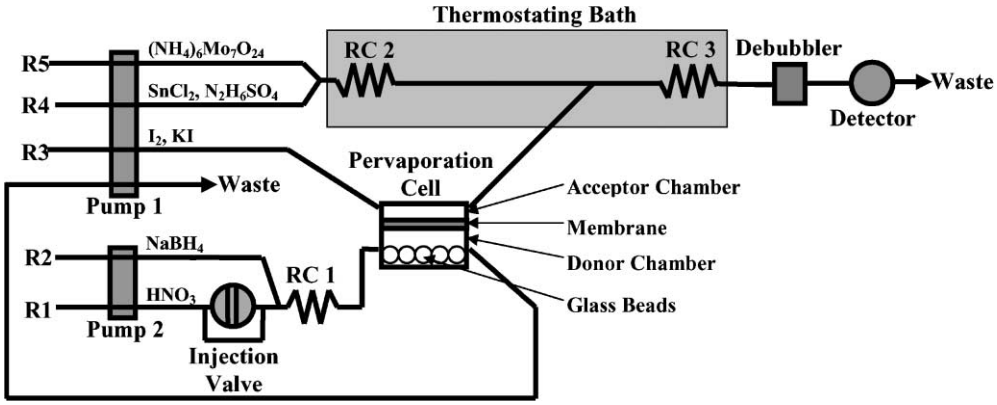

Fig. 1. Schematic of the PFI system for arsenic determination.

held together by stainless steel ring clamps and four stainless steel bolts. Both the acceptor chamber (0.3 mm deep) and donor chamber (5.0 mm deep) were hexagonal in shape and a single layer of glass beads (Fig. 1, 3.0 mm diameter, Selby-Biolab, Australia) was used to partially fill the donor chamber. The maintenance of a constant liquid level in the donor chamber is crucial for the reproducibility of PFI methods [28–38]. It has been established that a satisfactory control of the liquid level in the donor chamber can be achieved by the introduction of glass beads, the use of two peristaltic pumps connected to the inlet and the outlet of the donor chamber (Fig. 1), and by appropriate selection of the length of the tubing upstream and downstream of the donor chamber [36–38]. In the present study all these means were utilised for controlling the donor chamber liquid level. Circular semi-permeable PTFE membranes (40 mm diameter, 0.5, 0.9, 1.4 or 1.6 mm thickness, Trace, Germany) were used to separate the donor and acceptor chambers of the pervaporation unit (Fig. 1). In some cases a metal support for the membranes was used [36].

The temperature of reaction coils RC2 and RC3 (Fig. 1), where the colour chemical reaction takes place, was maintained constant by immersing the two coils in a water bath fitted with a thermoregulator (RATEK Instruments, Australia).

The PFI system was initially equipped with a home-made debubbler, which was a circular perspex block (35 mm outer diameter, 30 mm deep) with a flow-through cylindrical cavity (10 mm diameter, 15 mm deep) covered by PTFE tape (87 μm thickness). As a result of the higher pressure inside this cavity, dissolved gases and gas bubbles were released through the PTFE tape into the ambient air. Later, this debubbler was replaced by a 25 mm long gas-permeable (Accurel tubing, Pro-Tech, Australia) tube (2.4 mm i.d.).

2.2. Solutions

All chemicals were of analytical grade and were used as received. NANOpure deionised water (17.9 MΩ cm, Barnstead, USA) was used for all solutions preparation. Arsenic(III) and arsenic(V) stock solutions (1000 mg l^{-1}) were prepared by dissolving 0.1734 g of $NaAsO_2$ (Ajax, Australia) or 0.416 g of $Na_2HAsO_4{\cdot}7H_2O$ (Ajax, Australia) in 1 ml 5.0 M NaOH (BDH, UK). The solution was neutralised with 1.0 M H_2SO_4 (Ajax, Australia) using phenolphthalein (Ajax, Australia) as the indicator and diluted up to 100 ml with water. As(III) standards in the concentration range from 25 μg l^{-1} to 15.0 mg l^{-1} were prepared daily by appropriate dilutions of the stock solution.

Ammonium molybdate (R5, Fig. 1), stannous chloride, hydrazine sulfate and ascorbic acid (R4) solutions were prepared by dissolving the appropriate amount of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (BDH, Australia), $SnCl_2$ (M&B, Australia), $N_2H_6SO_4$ (BDH, Australia) or L-ascorbic acid (SIGMA, USA) in a mixture of 50 ml 1.0 M H_2SO_4 (BDH, Australia) and 10.0 ml glycerine (SIGMA, USA). The solutions obtained were diluted to 100 ml with water. The acceptor solution (R3, Fig. 1) containing I_3^- was prepared by dissolving the appropriate amounts of KI (M&B, Australia) and I_2 (UNILAB, Australia) in water. The acceptor solution (R3) and the two colour developing solutions mentioned above (R4, R5) were filtered through a 0.45 μm nylon filter (Alltech, Australia) and sonicated for 10 min before use. Sodium borohydride solution (R2) was prepared by dissolving $NaBH_4$ (BDH, Australia) in 0.025 M NaOH. Standard solutions of H_2SO_4, HNO_3 (BDH, Australia) or HCl (BDH, Australia) were used as carrier (R1) into which the samples were injected.

The potassium iodate solution used for the titration of sodium borohydride was prepared by dissolving 2.230 g of KIO_3 (M&B, UK) in 250 ml water. Sodium thiosulphate solution used as titrant and a starch indicator solution were prepared by dissolving 2.482 g of $Na_2S_2O_3$ (M&B, UK) and 2.0 g of Iotect Iodine indicator (M&B, UK) in 100 and 10 ml water, respectively.

2.3. Titration of sodium borohydride

An aliquot of 25 ml sodium borohydride in 0.025 NaOH solution was mixed with 35 ml 0.25 M KIO_3 in a 250 ml volumetric flask and swirled for about 30 s. After this, 2 g KI and 20 ml 2.0 M H_2SO_4 were consecutively added. The flask was allowed to stand for 2.0 min in the dark and the iodine liberated was titrated with standardised 0.10 M $Na_2S_2O_3$ solution using starch as the indicator [39].

2.4. PFI procedure

Samples and standards containing arsenite (As(III)) only were acidified to a final concentration of 0.5 M HNO_3 and injected into the PFI system (Fig. 1) while those containing arsenate (As(V)) were pretreated off-line with KI in a hydrochloric acid medium to reduce As(V) to As(III) [19]. The off-line reduction procedure involved the addition of 0.1 ml 20% (w/v) KI and 0.5 ml concentrated HCl to 5.0 ml of sample solution with a 30 min incubation before injection. All samples and standards were injected into an acidic carrier stream (R1, Fig. 1), which merged with a stream of sodium borohydride solution in 0.025 M NaOH (R2). The arsine formed in reaction coil RC1 evaporated into the headspace of the donor chamber of the pervaporation cell and diffused through the semi-permeable membrane into the acceptor chamber where it was oxidised to arsenate by I_3^-. The acceptor stream (R3) was merged with pre-mixed ammonium molybdate solution (R5) and a reducing solution (R4) and passed through a reaction coil (RC3) immersed in a thermostated water bath. After removing gas bubbles, the absorbance of the solution leaving the debubbler (Fig. 1) was monitored at 840 nm corresponding to the absorption maximum of the arsenomolybdenum blue complex.

2.5. Arsenic determination by hydride generation atomic absorption spectrometry (HG-AAS)

The hydride generation system was computer controlled and consisted of a GBC 933 atomic absorption spectrometer (GBC, Australia) coupled with a HG 3000 automatic hydride generator (GBC, Australia). As(III) standards in the concentration range from 1.0 to 20.0 $\mu g\,l^{-1}$ were prepared daily by appropriate dilutions of a 10.0 $mg\,l^{-1}$ As(III) stock solution. The dilution of the As(III) stock solution and the filtered samples was carried out using a solution of 2.0 M HCl (BDH, Australia) and 200.0 $mg\,l^{-1}$ KI (M&B, Australia) to reduce any As(V) present in the samples [19].

2.6. Samples

The arsenic concentration in four unfiltered effluent samples (Table 1) obtained from the mining industry was determined by both PFI and HG-AAS. Nitric acid was added to samples A, C and D to a final concentration of 0.1 $mol\,l^{-1}$. All four samples contained solid particles (30–50 $mg\,l^{-1}$ for A, C and D and 11,000 $mg\,l^{-1}$ for B) and their turbidity was between 0.2 and 2.0 NTU for A, C and D and 1900 for B. For this reason filtering of the samples was required prior to the HG-AAS measurements. The samples were analysed elsewhere for other chemical species and were found to contain Fe (2–50 $mg\,l^{-1}$), Cu (2–50 $mg\,l^{-1}$), Ni (less than 100 $\mu g\,l^{-1}$), SO_4^{2-} (20–100 $mg\,l^{-1}$ for A, C and D and 1000 $mg\,l^{-1}$ for B), and Cl^- (30–50 $mg\,l^{-1}$ for A, C and D and 1500 $mg\,l^{-1}$ for B).

3. Results and discussion

3.1. Optimisation of the system parameters

The flow system parameters that affect the sensitivity, reproducibility and sample throughput of the arsenic determination in the experimental PFI system

Table 1
Sample concentrations of As determined by the PFI and HG-AAS methods and recoveries of the added As concentrations determined by the PFI method (all measurements were performed in triplicate)

Sample	HG-AAS	PFI			
	Sample concentration ($\mu g\,l^{-1}$)	Sample concentration ($\mu g\,l^{-1}$)	Method used	Added concentration ($\mu g\,l^{-1}$)	Recovery (%)
A	N/A[a]	17.1 ± 0.5	Standard addition	22.5	98.9 ± 1.0
B	16.9 ± 0.3	16.9 ± 1.3	Standard addition	22.5	99.7 ± 4.9
C	233.4 ± 1.1	231.9 ± 4.2	Calibration curve	42.7	103.6 ± 1.5
D	152.8 ± 0.3	147.3 ± 7.1	Calibration curve	108.8	100.0 ± 4.9

[a] Not available due to insufficient sample volume.

Table 2
PFI system parameters optimised in the present study

Parameter	Range studied	Initial value	Optimal value
H^+ conc. (H_2SO_4, HNO_3, HCl) ($mol\,l^{-1}$) in R1	0.05–2.0	0.5	0.5 M HNO_3
$NaBH_4$ conc. (% (m/v)) in R2	0.25–4.0	0.25	0.50
$NaHCO_3$ conc. ($mol\,l^{-1}$) in R3	5.00×10^{-3} to 5.00×10^{-1}	1.00×10^{-1}	0.0
I_3^- conc. ($mol\,l^{-1}$) in R3	9.85×10^{-5} to 9.85×10^{-3}	1.97×10^{-3}	1.97×10^{-3}
$SnCl_2$ conc. (% (m/v)) in R4	0.005–0.025	0.02	0.02
$N_2H_6SO_4$ conc. (% (m/v)) in R4	0.050–0.250	0.20	0.20
Ammonium molybdate conc. (% (m/v)) in R5	0.2–2.0	1.0	1.0
Temperature of RC2 and RC3 (°C)	20–70	60	70
Sample volume (μl)	250–2500	500	500
Flow rate of R3 (R1 + R2 = R3) ($ml\,min^{-1}$)	0.2–1.4	0.4	0.6
Length of reaction coil RC1 (cm)	25–375	250	250
Length of reaction coil RC2 (cm)	25–100	25	25
Length of reaction coil RC3 (cm)	50–400	200	300
Membrane thickness (mm)	0.5, 0.9, 1.4, 1.6	1.4	1.4
Debubbler volume (ml)	0.11, 1.18	1.18	0.11

were studied separately according to their nature (i.e. chemical or physical). The initial value of these parameters, the range over which each was investigated and its optimal value are shown in Table 2. The order in which these parameters are listed in Table 2 corresponds to the actual order in which the optimisation took place. In studying the influence of each parameter on the sensitivity and sample throughput, the optimal values of the system parameters already investigated were used where appropriate.

3.1.1. R1 composition

The generation of arsine takes place in an acidic medium and in most AAS arsenic determinations, solutions of hydrochloric acid between 1.0 and $6.0\,mol\,l^{-1}$ were used [40–42]. In the present study, the influence of the hydrogen ion concentration on the arsine generation in the experimental PFI system was investigated in the range $0.05–2.0\,mol\,l^{-1}$ for nitric, sulfuric and hydrochloric acids. It was found that the absorbance increased with increasing hydrogen ion concentration up to $0.5\,mol\,l^{-1}$ after which the dependence levelled off. No significant difference between the three acids used was observed initially. However, it was found that with time the sensitivity of the method started to decrease considerably (e.g. down to 10–30% of the initial sensitivity after 3 h) when HCl or H_2SO_4 was used. A similar effect for HCl was observed by Nikolic et al. [40] and Tesfalidet and Irgum [41] and it was suggested that formation of volatile $AsCl_3$ caused the deterioration in the permeability of the PTFE membranes used [40]. The cause of the loss of sensitivity with H_2SO_4 solution is unknown. When nitric acid was used and the membrane was conditioned for 1 h, the repeatability was very good. For this reason, in all subsequent experiments 0.5 M HNO_3 was used as R1 (Fig. 1).

3.1.2. R2 composition

Various concentrations of sodium borohydride were used for arsine generation in different analytical techniques (e.g. 1.5% in FI-hydride generation [26]; 4.0% [41] in AAS; and 1.0% in FI-AAS [42]). The absorbance measured in the experimental PFI system was found to increase with increasing concentration of sodium borohydride in R2 up to 1% (m/v) after which it levelled off. However, for concentrations greater than or equal to 1% (m/v), the generation of hydrogen bubbles was very intensive and it was difficult to maintain a constant liquid level in the donor chamber of the pervaporation cell. Therefore, the optimum sodium borohydride concentration in R2 was selected as 0.5% (m/v).

3.1.3. R3 composition

In previous studies, arsine was absorbed and oxidised to arsenate in solutions of I_3^- in the concentration range from 9.85×10^{-4} to $1.97 \times 10^{-2}\,mol\,l^{-1}$ where the I_2:KI molar ratio was 1:2.5–3.0 [16,19,26]. In some cases, $NaHCO_3$ was added to those solutions

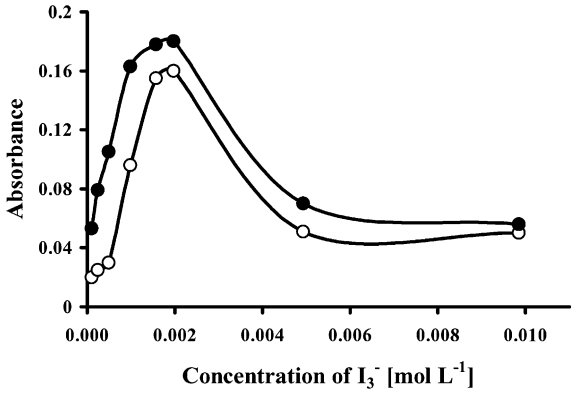

Fig. 2. Influence of the I_3^- concentration in the presence (○) and absence (●) of $NaHCO_3$ on sensitivity. (R1: 0.5 M HNO_3; R2: 0.5% (m/v) $NaBH_4$ in 0.025 M NaOH; sample concentration: 10 mg l^{-1} As(III); the remaining system parameters had their initial values (Table 2)).

[26]. In the present study, the concentration of I_3^- was varied between 9.85×10^{-5} and 9.85×10^{-3} mol l^{-1} maintaining the I_2:KI molar ratio equal to 1:2.5. In some of those solutions similar to [26], $NaHCO_3$ was present in a molar concentration approximately 50 times higher than that of I_3^- (Table 2). The results presented in Fig. 2 show that highest sensitivity was obtained at 1.97×10^{-3} M I_3^- and that the presence of $NaHCO_3$ in the concentration range studied (Table 2) reduced the sensitivity. This effect can be explained by the fact that the pH of the I_3^- solutions with and without $NaHCO_3$ ranged between 8.7 and 6.9, while the optimal pH for the oxidation of arsine is 6.5 [42].

3.1.4. R4 composition

The use of various reductants in the molybdenum blue reaction both under batch (potassium antimony tartrate and ascorbic acid [15,19], ascorbic acid [16], hydrazine sulfate [18]) and FI (ascorbic acid [23,24] and stannous chloride/hydrazine sulfate [24,26]) conditions were reported in the literature. When stannous chloride alone was used, it was found that the blue colour faded away rapidly. This undesirable effect was inhibited by the introduction of hydrazine sulfate into the stannous chloride solution in a 10-fold excess [15]. Linares at al. [23] found that the arsenomolybdenum blue complex did not precipitate if the reducing solution contained 10% (v/v) glycerine.

In the present study, the influence of stannous chloride, hydrazine sulfate and ascorbic acid and combinations of these reductants in 0.5 M H_2SO_4 solutions containing 10% (v/v) glycerine was investigated. Higher sensitivity was observed with ascorbic acid alone and the combination of stannous chloride and hydrazine sulfate. However, it was found that ascorbic acid caused the rapid formation of an insoluble blue deposit in the manifold tubings.

The effect of $SnCl_2$ and $N_2H_6SO_4$ on the sensitivity was studied in the concentration range between 2.0×10^{-3} and 2.5×10^{-2}% (m/v) with respect to $SnCl_2$ while maintaining a 10-fold excess of $N_2H_6SO_4$, as in [15]. It was found that the sensitivity increased initially with increasing concentration of $SnCl_2$ and for concentrations greater than 2.0×10^{-2}% it levelled off. For this reason, the optimal composition of R4 was selected as 2.0×10^{-2}% $SnCl_2$, 2.0×10^{-1}% hydrazine sulfate, 10% (v/v) glycerine and 0.5 M H_2SO_4.

3.1.5. R5 composition

Crouch and Malmstadt [43] recommended high acidity (e.g. pH 0.7) of the ammonium molybdate solution to prevent the direct reduction of Mo(VI). In accordance with this recommendation, Frenzel et al. [25] and Gomes et al. [26] used 1% (m/v) ammonium molybdate in 0.5 M H_2SO_4 solution having a pH close to 0.6. A higher baseline was obtained if HNO_3 was used instead of H_2SO_4 [26]. For this reason, sulfuric acid solutions of ammonium molybdate were utilised in subsequent experiments.

The influence of ammonium molybdate on the sensitivity was investigated in the concentration range from 0.2 to 2.0% (m/v). It was found that for concentrations higher than 1.0% (m/v) the absorbance remained unchanged and this value was selected as the optimal ammonium molybdate concentration. As for R4, the ammonium molybdate solution contained 10% (v/v) glycerine.

3.1.6. Temperature

In previous FI determinations of arsenic based on the molybdenum blue method, an elevated temperature of the manifold was found to accelerate the blue colour development (e.g. 50°C [23], 95°C [24] and 70°C [26]). In the present study, the temperature of the water bath was varied between 20 and 90°C. The optimal temperature was found to be 70°C since for

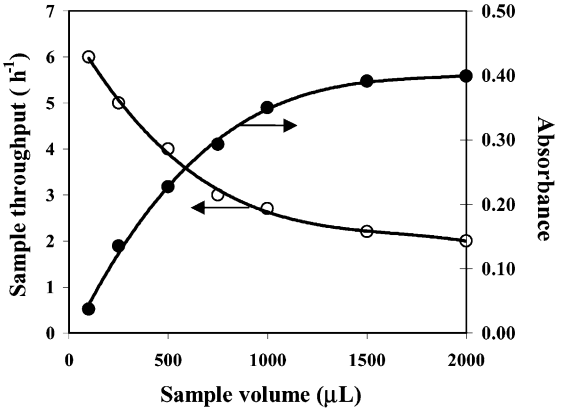

Fig. 3. Effect of the sample volume on the sensitivity (●) and the sample throughput (○) (R1–R5 had their optimal composition (Table 2); the remaining system parameters had their initial values (Table 2)).

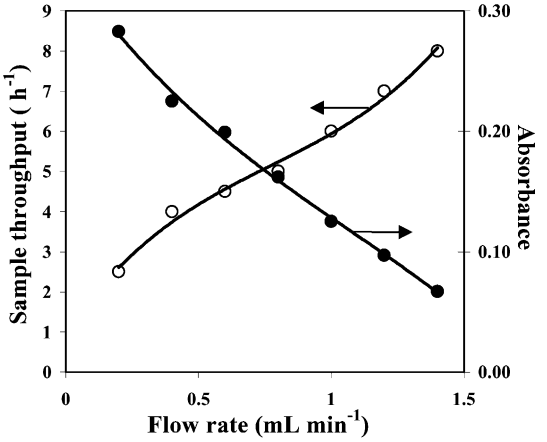

Fig. 4. Effect of the flow rate of R3 (R1 + R2 = R3) on the sensitivity (●) and the sample throughput (○) (sample volume: 500 μl; the remaining experimental conditions were as in Fig. 3).

temperatures higher than this the beneficial effect on sensitivity was negligible.

3.1.7. Sample volume

The influence of the sample volume in the range between 250 and 2500 μl on both sensitivity and sample throughput was studied (Fig. 3). As expected, small sample volumes increased the sample throughput, however, this led to a decrease in the sensitivity. A sample volume of 500 μl was selected as a compromise between the conflicting requirements for high sensitivity and sample throughput (Fig. 3).

3.1.8. Flow rates

To simplify the optimisation of the flow rates in the experimental PFI system (Fig. 1), it was decided that the flow rates of streams R1, R2, R4 and R5 should be equal while that of R3 should be twice this value. The latter selection was based on previous findings that best repeatability in PFI systems was achieved when the flow rates of the donor (R1 + R2, Fig. 1) and the acceptor (R3, Fig. 1) streams were equal [28–38]. As expected, higher flow rates increased the sample throughput and decreased the sensitivity (Fig. 4). Flow rates of 0.3 ml min^{-1} for R1, R2, R4 and R5 and 0.6 ml min^{-1} for R3 offer a reasonable compromise between sensitivity and sample throughput.

3.1.9. Reaction coils length

Reaction coil RC1 (Fig. 1) promoted mixing between HNO_3 (R1) and $NaBH_4$ (R2) on one hand and helped in maintaining a constant liquid level in the donor chamber of the pervaporation cell, which was crucial for obtaining reproducible results on the other. While in most cases satisfactory hydride generation was achieved in relatively short mixing coils (e.g. 30 cm [26,40]), a longer coil was very essential for good reproducibility of the PFI method. The length of RC1 (Fig. 1) was varied between 25 and 375 cm and as expected it did not affect the sensitivity substantially. However, for successfully maintaining a constant liquid level in the donor chamber, a length of 250 cm was chosen.

Reaction coil RC2 was necessary to promote mixing between streams R4 and R5 and its length, selected as 25 cm, did not affect the sensitivity or the sample throughput of the PFI system in the range between 25 and 100 cm.

The molybdenum blue reaction took place in reaction coil RC3. This reaction is not very fast and it can be expected that the length of the coil will affect the sensitivity of the method considerably. Since most researchers have used reaction coils between 100 and 400 cm [23–26] the influence of the length of RC3 on the sensitivity was investigated over the range from 50 to 500 cm. It was found that the sensitivity increased with increasing coil length. At the same time, longer

coils resulted in lower sample throughput. An RC3 length of 300 cm was chosen as an acceptable compromise between the sensitivity and sample throughput requirements.

3.1.10. Membrane thickness

The influence of the PTFE membrane thickness on the sensitivity was studied using membranes with thickness 0.5, 0.9, 1.4 and 1.6 mm. It was found that the thinner membranes (i.e. 0.5 and 0.9 mm) offered higher sensitivity but had relatively short life-times (e.g. 4 h) as a result of their lower mechanical strength. When a metal membrane support was used, the life-time was considerably prolonged, i.e. up to 1 week. However, the sensitivity decreased because the membrane support covered parts of the membrane thus reducing its surface area. For the 1.4 and 1.6 mm membranes, it was not necessary to use a membrane support and since the 1.4 mm membrane offered a slightly higher sensitivity, it was selected as the most appropriate one for the PFI system used. Its life-time was found to be at least 1 week.

3.1.11. Debubbler volume

The volume of the home-made debubbler incorporated initially in the experimental PFI system was 1.18 ml. It was found that by replacing it with a 25 mm long gas-permeable tube (2.4 mm i.d.) with an approximate volume of 0.11 ml, the sample throughput of the system increased by 60% without compromising its reproducibility or sensitivity.

3.2. Interferences

Arsenite (As(III)) is reduced preferentially to arsine by sodium borohydride compared to arsenate (As(V)). It was found that under the optimal experimental conditions (R1 containing 0.5 M H_2SO_4), the sensitivity of the method for arsenate was approximately 60% of that for arsenite when equivalent concentrations of each was injected. This effect was attributed to kinetic discrimination and it was found that the interference of As(V) can be reduced considerably at higher pH [5,6,25]. However, using pH as a means of inhibiting the reduction of As(V) is not practical because the results for the influence of the hydrogen ion concentration outlined earlier in this paper show that the sensitivity of the As(III) determination dramatically decreases at higher pH (e.g. at pH 1.6 the sensitivity is only 25% of its value at pH 0.87). For this reason, it was concluded that samples which might contain arsenate should be pretreated off-line to reduce As(V) to As(III) using KI in the presence of HCl. Experiments involving off-line pretreatment of synthetic samples containing As(III) and As(V) showed that in all cases the absolute error in total As recovery was less than 4% (Table 3). No difference in the analytical signal was observed between non-pretreated (containing 0.5 M HNO_3) and pretreated (containing KI and HCl) samples containing As(III) only.

Table 3
Recovery data for synthetic samples containing As(III) and As(V)[a]

As(III) concentration ($\mu g\,l^{-1}$)	As(V) concentration ($\mu g\,l^{-1}$)	Recovery (%)
100	0	101.6
75	25	102.0
50	50	99.0
25	75	100.3
0	100	100.6
100	100	102.5
500	0	102.2
0	500	100.2
0	1000	103.8

[a] Experimental conditions are the same as the optimal conditions in Table 2.

The effect of phosphate as KH_2PO_4, Ni(II), Cu(II), and Fe(II) which interfere with the arsenic determination based on the molybdenum blue reaction or AAS was studied using samples containing these chemical species in concentrations up to 1000 $mg\,l^{-1}$. No interferences were observed under the optimum PFI conditions.

3.3. Detection limit, sampling rate and linear detection range for the PFI system

Under the optimum working conditions (Table 2), the sampling rate for total arsenic of 10 $mg\,l^{-1}$ was found to be 8 h^{-1} with an R.S.D. less than 2.6% for arsenic based on measurements in triplicate. The calibration curve exhibited a sigmoidal shape characterised by two linear sections, i.e. between 2.0 and 15 $mg\,l^{-1}$ (absorbance $= -2.23 \times 10^{-2} + 1.95 \times 10^{-2}$ [As(III)], $R^2 = 0.999$) and between 25 and 1000 $\mu g\,l^{-1}$ (absorbance $= 8.14 \times 10^{-6}$ [As(III)], $R^2 = 0.997$). A detection limit of 15 $\mu g\,l^{-1}$ was

determined as three times the standard deviation of the blank.

3.4. Determination of total arsenic in effluent samples

The arsenic concentration in the four unfiltered effluent samples obtained from the mining industry (Table 1) was determined by the PFI system using the calibration curve for the linear range between 25 and 1000 $\mu g\,l^{-1}$. For two of the samples, the concentrations determined were considered as unreliable since they were very close to the detection limit. For these two samples, the concentration of As was determined by four point standard addition. In both cases very good linearity was observed ($R^2 > 0.995$). The results for all four samples are presented in Table 1. The reliability of the PFI method was checked by spiking all samples with a known concentration of As(III) and by determining the As concentration in the filtered samples by HG-AAS (Table 1). The concentration in the spiked samples was determined and the difference between the concentration before and after spiking for each sample was used to obtain the corresponding percentage recovery. The recoveries for all four samples did not differ by more than 3.6% from the theoretical value (Table 1). This finding together with the good agreement between the PFI and HG-AAS results (Table 1) shows the high degree of reliability of the PFI method developed in this study.

4. Conclusions

The PFI system for the determination of As(III) based on hydride generation and the molybdenum blue method was developed. A sampling rate of $8\,h^{-1}$ for As(III) of $10\,mg\,l^{-1}$ was achieved with two linear detection ranges between 2.0 and $15\,mg\,l^{-1}$ and 25 and 1000 $\mu g\,l^{-1}$ and a detection limit of $15\,\mu g\,l^{-1}$.

The PFI system was used successfully for the determination of arsenic in industrial effluent samples containing suspended solids and chloride, sulfate, nitrate, Ni(II), Cu(II), and Fe(II). Filtration of the samples was not required prior to injection. The reliability of the results obtained was confirmed by recovery PFI measurements after spiking the samples with As(III) and by HG-AAS.

Unlike standard colorimetric or HG-AAS methods, the PFI system proposed in this paper allows relatively straightforward and inexpensive automation of the determination of arsenic in turbid samples containing emulsions, suspensions and other interferents (e.g. phosphate, Ni(II), Cu(II), and Fe(II)).

The conversion of the off-line reduction of As(V) to As(III) into an on-line procedure is now in progress.

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