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Arsenic speciation in some environmental samples: a comparative study of HG–GC–QFAAS and HPLC–ICP–MS methods

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Some water and soil extracts polluted with arsenic, and a sewage sludge certified for total arsenic have been analysed by high-performance liquid chromatography–inductively coupled plasma–mass spectrometry (HPLC–ICP–MS) and hydride generation–gas chromatography–quartz furnace atomic absorption spectrometry (HG–GC–QFAAS techniques.) Detection limits in the range of 200–400 and 2–10 ng l^{-1} respectively allowed the determination of inorganic [As(III), As(V)] and methylated (DMA, MMA, TMAO) arsenic species present in these samples. Results obtained by both methods are well correlated overall, whatever the arsenic chemical form and concentration range (8–10 000 $\mu g\, l^{-1}$). Comparison of these results enabled us to point out features and disadvantages of each analytical method and to reach a conclusion that they are suitable for arsenic speciation in these environmental matrices. Copyright © 2000 John Wiley & Sons, Ltd.

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INTRODUCTION

Natural accumulations of arsenic occur in some parts of the world. Additionally arsenic is introduced into the different compartments of the environment by largescale industrial and agricultural use and also by mining activities.

Inorganic arsenic is predominant in soils and waters. Methylated forms such as monomethylarsonic acid (MMA), dimethylarsinic acid (DMA) and trimethylarsine oxide (TMAO) can be also found, due to the use of organic arsenicals as pesticides and to biological methylation.

In biological matrices more complex organic arsenic forms such as arsenocholine (AsC) and arsenobetaine (AsB) can occur. AsB may represent up to 95% of arsenic species in marine fish. In algae, arsenic is also present in arsenosugar forms, resulting from biotransformation of simpler arsenic compounds.

As for many other elements, the acute toxicity and environmental fate of arsenic compounds depend on their molecular forms. Inorganic arsenic is known to be particularly toxic, especially arsenite [As(III)]; the acute toxicity of arsenic compounds decreases in the order: arsenite $>$ arsenate $>$ MMA $>$ DMA, with a ratio of about 100 between the toxicity of inorganic and methylated forms. It is therefore important to determine the concentration of each of these species accurately.

Numerous analytical methods have been developed for that purpose in recent years and have been reviewed.[1] The oldest methods optimized for arsenic speciation are based on hydride generation.[2,3] However, the predominant methods nowadays consist of coupling the separation power of HPLC to detection with specific detectors such as atomic absorption spectrometry (AAS), inductively coupled plasma–atomic emission spectrometry (ICP–AES) or ICP–mass spectrometry (ICP–

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MS).[4] Numerous publications deal with the analysis of standard solutions but few with actual environmental samples. To calibrate these analytical methods for arsenic speciation, a standard solution certified in arsenobetaine content (CRM 626) and a tuna-fish tissue (CRM 627) certified in AsB and in DMA have been recently commercialized by the BCR (Commission of the European Communities, Brussels, Belgium. Because of the lack of reference materials certified for the more toxic arsenic compounds [As(III), As(V) and MMA], it was of particular interest to compare arsenic speciation determined by different methods on the same samples.

The aim of this paper is to quantify the major arsenic species present in some natural waters, soil and sludge water extracts by two different hyphenated techniques: hydride generation–gas chromatography–quartz furnace atomic absorption spectrometry (HG–GC–QFAAS) and high-performance liquid chromatography–inductively coupled plasma mass spectrometry (HPLC–ICP–MS). Comparison of the results will establish their validity and interest.

EXPERIMENTAL

Reagents and solutions

Arsenic trioxide (As_2O_3, p.a.) was obtained from Merck Darmstadt, Germany). Dimethylarsinic acid sodium salt trihydrate (DMA, purum) and standard solution ($1000\ mg\ As\ l^{-1}$) of arsenate (H_3AsO_4, spectrosol) were purchased from Fluka (Sigma–Aldrich, Buchs, Switzerland) and BDH (Poole, Dorset, UK), respectively. Methylarsonic acid (MMA) disodium salt [Puro (>98%)] was purchased from Carlo Erba (Milan, Italy).

Deionized water (Milli-RO/Milli-Q system from Millipore, 18 MΩ cm) was used to prepare the stock standard solutions and the eluent solutions. Arsenite stock standard solution ($1000\ mg\ As\ l^{-1}$) was prepared by dissolution of As_2O_3 in 0.2% (m/v) NaOH solution ($NaOH{\cdot}H_2O$, suprapur, Merck) leading to formation of sodium arsenite. The $1000\ mg\ As\ l^{-1}$ stock solutions of MMA and DMA were prepared in deionized water. All standards ($1000\ mg\ l^{-1}$) were used without any further purification and stored at 4 °C in the dark; their stability over several months has been confirmed.[5]

For the HPLC–ICP–MS method, working standard solutions, obtained daily by dilution in the chromatographic eluent just before use, were stored in the dark. Phosphate mobile phase ($12.5\ mmol\ l^{-1}$, pH 6.8) was prepared by dissolving diammonium hydrogen phosphate [$(NH_4)_2HPO_4$] in deionized water and pH adjustment was obtained by dropwise addition of 30% ammonia (NH_4OH); all were RPE quality (Carlo Erba). The mobile phase was filtered ($0.45\ \mu m$) and deaerated just before use.

For the HG–GC–QFAAS method, stock solutions were diluted daily to intermediate solutions containing $10\ mg\ As\ l^{-1}$ and to working solutions containing $100\ \mu g\ As\ l^{-1}$. Trimethylarsine (TMA) standard solution ($1000\ mg\ As\ l^{-1}$) and the working solution were prepared by solubilization of commercial trimethylarsine (Strem, 99% purity) in methanol (Merck, p.a.). A 6% $NaBH_4$ (Fluka, 99% purity) solution was prepared daily in deionized water and stabilized with 0.1 M NaOH ($NaOH{\cdot}H_2O$, Merck, suprapur). Oxalic acid (RPE quality) was purchased from Carlo Erba. Phosphate buffer (0.05 M) was prepared with KH_2PO_4 ($6.8\ g\ l^{-1}$; Merck, p.a.) and K_2HPO_4 ($8.7\ g\ l^{-1}$; Merck, p.a.).

All the vessels and sampling bottles used were decontaminated with 10% (v/v) HNO_3 (Merck, p.a.) and rinsed several times with deionized water.

Apparatus

HPLC–ICP–MS

The HPLC system consisted of a Varian 9012 (Varian) gradient solvent delivery unit fitted with a Hamilton PRP-X 100 (Hamilton, Reno, NV, USA) anion-exchange column (25 cm × 4.1 mm i.d.; spherical 10-μm particles of a styrene–divinylbenzene copolymer with trimethylammonium exchange sites; stable between pH 1 and 13; exchange capacity $0.19\ meq\ g^{-1}$). A 100-μL injection loop (PEEK; Interchim) was used in conjunction with a Rheodyne six-port injection valve. An Elan 6000 ICP/MS (Perkin-Elmer) was used to detect arsenic compounds in the chromatographic effluent.

HG–GC–QFAAS

The HG–GC–QFAAS system was an automatic device optimized in our laboratory for organotin[6,7] and arsenic speciation.[8] It consists of a hydride generation flask made of Pyrex (50 ml) linked to a glass U-tube (705 mm×4 mm i.d.) packed with 10% OV 101 on Chromosorb 80/100-mesh. This glass column could be immersed in liquid nitrogen. It was connected to a T-quartz cell (14 cm×12 mm

Table 1 Operating conditions

ICP–MS: Elan 6000	
R.f. power	$\simeq$ 1100 W
Nebulizer	Cross-flow
Spray chamber	Ryton Scott-type
Ion sampling:	
Sampler cone	Nickel, 1 mm orifice
Skimmer cone	Nickel, 0.75 mm orifice
Argon flow rates:	
Outer	15 l min^{-1}
Intermediate	0.80 l min^{-1}
Aerosol carrier	$\cong$0.95 l min^{-1}
Acquisition parameters:	
Dwell time per mass	50 ms
Sweeps per reading	2
Readings per replicate	535
Replicates	1
Acquisition mode	Peak jumping
Data acquisition	Turbochrom (Integration software)
HPLC: Varian 9012	
Anion-exchange column	PRP-X 100 (250 mm × 4.1 l mm i.d.)
Mobile phase	12.5 mm $(NH_4)_2HPO_4$ in water
pH	
Flow rate	8.5 with NH_4OH
Injected volume	1.5 ml/min^{-1}
	100 μl

HG–GC–QFAAS	
Hydride generation:	
Acid:	
Expt I: As(III+V), MMA, DMA	1% Oxalic acid (50 ml)
Expt II: As(III) only	0.05 M Phosphate buffer (50 ml)
$NaBH_4$	
Concentration	6% in 0.1 M NaOH
Flow rate (time)	2 ml min^{-1} (5 min)
Trapping:	
Column	Glass U- tube (Pyrex, 705 mm × 4 mm i.d.)
Packing	10% OV 101 on Chromosorb W-HP (80/100 mesh)
Trapping time	5.5 min
Room temperature time	3 min
Heating time	3 min (40 °C min^{-1})
Initial helium flow rate:	
Expt I	100 ml/min^{-1}
Expt II	600 ml/min^{-1}
Detection:	
Lamp current	8 mA
Wavelength	197.3 nm
Quartz cell temperature	800 °C
O_2 flow rate	5 ml/min^{-1}
H_2 flow rate	300 ml min^{-1}

Table 2 Retention times (R_t) and performances of the anion-exchange HPLC–ICP–MS method

		Calibration curves		Detection limits[b]	
Species	$R_t \pm SD$(s)	Slope[a] (cps/μg l^{-1})	r^2	Relative[c] (ng l^{-1})	Absolute (pg as element)
As(III)	110 ± 1	271	0.9998	250	25
As(V)	430 ± 2	180	0.9999	380	38
DMA	150 ± 1	289	0.9999	240	24
MMA	195 ± 1	315	0.9997	220	22

[a] Mean for three replicate experiments (peak height).
[b] Defined as 3 × SD of 10 blanks/slope of calibration curve.
[c] Injection loop: 100 μl.

i.d.) heated by a ceramic furnace (Perkin-Elmer). Tygon tubing connected the reaction vessel, the trap and the quartz cell. The mixture in the hydride generation flask was homogenized with a magnetic stirrer. Absorbance signals were detected by a SpectrAA-10 atomic absorption spectrometer (Varian) and a Shimadzu CR4A-Chromatopac Integrator; a PC16 N I/O card drove the process.

Analytical methods

HPLC–ICP–MS

The mass spectrometer was set to sample ion intensities (peak jumping mode) at the analyte mass-to-charge ratio (*m/z*) 75 (^{75}As$^+$). Instrument sensitivity was first optimized using standard solutions introduced with a peristaltic pump delivering a 1.5 ml min^{-1} flow of solution. Instrument adjustments included physical *x,y* mass spectrometer positioning relative to the plasma, the ion lens voltage, argon aerosol carrier gas flow and radio-frequency (r.f.) power input to the argon plasma. The chromatographic system was interfaced with the ICP–MS instrument through a 10-cm Teflon capillary tube (0.5 mm i.d.) connecting the HPLC column outlet to the inlet of the nebulizer. The chromatographic flow rate of 1.5 ml min^{-1} was compatible with the sample uptake rate of the ICP–MS instrument. The chromatographic conditions used in this study were previously optimized.[9]

The optimized HPLC and ICP–MS settings, the analytical performances of the HPLC–ICP–MS method and a typical chromatogram obtained for standard solutions are given in Tables 1 and 2 and Fig. 1 respectively.

Sensitivities as peak heights were very similar for the three less-retained species As(III), DMA and MMA (differing by less than 8%). These differences are in the order of magnitude of the day-to-day repeatability of the measurements by this method.

HG–GC–QFAAS

This method was optimized in order to quantify As(III), As(V), MMA, DMA and TMA species. The principle can be summarized as follows.

An aliquot of sample (0.05–50 ml) was introduced into a Pyrex reactor, containing 50 ml of an appropriate buffer, to which $NaBH_4$ solution was progressively added using a peristaltic pump under continuous stirring. Arsines and alkylarsines formed were flushed by the helium carrier gas to be trapped in the U-column maintained in liquid nitrogen. After purging, the column was removed from liquid nitrogen and then warmed up at room temperature over 3 min. Volatilized hydrides were carried to an electrically heated quartz cell where they were atomized in a H_2–O_2 flame. Water vapour condensed in the trap was removed by

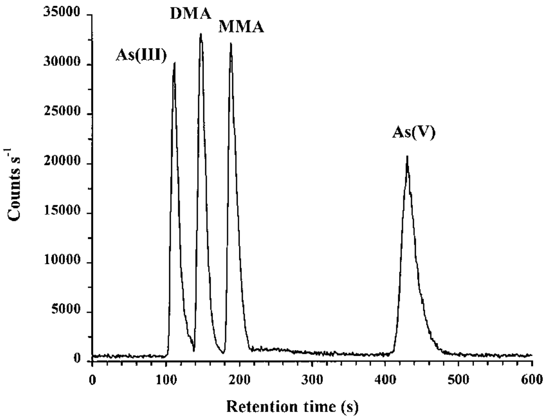

Figure 1 Typical HPLC–ICP–MS chromatogram obtained with the instrumentation conditions described in Table 1. Amount of each standard injected: 100 ng ml^{-1} (as As).

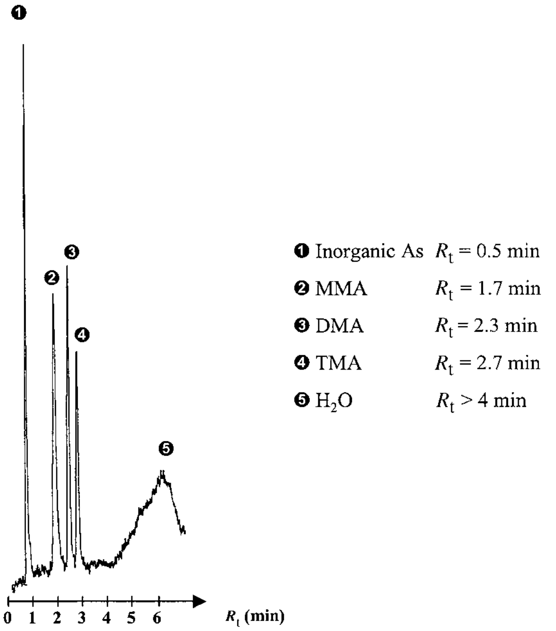

Figure 2 Typical HG–GC–QFAAS chromatogram obtained with the instrumentation conditions described in Table 1. Amount of each standard injected: 10 ng (as As). R_t, retention time.

controlled heating via a nichrome wire. The equipment was fully automated except for sample handling and a modified Shimadzu integrator determined all successive events and proceeded to data storage, plotting and calculations.

A pH-selective reduction was used for the speciation of As(III) and As(V). It necessitated two steps:

(1) In a 1% (m/v) oxalic acid solution (pH 1.5), inorganic arsenic As(III + V) and MMA, DMA and TMA species were reduced by $NaBH_4$ to corresponding arsines (Fig. 2).
(2) In a 0.05 M phosphate buffer (pH 6.8), As(III) was reduced to AsH_3. As(V) quantification was then obtained from the difference between the total inorganic arsenic concentration previously determined and the concentration obtained for As(III) in this step.

The operating parameters are detailed in Table 1 and analytical performances are given in Table 3.[10] A direct comparison of analytical performances with standard solutions can be made by considering Tables 2 and 3.

Absolute (mass) detection limits (DL) are much lower for HPLC–ICP–MS; however—owing to the much larger sample volume (50 ml vs 100 μl) used—HG–GC–QFAAS allows much lower relative (concentration) DL values. Moreover trimethylarsine (TMA) and TMAO may be determined by HG–GC–QFAAS and not by HPLC–ICP–MS, as these neutral arsenic species were not retained by the anion-exchange HPLC procedure used here. This limitation is of little importance for our purposes as neither TMA nor TMAO has ever been detected in the matrices studied in this work.

Water samples

Sampling and storage

Polycarbonate bottles were used for sampling and storage. They were first decontaminated with 10% HNO_3 over one week and rinsed several times with deionized water before use. The samples were stored in the dark at 4 °C and filtered (0.45 μm) just before analysis.

Table 3 Retention times (R_t) and performances of the HG–GC–QFAAS method

			Calibration curves		Detection limits*	
Species	R_t (min)	RSD[a] (%)	Linearity range (ng As)	r^2	Relative[b] (ng l^{-1})	Absolute (pg as element)
As(III), pH 1.5	0.5	3	0.5–20	0.997	10	500
As(V), pH 1.5	0.5	3	0.5–20	0.999	10	500
As(III), pH 6.8	0.6	4	0.2–25	0.998	4	200
DMA	2.3	5	0.2–20	0.999	3	150
MMA	1.7	4	0.1–20	0.999	2	100
TMA	2.7	6	0.3–20	0.996	6	300

[a] Peak area repeatability of 10 ng of standard solutions (five replicates).
[b] Defined as 3 × SD of 20 blanks/slope of calibration curve (IUPAC, $k = 3$; Ref 10.).
[c] Sample volume = 50 ml.

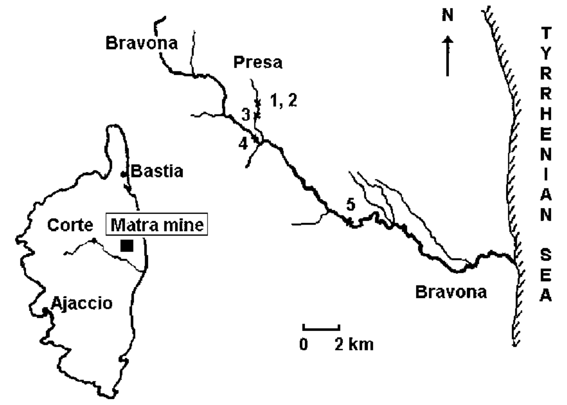

Figure 3 Simplified map of the Matra site in Corsica. Sample sites 1–5 are indicated.

Sampling sites

Three different sites were used for water sampling.

Matra (Corsica)

The first site was situated in High Corsica near the mining site of Matra, where arsenic sulphide, realgar (As_4S_4), was extracted until 1945. Five samples were taken, the sites of which are indicated on a simplified map of the site (Fig. 3).

Salsigne

There are serious arsenic-associated environmental problems in the region of Salsigne (Aude, France) situated near an old gold and arsenic mine.[11] Three samples of water were taken in December 1996. Sample 6 was taken from the Orbiel river upstream of the mine, sample 7 downstream of the mine and sample 8 from the lagoon, situated close to the Orbiel river. Because of torrential rains during the sampling, the Orbiel river was in spate and the lagoon was in danger of overflowing, leading to very particular hydrological conditions, and data presented in this paper cannot be extrapolated to represent the general situation.

Thermal water

A thermal water sample was provided by the Department of Toxicology, Hydrology and Hygiene of the Pharmaceutical and Biological Science Faculty of Lille.

Soil sample extracts

Three industrially contaminated soils were sampled with a spade from confidential sites, and carried in refuse sooks. A sewage sludge reference material (CRM 007-040), certified the total arsenic ($5.74\ \mathrm{mg\ kg^{-1}}$), was also analysed.

These samples were treated via simple water extraction using experimental conditions as close as possible to those described in AFNOR X 31-210 (December 1992).

Before analysis extracts were centrifuged at 3400 rpm for 15 min, then filtered through a 0.45-μm membrane. The pH and the redox potential (E_h) of the samples were measured in the water extracts, which were then stored in airtight polyethylene boxes in the dark.

RESULTS AND DISCUSSION

HG–GC–QFAAS results were obtained using the standard additions method in peak area mode. With the HPLC–ICP–MS device MMA was used as internal standard (to improve accuracy and reduce analysis time) when it was not present in the samples. In the other cases, the internal standard used was Te(VI) (*m/z* 126) in peak height mode.

Before analysis of real samples, the performances of the two methods were tested by blind analysis of a mineral water containing no significant arsenic species and spiked by another worker with As(III), As(V), MMA and DMA at an undisclosed level. Results obtained (Table 4) are satisfactory with recoveries in the range 106–107 % (HPLC–ICP–MS) and 96–119 % (HG–GC–QFAAS). Clearly, As(V) recovery by HG–GC–QFAAS method is less good because of the method of determination, which leads to a lower precision. For all other arsenic species, relative standard deviations are below 5%, whatever the analytical method.

Water samples

Waters sampled at the Matra and Salsigne sites had a pH in the range 6.8–7.7. Matra waters were acidified with 0.5% of nitric acid, for better stability during transport. These two sites contained only As(V) species, in accordance with results found in the literature concerning aerated waters such as rivers or lakes.[11] From the theoretical results of Sadiq *et al.*,[12] in oxidizing waters ($0.2\ \mathrm{V} < E^0 < 0.5\ \mathrm{V}$) and at a range of pH from 5 to 8, As(V) is predominant (in the molecular forms $H_2AsO_4^-$ and $HAsO_4^{2-}$). In reducing conditions (0–0.1 V), As(III) (H_3AsO_3) is the more stable species and its presence has been confirmed in

Table 4 Theoretical and experimental arsenic species concentrations in a spiked mineral water determined by HPLC-ICP-MS and HG-GC-QFAAS

		Species			
		As(III)	DMA	MMA	As(V)
Theoretical (spiked) value (ng As ml^{-1})		150	300	200	100
HPLC–ICP–MS	Mean[a] ± SD (ng As ml^{-1})	159 ± 10	322 ± 13	214 ± 11	106 ± 6
	Recovery ± SD (%)	106 ± 7	107 ± 4	107 ± 6	106 ± 6
HG–GC–QFAAS	Mean[b] ± SD (ng As ml^{-1})	144 ± 7	312 ± 16	208 ± 10	119 ± 20
	Recovery ± SD (%)	96 ± 4	104 ± 2	104 ± 5	119 ± 20

[a] $n = 5$ (determined by external calibration).
[b] $n = 3$ (determined by standard additions).

groundwaters.[13] However, redox and pH conditions were not sufficient to determine the As(III)/As(V) ratio, which also depends on the chemical and biological composition of the sample.

Matra site

The results (Table 5) obtained by both speciation methods or by ICP–MS for total arsenic were in good agreement except for sample 4 by HPLC–ICP–MS. The total arsenic content of this sample was very low (0.9 μg l^{-1}), slightly below the quantification limit of As(V) by HPLC–ICP–MS (3.8 μg l^{-1}) established with standard solutions. The discrepancy between HPLC–ICP–MS and HG–GC–QFAAS therefore has no real meaning. This result points to an advantage of HG–GC–QFAAS: the sample volume could be increased to 50 ml (hydride generator volume), decreasing the relative detection limit, whereas in the HPLC–ICP–MS method the injection loop volume (100 μl) cannot be easily increased.

As expected, samples 1–3 taken near the realgar mine contained a high arsenic concentration. The low concentration (about 1 μg l^{-1}) in sample 4 indicated that the Bravona river was not contaminated by arsenic upstream of the confluence with the Presa river. Sample 5, far downstream, still contained 100 μg As l^{-1}, quite a high value. Finally, the results of this survey are in good agreement with those of previous work concerning total arsenic only.

Salsigne site

Whatever the speciation or total method used and the concentration range, results obtained were similar. Despite the high flow of the Orbiel river, the pollution noted upstream of the mine was not negligible (sample 6). Moreover, although the lagoon was at risk of overflowing, sample 8 contained a very high arsenic concentration.

Thermal water

In the thermal water also, As(V) was by far the predominant form (more than 99.9%) but traces of As(III), DMA and MMA were also detected. The presence of these forms suggested biological activity (reduction, methylation) occurring in this water.[14] The DMA could not be quantified. As(III) and MMA concentrations determined by both methods differed significantly. As regards MMA, the discrepancy probably had the same origin as given for the Matra water samples: the HPLC–ICP–MS value was close to the limit of quantification. The very high mineralization of this sample probably accounted for another part of the discrepancy. The case of As(III) was more complicated, as both methods were facing their extreme limitations for different reasons. HPLC–ICP–MS was again close to its limit of quantification. HG–GC–QFAAS probably suffered from interference due to the high As(V) content of the sample: the reduction rate of As(V) to AsH_3 in step II was not absolutely zero. Further experiments (Fig. 4) indicated that As(III) values may have been noticeably overestimated when the As(V) content in the hydride-generating reactor was higher than 200 ng, a limit widely trespassed with this sample. Both methods nevertheless appeared able to show at least semi-quantitatively the presence of extremely minor arsenic species (less than 0.1%) in the presence of a very high concentration of As(V).

Taking into account these considerations, the results obtained by both speciation methods were on the whole well correlated and fitted well with total arsenic, validating their use over a large concentration range.

Table 5 Arsenic speciation in water samples (μg l^{-1})

Water	Mode[a]	As(III)	DMA	MMA	As(V)	Total As
Matra site						
Sample 1	I	<LD[b]	<LD	<LD	2070 ± 60[c]	2070 ± 60
	II	<LD	<LD	<LD	2100 ± 200	2100 ± 200
	III	—	—	—	—	2160 ± 40
Sample 2	I	<LD	<LD	<LD	1860 ± 30	1860 ± 30
	II	<LD	<LD	<LD	1900 ± 200	1900 ± 200
	III	—	—	—	—	1950 ± 30
Sample 3	I	<LD	<LD	<LD	2180 ± 50	2180 ± 50
	II	<LD	<LD	<LD	2300 ± 200	2300 ± 200
	III	—	—	—	—	2310 ± 30
Sample 4	I	<LD	<LD	<LD	3.6[d]	3.6 ± 0.5
	II	<LD	<LD	<LD	0.96 ± 0.04	0.96 ± 0.04
	III	—	—	—	—	0.89 ± 0.03
Sample 5	I	<LD	<LD	<LD	101 ± 8	101 ± 8
	II	<LD	<LD	<LD	95 ± 5	95 ± 5
	III	—	—	—	—	94 ± 3
Salsigne site						
Sample 6	I	<LD	<LD	<LD	36 ± 3	36 ± 3
	II	<LD	<LD	<LD	35 ± 1	35 ± 1
	III	—	—	—	—	33 ± 1
Sample 7	I	<LD	<LD	<LD	60 ± 1	60 ± 1
	II	<LD	<LD	<LD	60 ± 3	60 ± 3
	III	—	—	—	—	56 ± 2
Sample 8	I	<LD	<LD	<LD	7560 ± 210	7560 ± 210
	II	<LD	<LD	<LD	7600 ± 300	7600 ± 300
	III	—	—	—	—	7570 ± 40
Thermal water	I	3.2[d]	<LQ[b]	4.3 ± 0.5[d]	5260 ± 60	5270[e] ± 60
	II	25 ± 2	<LQ	8.0 ± 0.5	5300 ± 200	5330[e] ± 200
	III	—	—	—	—	5310 ± 40

[a] Mode I, HPLC–ICP–MS; mode II, HG–GC–QFAAS; mode III, ICP–MS.
[b] <LD, not detected; —, not determined; <LQ, not quantified.
[c] Means and standard deviations were obtained with (I) $n = 5$; II, $n = 3$; III, $n = 10$.
[d] Close to LQ (defined as 10 × LD).
[e] Obtained by addition of individual concentrations of the species.

Soil sample extracts

As in the water samples, As(V) was always the predominant species detected (Table 6). However, As(III) was present in all extracts analysed, up to 40% of total arsenic in soil 1 extract. Inorganic arsenic speciation in soils depended on the thermodynamic characteristics of the sample[15] but also on its chemical and biological composition. However, the As(III)/As(V) ratios determined in these water extracts were certainly not representative of the real soils because of the difference in water extraction yield for each inorganic species.

Significant concentrations of the methylated species MMA and DMA were detected in soil 2, and moreover in the sewage sludge extracts. The presence of these species was probably due to important microbiological activity especially in the sludge. Comparison of the total arsenic concentration extracted from the sludge by water with the certified value (5.74 mg kg^{-1}) led to a percentage of arsenic water extraction of about 11%.

Both speciation methods and the total arsenic determination were in good agreement for the soil 1 extract analysis.

Speciation in the soil 2 extract indicated a good coherence of MMA and DMA data; different sample handling and storage delays probably accounted for a partial interconversion between the various inorganic arsenic forms. However, total arsenic determination by direct HPLC–ICP–MS led to a slightly higher value.

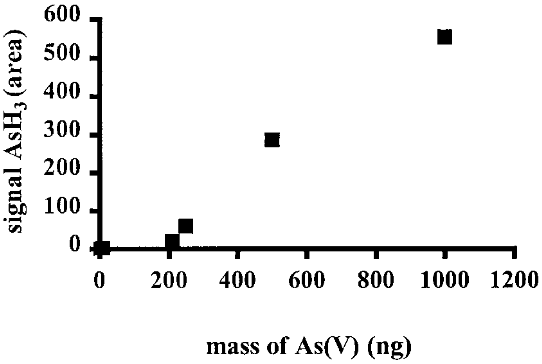

Figure 4 Effect of high As(V) concentrations on As(III) determination in phosphate buffer (pH 6.8) by HG–GC–QFAAS.

Difficulties with the stability of the inorganic forms were also encountered with soil 3 and sludge CRM 007-040 extracts.

On the whole a very good general agreement may be noted for MMA and DMA determinations. The balance of As(III)/As(V) is much more difficult to ascertain. From these data and many other experiments it appears that the kinetics of this redox process are considerably enhanced in soil extracts as compared with natural waters and that extremely close attention should be given in further work to the preservation of the As(III)/As(V) ratio in such experiments.

CONCLUSIONS

HPLC–ICP–MS and HG–GC–QFAAS methods used to determine arsenic speciation in natural freshwater samples and in soil or sludge water extracts gave similar qualitative and quantitative results in an important concentration range varying from 1 to 7000 $\mu g\,l^{-1}$ for water and from 0.1 to 40 $mg\,kg^{-1}$ for soils and sludge. They were both able to detect trace components [As(III), MMA and DMA] in the presence of very high concentrations of As(V). As(III) determination by HG–GC–QFAAS was nevertheless impeded by interference.

The main difficulty concerned sample preparation, handling and storage when dealing with soil extracts as redox processes may sometimes have occurred at unexpected speed, perhaps owing to catalysis.

HG–GC–QFAAS is an easy method to apply. Its high sensitivity allows dilution of natural samples for the determination of major species, thus reducing matrix interferences. The separation of volatile components from the matrix and their preconcentration in a cryogenic trap prior to detection makes it suitable to analyse successfully complex environmental samples. This is an inexpensive method compared with HPLC–ICP–MS, which requires significant investment and functioning costs. However HG–GC–QFAAS analysis time (taking 13 min) is longer than that of HPLC–ICP–MS (9 min), and inorganic arsenic speciation necessitates two independent determinations.

Table 6 Arsenic speciation in soil sample extracts ($mg\,kg^{-1}$)

Water extract	Mode[a]	As(III)	DMA	MMA	As(V)	Total As
	I	14 ± 1[c]	<LQ[b]	<LQ	23 ± 1	[a]37 ± 2
Soil 1	II	14 ± 1	<LQ	<LQ	30 ± 4	[a]44 ± 3
	III	—[b]	—	—	—	37 ± 3
	I	0.164 ± 0.008	0.048 ± 0.005	0.038 ± 0.003	1.43 ± 0.12	[a]1.68 ± 0.12
Soil 2	II	0.369 ± 0.044	0.055 ± 0.003	0.050 ± 0.003	1.31 ± 0.14	[a]1.79 ± 0.19
	III	—	—	—	—	2.20 ± 0.16
	I	0.065 ± 0.010	<LQ	<LQ	0.110 ± 0.009	[a]0.175 ± 0.013
Soil 3	II	0.086 ± 0.012	<LQ	<LQ	0.052 ± 0.041	[a]0.138 ± 0.029
	III	—	—	—	—	0.125 ± 0.016
	I	0.130 ± 0.006	0.121 ± 0.001	0.159 ± 0.003	0.198 ± 0.004	[a]0.608 ± 0.008
CRM 007–040	II	0.064 ± 0.012	0.130 ± 0.008	0.184 ± 0.005	0.245 ± 0.012	[a]0.623 ± 0.019
	III	—	—	—	—	0.616 ± 0.010

[a] Modes as in Table 5.
[b] <LQ, not detected; —, not determined.
[c] Means and standard deviations were obtained (three replicates) with (I) $n = 3$; (II) $n = 3$; (III) $n = 10$.
[d] Obtained by addition of individual concentrations of the species.

Moreover, HG–GC–QFAAS equipment, although easy to make, is not available on the market.

Another advantage of the HPLC–ICP–MS method is the possible simultaneous multi-elemental speciation of As [As(III), As(V), MMA and DMA] and other elements such as Se [Se((IV), Se(VI)], Te(VI) and Sb(V) in a single analysis.[16]

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