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Talanta 69 (2006) 1112–1117
Talanta
www.elsevier.com/locate/talanta

Flow injection hydride generation electrothermal atomic absorption spectrometric determination of toxicologically relevant arsenic in urine

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Received 26 July 2005; received in revised form 1 December 2005; accepted 7 December 2005
Available online 26 January 2006

Abstract

Analytical procedure for the determination of toxicologically relevant arsenic (the sum of arsenite, arsenate, monomethylarsonate and dimethylarsinate) in urine by flow injection hydride generation and collection of generated inorganic and methylated hydrides on an integrated platform of a transverse-heated graphite atomizer for electrothermal atomic absorption spectrometric determination (ETAAS) is elaborated. Platforms are pre-treated with 2.7 μmol of zirconium and then with 0.10 μmol of iridium which serve both as an efficient hydride sequestration medium and permanent chemical modifier. Arsine, monomethylarsine and dimethylarsine are generated from diluted urine samples (10–25-fold) in the presence of 50 mmol L^{-1} hydrochloric acid and 70 mmol L^{-1} L-cysteine. Collection, pyrolysis and atomization temperatures are 450, 500, 2100 and 2150 °C, respectively. The characteristic mass, characteristic concentration and limit of detection (3σ) are 39 pg, 0.078 μg L^{-1} and 0.038 μg L^{-1} As, respectively. The limits of detection in urine are ca. 0.4 and 1 μg L^{-1} with 10- and 25-fold dilutions. The sample throughput rate is 25 h^{-1}. Applications to several urine CRMs are given.

Keywords: Electrothermal atomic absorption spectrometry; Flow injection hydride generation; In-situ trapping; Arsenic; Monomethylarsonate; Dimethylarsinate; Urine; Permanent modification; Zirconium and iridium treated graphite platform; Automation

1. Introduction

Arsenic is a ubiquitous toxic trace element, representing a major toxicological and environmental concern [1,2]. It has been permanently among the most popular analytes in recent decades and substantial progress in its quantification and speciation analysis has been reached (reviews [3–6]). Despite the remarkable methodological improvements, arsenic remains one of the most difficult analytes [3]; its concentration levels, oxidation and binding states, ionic and molecular forms and metabolic pathways vary strongly in different environmental compartments, food chains and ultimately in mammals.

Urine is a major route of excretion of arsenic from human organism, being an important and indispensable toxicokinetic test for monitoring of occupational, environmental, dietary, accidental and other exposure sources [1,5–7]. Four arsenic species represent main toxicological interest and are well recognized in human urine—in declining order of their toxicity: inorganic (i) arsenic(III) (i-As(III), arsenite), i-As(V) (arsenate), monomethylarsonate (MMA, $CH_3As(OH)_2O^-$) and dimethylarsinate (DMA, $(CH_3)_2As(OH)O^-$), the latter one being the prevailing yet the least toxic metabolite. Whereas these four species could nowadays be differentiated quantitatively by means of advanced separations such as liquid chromatography, ion exchange, selective hydride generation (HG), cryotrapping with subsequent fractional vaporization, etc. (reviews [4–6]), the determination of their sum, denoted as 'first order speciation' [8] or 'toxicologically-relevant arsenic' [9,10] is likely to gain popularity. Attractive features of this approach could be summarized: (i) its toxicological grounds and significance; (ii) this sum is essentially the 'hydride-reactive' fraction, since i-As(III), i-As(V), MMA and DMA are derivatized to their corresponding hydrides (AsH_3, AsH_3, CH_3AsH_2 and $(CH_3)_2AsH$, respectively, under well-defined conditions of HG [11,12]; (iii) very simple pre-treatment of urine samples is involved, e.g. dilution with appropriate reagent such

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doi:10.1016/j.talanta.2005.12.015

as L-cysteine [9–15]; (iv) lengthy decomposition procedures are avoided (MMA and DMA are rather resistant to wet mineralization treatments and could be seriously underestimated, even in microwave oven digests [3,12,16,17]); (v) differentiation from some dietary exposure sources with low toxicity and bioavailability such as seafood-derived arsenic (arsenobetaine, arsenocholine, tetramethylarsonium) can be achieved, hence reliability of occupational monitoring is improved; (vi) instrumental measurements could be automated and sampling frequencies greatly improved, especially in flow injection mode of operation [8–11]. Potential disadvantages of this approach are the narrow acidity interval for simultaneous hydride generation from arsenite, arsenate, MMA and DMA (compromise conditions), dependence of final pH on different acid/base buffering properties of individual urines at low dilution factors and individual foaming pattern of different urine samples. As long as other hydride forming species (e.g. phenylarsinic acid and derivatives [18,19]) are not metabolite products in arsenic detoxication and are hardly found in human body and body fluids, they are not in the scope of this study, moreover they could entrain the body only in case of specific compound poisoning. Their excretion is without conversion to above-mentioned four species [1].

The aim of this work was to elaborate a sensitive and robust atomic absorption spectrometric procedure for the determination of toxicologically relevant metabolite arsenic (sum of arsenite, arsenate, MMA and DMA) in human urine [1] by flow injection hydride generation and collection of generated inorganic and methylated hydrides on Zr–Ir treated platforms of graphite atomizer. To the authors' best knowledge, this approach has not been realized in analytical practice.

Expected advantages of the FI-HG–ETAAS coupling are: (i) better sensitivity owing to hydride trapping and electrothermal atomization, thus applying higher dilution factors and providing better tolerance to pH adjustment, foaming, kinetic effects on HG/stripping; (ii) elimination of atomization interferences; (iii) improved precision and long term stability; (iv) automated, high sample throughput measurements. These carbide–iridium modified platforms have already shown good performance for trapping and stabilization of hydride-forming elements (As, Sb, Se, Sn) and some organoelement species in hyphenated hydride-generation–ETAAS [13,14,20].

2. Experimental

2.1. Apparatus

A Perkin-Elmer AAnalyst 600 atomic absorption spectrometer (Perkin-Elmer, Norwalk, CT, USA) equipped with a Model 4100 ZL transverse-heated graphite atomizer with integrated, pyrolytic graphite coated platform (THGA®) and longitudinal Zeeman-effect background corrector [21–23] with an AS 800 Autosampler, a FIMS 100 Mercury Analysis System with an AS 93 Plus Autosampler, an electrodeless discharge lamp (EDL) powered by EDL System II were employed. 'End-capped' THGA® tubes (Part No. B300-0655) [24,25] were used for better sensitivity (ca. 1.3–1.4-fold versus normal tubes) and improved precision. Optimized instrumental parameters and temperature programs are given in Tables 1 and 2.

Table 1
Optimized instrumental parameters for HG–ETAAS measurements

Parameter	Setting
Wavelength (nm)	193.7
Bandpass (nm)	0.7 (low)
EDL System 2 power (mA)	380
Signal measurement	AA–BG (peak area)
Smoothing	5 points
Baseline offset correction (BOC) time (s)	2
Read delay (s)	0
Sample coil volume	500 μL, PTFE tubing, 1 mm i.d., 64 cm
Sample load conduit	Tygon tubing, "yellow/blue", 1.52 mm i.d., 7.0 mL min^{-1} at 80 rev min^{-1}
Carrier conduit	Tygon tubing, "yellow/blue", 1.52 mm i.d., 4.0 mL min^{-1} at 50 rev min^{-1}
Reductant conduit	Tygon tubing, "red/red", 1.14 mm i.d., 2.0 mL min^{-1} at 50 rev min^{-1}
Waste from GLS	Tygon tubing, "white/black", 3.18 mm i.d., 10.5 mL min^{-1} at 80 rev min^{-1}
Reaction coil	PTFE tubing, 1.3 mm i.d., 100 cm
Argon flow rate (mL min^{-1})	125

THGA® graphite tubes with integrated platform were pretreated with 2.7 μmol of Zr (250 μg) and then with 0.10 μmol of Ir (20 μg) by successive multiple injections of modifiers on platform and multi-stage thermal treatments as detailed elsewhere [20,26]. The amounts of permanent modifier components was increased in this work (versus 1.2 μmol of Zr and 10 nmol of Ir in original papers [13,14], thus providing better long-term stability of measurements and lifetimes of THGA® tubes up to 700–800 firings. Noteworthy, the *critical* values of atomization (2100 °C) and clean temperatures (2150 °C) may not be exceeded, in order to avoid vaporization and redistribution of permanent modifier. The quartz pipette tip was adjusted to deliver hydrides about 1.3 mm above the platform. All results are based on integrated absorbance (A_{int}) measurements.

The standard gas–liquid separator (GLS) made of polymethylpentene with internal volume of 2.15 cm^3 and PTFE membrane (Fig. 1(A)) was replaced in this work with a larger custom-made GLS (20 cm^3), which exhibited better tolerance to flooding and aerosol formation (Fig. 1(B)). This GLS is made of borosilicate glass tube (height 155 mm, i.d. 16 mm, o.d. 19 mm) and has one side-arm input (I) and two outlets: a central one for waste (W) and a side-one for the gas–vapor flow (O), all made of borosilicate glass tubes (i.d. 4 mm, o.d. 6 mm). The GLS is fed and drained by means of two PTFE capillaries (I, i.d. 1.0 mm and W, i.d. 1.3 mm) fitted into the side arm (I) and the central tube (W) of the GLS, respectively.

Table 2
The optimized FIAS (a) and THGA® program (b) and sequence (c) for HG–ETAAS determination of toxicologically relevant arsenic

Step	Time (s)	Pump speed (rev min^{-1})	Valve position
(a) FIAS			
Prefill	10	80	Fill
1	10	80	Fill
2	5	80	Fill
3	40	50	Inject

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Internal Ar flow (mL min^{-1})	Read
(b) Furnace program					
1	450	1	50	0	–
2	500	1	20	250	–
3	2100	0	4	0	Yes
4	2150	1	2	250	–

Step	Actions and parameters
(c) Autosampler and furnace sequence	
A	Run FIAS steps 1 to 1
B	Run furnace step 1 with FIAS step 2
C	Stop FIAS pumps
D	Move autosampler arm into furnace for FIAS steps 3 to 3
E	Move autosampler arm out of furnace
F	Run furnace steps 2 to 4

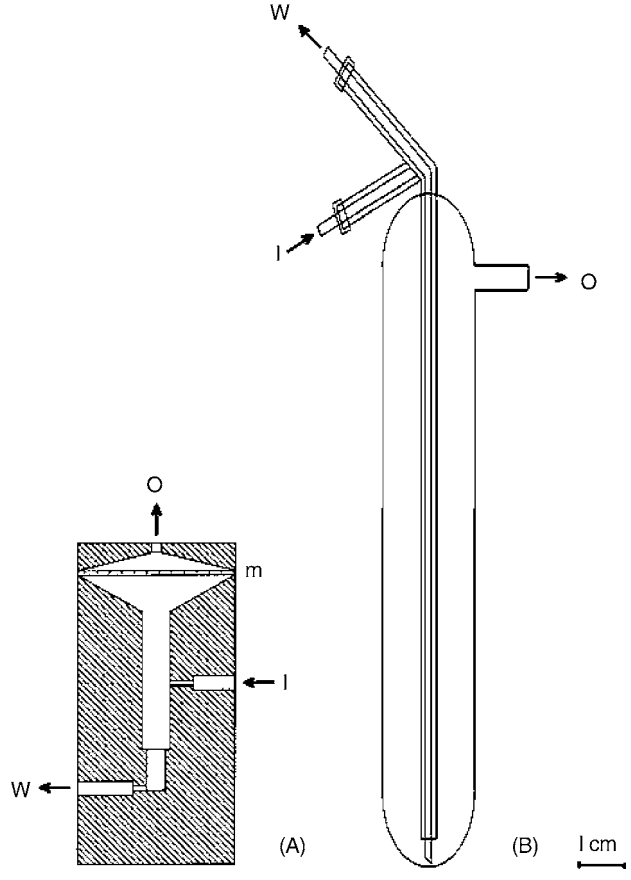

Fig. 1. Gas–liquid separators. (A) The standard GLS made of polymethylpentene with PTFE membrane (m) (internal volume 2.15 cm^3), supplied by the manufacturer. (B) Custom-made GLS with internal volume of 20 cm^3, fed and drained by means of two PTFE capillaries: (I) inlet; (O) outlet of GLS to an AS 800 autosampler and THGA® furnace; (W) waste.

2.2. Standards and reagents

Reagents of analytical grade or higher quality were used. Stock standard solutions used for arsenic measurements (1 g As L^{-1}) were: 1000 μg mL^{-1} As(III) atomic absorption spectroscopy standard solution No. 11082 (Fluka, Buchs); 1000 μg mL^{-1} As(V), As standard solution traceable to SRM from NIST, H_3AsO_4 in 0.5 mol L^{-1} HNO_3 (CertiPUR®, Merck, Darmstadt); organoarsenicals were prepared by dissolving of sodium methylarsonate (MMA), $CH_3AsO(ONa)_2{\cdot}6H_2O$ (Cod. 371205, Carlo Erba, Milan), 0.3896 g in 100 mL aqueous solution; sodium cacodylate (DMA), $C_2H_6O_2AsNa{\cdot}3H_2O$ (Cod. 367455, Carlo Erba), 0.2857 g in 100 mL aqueous solution. Stock solution of sodium tetrahydroborate(III), 1.2 mol L^{-1} $NaBH_4$ (45 g L^{-1}) was prepared by dissolving the solid reagent (Fluka) in 0.125 mol L^{-1} NaOH (5.0 g L^{-1}); it was kept in refrigerator for up to one week and was diluted with water (1 + 9) before analysis. Silicon antifoaming agent (Merck) was added to sodium tetrahydroborate solution in preliminary experiments (1 mL L^{-1} in final reductant solution). Stock aqueous solutions of L-cysteine, 0.7 or 0.9 mol L^{-1}, were prepared fresh daily from solid reagent (>99.5%, Fluka) and diluted as required. Graphite platforms were pre-treated with Zr and Ir [20,26], employing solutions prepared from zirconyl nitrate, $ZrO(NO_3)_2{\cdot}nH_2O$ (Erba) and iridium AA standard solution, 1000 μg mL^{-1} in 20% HCl (Alfa Johnson Mathey). Working standard solutions were prepared before use. Carrier solution was 45 mmol L^{-1} HCl. The water used in all operations was prepared by means of a Milli-Q system (Millipore).

2.3. Certified Reference Materials

The Certified Reference Materials (CRM) were obtained from the following manufacturers: "Lyphochek® Urine Met-

als Control", Level 1, Lot No. 69031; Level 2, Lot No. 69032; Level 1, Lot No. 69071 from Bio-Rad Laboratories (Munich, Germany); "Seronorm^{TM} Trace Elements–Urine Blank" Lot No. 2524 and "Seronorm^{TM} Trace Elements Urine" No. 2525 from Sero AS (Billingstad, Norway).

2.4. Sample treatment

Urine samples were treated with dilute HCl and L-cysteine reagents, yielding final concentrations of 50 mmol L^{-1} HCl and 70 mmol L^{-1} L-cysteine reagents in 10–25-fold diluted urine matrix. Sample treatment for 10-fold diluted urine: 2 mL aliquot of urine sample is pipetted into a 20 mL flask, 2 mL of 0.5 mol L^{-1} HCl and 2 mL of 0.7 mol L^{-1} L-cysteine are added, contents are diluted to 20 mL, mixed (without vigorous shaking), loaded in autosampler rack and left for 1 h at room temperature.

3. Results and discussion

3.1. Optimization of instrumental and chemical parameters

Optimized parameters are given in Tables 1 and 2.

Previous experience has shown that somewhat higher levels of the $NaBH_4$ reductant are beneficial [9,13–15]. An optimal concentration of 0.12 mol L^{-1} $NaBH_4$ was adopted in this work. The ruggedness test with ±20% lower and higher $NaBH_4$ levels, viz. 0.096 and 0.144 mol L^{-1} did not reveal significant effects on A_{int} signals and recoveries. A slight impairment of blank levels has been noted at higher reductant levels, e.g. 47, 49 and 54 pg per assay at 0.096, 0.120 and 0.144 mol L^{-1} concentrations of $NaBH_4$.

The flow rate of Ar has been expected to affect efficiency of striping-out the hydrides and their delivery to the graphite atomizer, especially for less volatile methylated hydrides—cf. the boiling points of −55, 2 and 35.6 °C for AsH_3, CH_3AsH_2 and $(CH_3)_2AsH$, respectively. Experimentally, higher Ar flow rates impair sensitivity for all three species, e.g. a signal decrease by 7.2, 5.5 and 6.5% for i-As, MMA and DMA, respectively, at 155 mL min^{-1} Ar versus 100 mL min^{-1} Ar. Therefore, the flow rate was adjusted between 115 and 130 mL min^{-1} in the course of this work.

According to most previous studies, the concentration of HCl in final solutions should be adjusted within relatively narrow interval between 10 and 100 mmol L^{-1} [9–15]. The effect of acid concentration was evaluated within the optimal interval for this system, 30–75 mmol L^{-1} HCl (Fig. 2). Recoveries (*R*%) for all four arsenic species were between 88 and 100%, being persistently lower (by 6–12%) for DMA. Heating of the reaction coil (1 m, 1 mm i.d.) in boiling water bath does not bring improvement in recoveries of DMA. Possible explanation should be sought in lower chemical yield and different kinetics of $(CH_3)_2AsH$ generation and transport, since similar recoveries for DMA (≤96%) are found with batch-type HG with externally-heated quartz tube atomizer (QTA) [15]. Efficient quantitative trapping of $(CH_3)_2AsH$ between 200 and 600 °C and thermal stabilization of DMA in the graphite atomizer up to pyrolysis temperatures of 1300 °C has been demonstrated earlier [13].

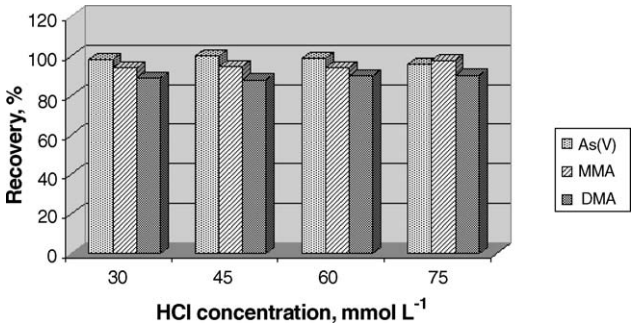

Fig. 2. Effect of HCl concentration on normalized integrated absorbance signals of 4 μg L^{-1} As at fixed concentration of L-cysteine, 90 mmol L^{-1}.

Fortunately, ETAAS with in-situ hydride trapping is more robust towards pH adjustment as compared to HGAAS with QTA. This could be attributed to completely different atomization mechanisms for As in the QTA (supposedly by means of hydrogen radicals) [12], which is strongly affected by total gas flow rate (Ar + H_2) and the amount of the generated H_2 from the hydrolyzed $NaBH_4$. pH normally varies within a relatively broad interval of pH 4.8–8.0 in human urine. Higher sensitivity of ETAAS also allows higher urine dilution factors (10–25×), hence decreasing the buffer capacity of urine constituents and allowing better adjustment of final acidity of individual diluted urines. The problem with critical pH effect as well as individual foaming pattern of different urine samples has been encountered in previous studies on hydride forming elements which exhibit strong pH dependence of hydride generation such as Sn [27], Pb [27] and As [15].

Employing a custom-made, larger volume GLS (Fig. 1–B) and larger dilution factors for urine samples (>10-fold) has allowed working without antifoam addition, since no visible foaming was observed.

Spike experiments were performed at the optimal conditions with i-As, MMA and DMA at 4 μg L^{-1} As in 10-fold diluted human urine (Fig. 3). The toxicologically relevant arsenic in sample was estimated at 10.7 ± 0.1 μg L^{-1}. Recoveries from diluted urine matrix were similar to those of aqueous solutions, with the lowest value of 91.8% for DMA. Admittedly, the worst case of DMA recovery around 92% may contribute

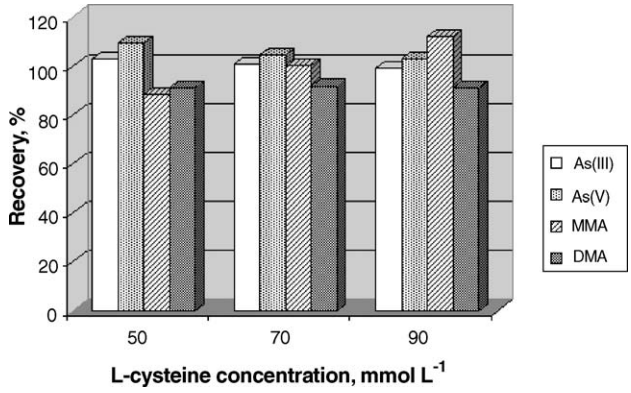

Fig. 3. Effect of L-cysteine concentration on normalized integrated absorbance signals of arsenic species (4 μg L^{-1}) spiked in 1 + 9 diluted urine at fixed concentration of HCl, 50 mmol L^{-1}.

Table 3
Determination of toxicologically relevant As in urine CRMs ($\mu g\,L^{-1}$)

CRM	Certified	Range	Method	Found[a]	Dilution factor	R.S.D. (%)	Data from speciation analysis (Sloth et al. [28])
Bio-Rad Lyphochek® Urine Metals Control Level 1, Lot No. 69031	50	40–60[b]	AAS	54.6 ± 0.6	10	0.6	–
Bio-Rad Lyphochek® Urine Metals Control Level 2, Lot No. 69032	154	123–185[b]	AAS	160 ± 2	25	0.5	–
Bio-Rad Lyphochek® Urine Metals Control Level 2, Lot No. 69071	51	41–62[b]	AAS	53.4 ± 0.2	10	0.2	–
Bio-Rad Lyphochek® Urine Metals Control Level 2 Lot 69071	59	47–71[b]	ICP-MS			–	
Seronorm™ Trace Elements Urine Blank, Lot No. 2524	83 ± 7[c]	76–90[d]	ICP-SFMS[e]	6.9 ± 0.2	10	1.3	As(III) 0.32 ± 0.01[f]; As(V) 0.30 ± 0.01[f]; MMA 0.32 ± 0.02[f]; DMA 9.1 ± 0.4[f]; sum of four species 10.3 ± 0.5[f]; DMA 8.2 ± 0.3[g]
Seronorm™ Trace Elements Urine Blank, Lot No. 2525	184 ± 17[c]	167–201[d]	ICP-SFMS[e]	107 ± 2	25	1.1	As(III) 0.10 ± 0.01[f]; As(V) 97 ± 2[f]; MMA 0.28 ± 0.02[f]; DMA 9.7 ± 0.4[f]; sum of four species 107 ± 2[f]; DMA 8.0 ± 0.3[g]

[a] ±2 standard deviations, based on two parallel sample digests, each measured three times.
[b] Acceptance range.
[c] ±Uncertainty.
[d] 95% Confidence interval.
[e] Inductively coupled plasma-sector field mass spectrometry.
[f] By means of HPLC–ICP-MS with anion exchange chromatography.
[g] By means of HPLC–ICP-MS with cation exchange chromatography.

to a maximum (negative) bias of −2, −4 or −6% in results for the sum of As(III) + As(V) + MMA + DMA by this procedure, supposing that the DMA fraction of the urinary arsenic reaches 25, 50 or 75%. Persistence of such a small systematic error could be considered as a minor disadvantage of this proposed assay.

Applications to several urine CRMs are summarized in Table 3. Results for Bio-Rad Lyphochek® urine CRMs are within the confidence intervals of certified values. Recoveries for Sero AS Seronorm™ urines are apparently low (8.3 and 58%, respectively). Explanation of these low recoveries could be that the As contents in these samples have been certified by means of ICP-SFMS and the *total* amount of As in No. 2524 sample probably consists of mainly non-hydride forming species. Subtraction of concentrations of Nos. 2525 and 2524 gives a difference of 101 $\mu g\,L^{-1}$, which could be assumed to be an inorganic As spike. Comparison for those particular lots of Seronorm™ urine between our results and experimental data from recent literature on arsenic speciation analysis (Sloth et al. [28]) is given in Table 3. The individual As species have been determined by means of HPLC–ICP-MS with anion exchange and cation exchange chromatography—cf. the sum of arsenite + arsenate + MMA + DMA by HPLC–ICP-MS equal to $10.3 \pm 0.5\,\mu g\,L^{-1}$ and $107 \pm 2\,\mu g\,L^{-1}$ for CRM Nos. 2524 and 2525 [28] and $6.9 \pm 0.2\,\mu g\,L^{-1}$ and $107 \pm 2\,\mu g\,L^{-1}$ by this method, respectively.

3.2. Figures of merit

The characteristic mass, characteristic concentration and limits of detection (3σ) and quantification (10σ) are 39 pg, 0.078 $\mu g\,L^{-1}$, 0.038 $\mu g\,L^{-1}$ and 0.13 $\mu g\,L^{-1}$ As, respectively. The limits of detection in urine are ca. 0.4 and 1 $\mu g\,L^{-1}$ with 10- and 25-fold dilutions. Procedural blank levels are ca. 0.30 ng and 0.15 $\mu g\,L^{-1}$ As. The regression equation for calibration curve was $A_{int} = 0.5622$ [As(III), $\mu g\,L^{-1}$] with correlation coefficient, $r^2 > 0.998$.

Within-batch and between-batch R.S.D.s are <0.9 and <1.3% at 4 $\mu g\,L^{-1}$ As level, respectively. About 5.5–6.0 mL of diluted urine is required for duplicate measurements. The sample throughput rate is 25 h^{-1}.

4. Conclusions

Owing to its high sensitivity, precision and robust operation, the ETAAS with in-situ collection of arsine, monomethylarsine and dimethylarsine generated from diluted urine samples in the presence of 50 mmol L^{-1} HCl and 70 mmol L^{-1} L-cysteine represents an on-line, fast and automated analytical method for the determination of toxicologically relevant arsenic, i.e. the sum of arsenite, arsenate, monomethylarsonate and dimethylarsinate. Employment of a custom-made, large-volume gas–liquid separator and high dilution factors (10–25×) results in much

better tolerance to flooding, foaming and aerosol formation. Pre-instrumental sample treatment is conveniently performed in a batch mode and involves only additions of stock solutions of HCl and L-cysteine to a urine sample aliquot.

Acknowledgments

The authors gratefully acknowledge the partial financial support provided by Bulgarian Ministry of Education (No. N2405) and by the Ministry of Education and Science of the Republic of Macedonia (No. 17-2633) in the frame of bilateral cooperation project "Development of methods for the determination of chemical species of toxic and essential elements in food and environmental samples". Thanks are due to the Referee 1 who called the authors' attention to the behaviour of phenylated arsenic species in hydride generation.

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