Determination of arsenic in organic solvents and wines using microscale flow injection inductively coupled plasma mass spectrometry

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The presence of carbon-containing substances can enhance As signals and elevate background levels observed in inductively coupled plasma mass spectrometry (ICP-MS), thus causing potential errors in the quantification of As. Most approaches for eliminating these interferences are tedious and time consuming and increase the risk of sample contamination and analyte loss. A microscale flow injection (μFI) system employing a microconcentric nebulizer (MCN) for efficient sample introduction into the ICP-MS system was used to reduce signal enhancement effects. Also investigated was the suitability of several elements (Se, Y, In and Sb) to be used as internal standards for As in samples containing organic solvents. The μFI-ICP-MS system developed in this study was shown to reduce the signal enhancement caused by organic solvents by a factor of 2–3 compared with a conventional FI-ICP-MS system. Sample volumes of 0.2, 0.5 or 1.0 μl were injected into the μFI-ICP-MS system at carrier flow rates ranging from 50 to 200 μl min^{-1}. Response profiles obtained following the injection of 1.0 μl solutions containing 20 pg μl^{-1} As at carrier flows of 50, 100 or 200 μl min^{-1}, allowed for throughputs of approximately 80, 140 or 180 samples per hour, respectively. The relative standard deviation (%RSD) of the transient signals, determined over a 20 min period at the previously mentioned flow rates, ranged from 2 to 5%. The calculated absolute limit of detection of the μFI-ICP-MS system, ranging from 25 to 59 fg As, demonstrates the method's potential for determining As at ultratrace levels. The μFI-ICP-MS method was subsequently used to determine As in red and white wines. Diluted wine samples (1 + 1 dilution in de-ionised water) were analysed without any further sample preparation. When using In as the internal standard the average recovery of As was found to be 100 ± 2%. The concentration of As was determined to be between 7 and 13 pg μl^{-1} for all wines examined. These values are significantly lower than the reported maximum permissible concentration limits for As in wine.

Introduction

Arsenic, a well-known poison and suspected carcinogen, is found in its various forms in food products, and biological and environmental materials, at trace and ultratrace levels.[1–4] Despite the fact that As is ubiquitous in the environment, little is known about its chronic sub-lethal effects. Since considerable interest is currently directed towards understanding these effects it is of particular importance to develop robust analytical techniques suitable for providing high sensitivity, accuracy, precision, and sample throughput. Inductively coupled plasma mass spectrometry (ICP-MS), one of the most sensitive techniques for elemental determinations, has been used extensively for determining As in a wide range of materials.[1,2,5–9] Unfortunately, however, both spectral and non-spectral interferences have been reported for this element.[6,8,10–12] One particular non-spectral interference originates from carbon-containing substances, which have been reported to cause pronounced effects on the intensity of As signals in ICP-MS.[8,11–13] Although the mechanism responsible for the signal variation is not fully understood, it is believed to involve changes in plasma conditions which cause modification of the elemental ionisation equilibrium over a limited range of ionisation energies.[11] In practice, this can cause errors in the quantification of As in samples containing elevated levels of organic substances.

Measures taken to eliminate quantification errors may include using matrix-matched standards or internal standards capable of compensating for As signal variations. The use of matrix-matched standards, however, is only possible if the exact composition of the sample matrix is known and can be prepared easily. Most often this is not the case, especially when analysing waste materials containing unknown amounts of organic solvents. On the other hand, employing an internal standard to correct for As signal variation is not always a straightforward procedure. This is mainly because As and the element used as the internal standard do not always respond identically towards matrix interferences. Selecting an appropriate internal standard becomes even more difficult when samples containing high levels of dissolved solids cause additional interferences. Other approaches for reducing or even eliminating non-spectral interferences may include the partial removal of organic components from the sample. This approach is time consuming and tedious, and also adds to the overall complexity of the analysis by increasing the risk of sample contamination and analyte loss. To emphasise further the effects of introducing large amounts of volatile solvents into an ICP, it should be mentioned that this can cause plasma instability because of energy withdrawal, formation of carbon-containing molecular species and carbon deposition on the torch and sample cones. Prevention of such effects requires specialised equipment suitable for spray desolvation, addition of oxygen gas, and spray chamber chilling.[14–16] In many cases the cost and complexity of additional equipment has restricted their usefulness and general applicability.

The purpose of this study was to investigate the effects of carbon-containing solvents, *i.e.*, methanol and isopropyl alcohol, on As signals obtained using ICP-MS. In addition, a

microscale flow injection (μFI)-ICP-MS technique was developed and evaluated for overcoming the aforementioned effects. The technique is based on the efficient introduction of 0.2, 0.5 or 1.0 μl samples into the ICP-MS system *via* a commercially available microconcentric nebuliser (MCN). The μFI-ICP-MS technique was characterised initially and subsequently evaluated for its suitability for determining As in organic solvents and wine samples.

Experimental

Instrumentation

A VG PlasmaQuad II ICP-MS instrument (VG Elemental, Winsford, Cheshire, UK) was used throughout this study. The quadrupole mass filter was operated in the single-ion monitoring mode (*m*/*z* 75) when monitoring As^+ and in the peak jump mode for multi-element detection. Multi-element detection was applied when Se^+ (*m*/*z* 77), Y^+ (*m*/*z* 89), In^+ (*m*/*z* 115) and Sb^+ (*m*/*z* 121) were used as internal standards. The instrument operating conditions were optimised for maximum As^+ signal (*m*/*z* 75). Typical operating conditions and data acquisition parameters are given in Table 1.

Throughout this study the MCN-100 (CETAC Technologies, Omaha, NE, USA) was used. It has been demonstrated that this nebulizer allows for the efficient introduction of analytes into the ICP at low μl min^{-1} flow rates.[17,18] The MCN was mounted directly onto a standard double-pass water-cooled spray chamber without the need for any modifications. A reciprocating pump (Shimadzu, LC-5A, Kyoto, Japan) was used to deliver carrier liquid into the ICP-MS system at flow rates between 50 and 200 μl min^{-1}. Samples were introduced into the carrier stream *via* an internal chamber micro-injector (Rheodyne 7520, Cotati, CA, USA). Internal chambers of 0.2, 0.5 and 1.0 μl were used in this study. The μFI-ICP-MS response was optimised for maximum signal at *m*/*z* 75 using a 190 μl loop fitted onto a Rheodyne 7125 injector. This sample volume was sufficient to provide a quasi-continuous signal that lasted long enough for signal optimisation.

Reagents and samples

Inorganic As, Se, Y, In and Sb standard solutions were prepared by diluting individual standards (VHG Lab, Manchester, UK) containing 10 000 μg ml^{-1} of each element in de-ionised water acidified to 0.05% v/v nitric acid (69% m/m, AnalaR, BDH, Poole, Dorset, UK). Methanol (99.8%, BDH) and isopropyl alcohol (99.7%, BDH) were used to provide a convenient carbon source that was miscible with water. Individual solutions containing 20 pg μl^{-1} of As and 5–100% v/v methanol or 3.5–100% v/v isopropyl alcohol were prepared and used for investigating the effect of carbon-containing substances on As signals in ICP-MS. These solutions were also used to test for As recoveries. Wine samples were diluted 1+1 with de-ionised water and acidified to 0.1% v/v nitric acid. Aqueous calibration standards were also prepared to contain the same amount of acid. All wines used in this study were commercially available. All wine samples were filtered, through a 0.45 μm pore size membrane, prior to injection.

Table 1 Typical ICP-MS operating conditions

Argon coolant flow	12.5–14.5 l min^{-1}
Argon auxiliary flow	1.2–2.0 l min^{-1}
Argon nebulizer flow	0.76–0.80 l min^{-1}
Rf forward power	1350 W
Reflected power	< 5 W
Nebulizer	Microconcentric nebulizer (MCN)-100
Spray chamber	Water-cooled (5 °C) Scott-type (double-pass)
Sample cone	Nickel; aperture diameter 1.0 mm
Skimmer cone	Nickel; aperture diameter 0.75 mm
μFI carrier flow rate	50–200 μl min^{-1}
Data acquisition mode	Peak jump or single-ion monitoring (SIM)
Dwell time	10.24 ms

Results and discussion

Performance characteristics of the μFI-ICP-MS system

Responses obtained for As by using μFI-ICP-MS were evaluated at carrier flow rates of 50, 100 and 200 μl min^{-1}. A typical response profile obtained following consecutive 0.5 μl injections of solutions containing 20 pg μl^{-1} As is presented in Fig. 1. It is evident from this profile that the resulting narrow peaks allow for high sample throughput. More specifically, when running the carrier at a flow of 50, 100 or 200 μl min^{-1} and injecting 1.0 μl samples it was possible to make 80, 140 or 180 injections per hour, respectively. The relative standard deviations (%RSD) of the transient signals determined over a 20 min period, at the previously mentioned flow rates, ranged from 2 to 5%. The system dispersion was determined to be 10. Dispersion was calculated as the ratio of the net As signal obtained following continuous sample introduction to the peak height of the As transient signal obtained following μFI using a 1.0 μl internal chamber injector.

The limits of detection (LOD) obtained for As using the MCN-based μFI-ICP-MS system are summarised in Table 2. All reported LOD were determined at a carrier flow rate of 200 μl min^{-1}. The concentration LOD (cLOD) obtained for 0.2 and 0.5 μl samples were, on average, a factor of 15 higher than those typically obtained for 20 μl samples. However, the absolute LOD (aLOD) obtained after injecting 0.2 and 0.5 μl samples were, on average, 6 and 2.5 times, respectively, better than those obtained for 20 μl samples. The aLOD, ranging from 25 to 59 fg As, demonstrate the potential of μFI-ICP-MS for determining As at ultratrace levels.

The performance characteristics, *i.e.*, LOD, %RSD and

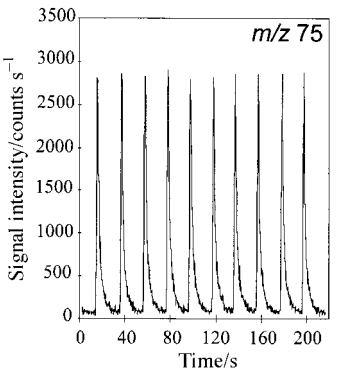

Fig. 1 Peak profiles for 0.5 μl injections ($n = 10$) of 20 pg μl^{-1} As; carrier flow rate was 200 μl min^{-1}.

Table 2 Limits of detection[a] obtained for As by using MCN-based FI-ICP-MS

Injected volume/ μl	Concentration LOD[b]/ fg μl^{-1}	Absolute LOD[b]/ fg
0.2	125[c]	25[c]
0.5	118[d]	59[d]
20	8[e]	160[e]

[a]Calculated as three times the background standard deviation. [b]All LOD were determined at 200 μl min^{-1} carrier flow. [c]Calculation based on the peak area corresponding to 50 pg μl^{-1} As. [d]Calculation based on the peak area corresponding to 10 pg μl^{-1} As. [e]Calculation based on the peak area corresponding to 2 pg μl^{-1} As.

sample throughput, of the MCN-based μFI-ICP-MS system compare well with those previously reported for a high-efficiency nebulizer (HEN)-based μFI-ICP-MS system.[5] Judging from the systems' analytical figures of merit both the MCN and the HEN perform equally well when used for determining As at ultratrace levels. However, the obvious advantage of the MCN, over the HEN, is that it does not require a high-pressure nebulizer gas line and a mass flow controller capable of withstanding approximately 175 psi back-pressure. The MCN can operate efficiently with a mass flow controller that can deliver nebulizer gas at back-pressures of about 50 psi. This type of mass flow controller is a standard component of almost all commercial ICP-MS instruments. It should, however, be mentioned that the additional hardware required for the efficient operation of the HEN is no longer required for a modified version of the HEN; the direct injection HEN (DI-HEN).[19] The DI-HEN sits directly inside the ICP torch and maintains its efficiency even at low nebulizer gas flows, $\approx 0.25\ l\ min^{-1}$ compared with $1.0\ l\ min^{-1}$ required typically by most other types of nebulizers. The DI-HEN has been reported to provide excellent cLOD for As ($17\ fg\ \mu l^{-1}$) in the continuous flow mode; however, aLOD for As in the FI mode have not yet been published.[19]

Effects of carbon on arsenic signal

It has been shown that carbon-containing substances can cause signal enhancement for partially ionised elements when analysed by ICP-MS.[11] Although the mechanism responsible for this effect is not fully understood, it is currently believed that the presence of carbon in the plasma induces changes in the thermo-ionisation of some elements over a limited range of ionisation energies. Allain *et al.*[11] first reported signal enhancements for partially ionised elements (Au, As, Hg, Se, Te) in the presence of organic substances and briefly commented on the difficulty associated with finding suitable internal standards to compensate for this. In view of these and later findings it is apparent that signal variations originating from the carbon present in samples can cause errors when quantifying As by ICP-MS. To correct for signal variations, samples must either be pre-treated to reduce their carbon content or analysed along with matrix-matched standards or with appropriate internal standards. All three approaches, however, exhibit limitations. As already discussed, sample pre-treatment is not only time consuming but also involves additional sample preparation steps that can lead to analyte loss or sample contamination. Employing matrix-matched standards is extremely difficult, especially for samples containing unspecified or variable amounts of carbon, *e.g.*, waste mixtures or alcoholic beverages. Also, samples containing large amounts of dissolved solids can cause additional non-spectral interferences.

As part of this study a μFI-ICP-MS system was used to examine the effects of organic solvents on the intensity of As signals. The investigation was carried out by analysing solutions containing constant amounts of As along with various amounts of carbon. In these experiments methanol and isopropyl alcohol were used as carbon sources. Initially, the effects of increasing concentrations of methanol and isopropyl alcohol on As signal intensity, for 0.2 and 20 μl samples, were investigated. The results obtained from these experiments are summarised in Fig. 2. As expected, non-spectral interferences, manifested as signal enhancements, were observed when samples containing organic solvent were introduced into the ICP-MS system *via* FI. The signal enhancement was significantly greater for 20 μl samples compared with 0.2 μl samples, even though the organic solvent concentration was the same in both cases [Fig. 2(a) and (b)]. Since the carrier flow rate was also the same in both cases, *i.e.*, $200\ \mu l\ min^{-1}$, the rate of carbon aspiration into the ICP-MS system was identical in both cases. In order to explain the greater signal enhancement observed for the 20 μl sample we propose that the presence of carbon in the plasma causes accumulative effects, which most likely occur because of the long washout times required to remove the carbon from the plasma. In studies reporting on the development of liquid chromatographic methods for separating As species it was mentioned that even when the introduction of organic solvent into the plasma was discontinued, a relatively long period of time was required before the ICP-MS sensitivity returned to its pre-solvent level.[9,20]

When the absolute amount of carbon injected into the ICP-MS system is plotted against the recorded As signal intensity, a continuous increase in As signal intensity with increasing amount of carbon injected is observed [Fig. 2(c) and (d)]. A maximum occurs when approximately 1 mg of carbon is injected; signals start to decrease when higher amounts of carbon are aspirated. The fact that the signal intensity for In and Y also starts to decrease at these levels of organics is a strong indication that plasma overloading is occurring.

Together these findings oppose the hypothesis that signal enhancements originate solely from increased nebulization efficiencies resulting from organic solvents present in the aspirated solution. If signal enhancements were caused exclusively because of increased nebulization efficiencies then signal enhancements would be expected to be equal for samples containing the same concentration of carbon. Our present findings, however, do not support this theory. The report by Allain *et al.*,[11] in which signal enhancements for partially ionised elements were still observed when a post-nebulizer methane gas was added to the plasma, also supports the hypothesis that signal enhancement is mainly caused because of the presence of carbon in the plasma and not because of increases in nebulization efficiencies.

After comparing signal intensities obtained on injecting 20 and 0.5 μl solutions, both containing the same absolute amount of carbon, it was observed that signal enhancement was approximately the same for both sample sizes [Fig. 2(e) and (f)]. However, on further inspection a slightly greater enhancement was observed for 0.5 μl samples. This minor difference is believed to occur as a result of differences in the rates at which carbon is nebulized into the ICP-MS system for the two different sample sizes. For example, on injecting samples containing identical absolute amounts of carbon, a 20 μl sample results in a 40-fold lower rate of carbon introduction compared with a 0.5 μl sample. In practice, this suggest that similar reductions in signal enhancement for As in samples with elevated levels of carbon can be achieved by using either μFI (0.5 μl internal volume injector) or by diluting the sample 40-fold and using conventional FI (20 μl injection loop). Of course some disadvantages associated with sample dilution include the risk of contamination and additional time required per analysis. Also, larger injection loops give broader peaks, which result in reduced sample throughput.

Selection of internal standard

As part of this study, the use of μFI-ICP-MS for overcoming interferences caused by organic compounds was also investigated. The fact that the μFI system only requires small sample volumes ($\leqslant 1\ \mu l$), and, as a consequence, only introduces a small absolute amount of sample matrix into the ICP-MS system, prompted us to evaluate μFI-ICP-MS for its suitability to eliminate or reduce non-spectral interferences caused by organic substances. However, as already mentioned, in the presence of elevated levels of organic substances, accurate quantification of As can only be achieved if a suitable internal standard is used to compensate for all non-spectral interferences. In general, an internal standard should be selected with consideration to the type of sample to be analysed and the ionisation efficiency of the element. The elements evaluated in this study as internal standards for As were Se, Y, In and Sb.

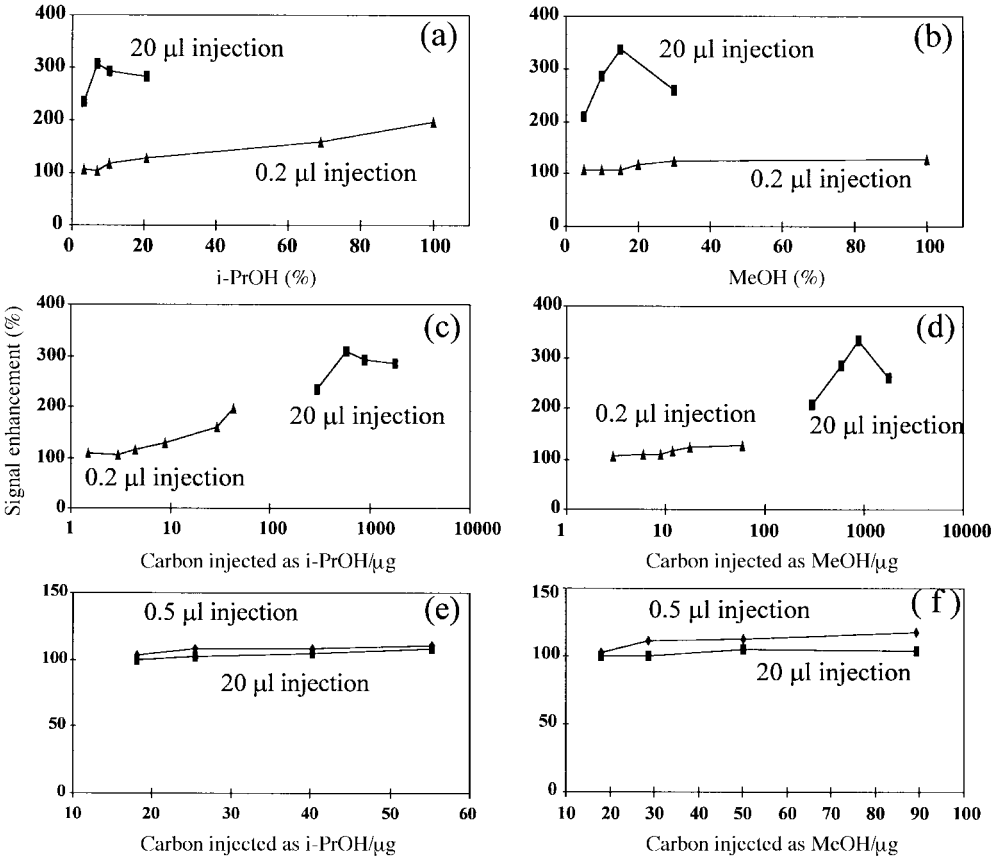

Fig. 2 Comparison of the effect of carbon-containing compounds on As signal intensity for solutions containing 20 pg μl^{-1} As: (a), (c) and (e) with isopropyl alcohol (i-PrOH) as carbon source; (b), (d) and (f) with methanol (MeOH) as carbon source.

The effects of methanol and isopropyl alcohol on the response ratios of As-to-internal standard were investigated in detail (Table 3). When Se was used as the internal standard it compensated successfully for the enhancement of As signals caused by elevated levels of organics. The measured As^+/Se^+ ratio remained relatively constant ($99 \pm 3\%$) for both 0.2 and 0.5 µl samples containing 0–100% v/v isopropyl alcohol or methanol. When larger samples, *i.e.*, 20 µl samples, containing 69.3% v/v isopropyl alcohol or 30% v/v methanol, were analysed using FI-ICP-MS the response ratio As^+/Se^+ deviated from the reference value of 100%, reaching a maximum of 129%. This finding indicates that Se can only compensate partially for the enhancement of As signals caused by elevated levels of organics. Also, unacceptably high standard deviations were observed for triplicate 20 µl injections of these samples. This was most likely caused because organic solvents remain in the plasma for a prolonged time, thus affecting samples injected subsequently.

Table 3 Effect of organic solvents on the As-to-internal standard ratio for different sample volumes (mean $\pm s$; $n=3$)[a]

	% of original ratio[c]											
	As^+/Se^+			As^+/Y^+			As^+/In^+			As^+/Sb^+		
	Volume injected/µl			Volume injected/µl			Volume injected/µl			Volume injected/µl		
Solvent[b]	0.2	0.5	20	0.2	0.5	20	0.2	0.5	20	0.2	0.5	20
i-PrOH (%):												
3.5	96±1	101±1	90±5	98±1	108±1	135±7	103±1	108±1	132±4	89±3	106±1	134±6
6.9	101±3	100±1	95±5	102±2	110±2	178±6	103±5	109±3	166±3	112±2	107±2	166±4
10.4	97±7	101±3	98±9	102±1	108±2	234±8	104±6	108±3	202±5	114±6	105±2	185±8
20.8	93±4	98±4	106±8	106±5	106±5	241±12	102±13	111±6	222±9	124±9	102±5	209±18
69.3	98±6	99±4	110±15	119±5	124±5	474±23	101±20	124±6	403±17	142±11	112±15	208±25
100	94±6	107±6	n.d.[d]	85±12	127±12	n.d.	107±24	134±19	n.d.	174±15	168±21	n.d.
MeOH (%):												
5	101±1	101±1	96±4	102±3	106±3	135±5	102±1	108±2	134±5	102±2	106±2	124±4
10	98±1	99±1	100±5	101±1	107±2	171±5	102±1	109±1	167±3	102±1	107±2	151±5
15	101±3	98±2	107±4	105±2	103±3	216±7	110±3	108±3	199±6	105±2	104±2	178±6
20	99±2	98±2	104±7	103±2	100±6	265±15	104±4	106±3	242±11	104±1	102±5	201±14
30	102±3	98±2	129±13	108±3	106±6	364±18	106±7	111±6	305±16	107±6	106±7	249±19
100	98±4	103±4	n.d.	86±3	116±8	n.d.	121±9	127±5	n.d.	99±7	137±7	n.d.

[a]Carrier flow at 200 µl min^{-1}. [b]i-PrOH = Isopropyl alcohol; MeOH = methanol. [c]Original ratio is defined as the ratio of As signal intensity to that of Se, Y, In or Se in aqueous solutions. [d]n.d.: Not determined.

When the As^+/Y^+ ratio was examined it was observed that Y did not compensate adequately for As signal fluctuations in the presence of elevated levels of organic solvents (Table 3). When injecting 0.2 or 0.5 μl samples the As^+/Y^+ ratio only remained close to the reference value for solutions containing up to 20.8% isopropyl alcohol or 20% methanol. Yttrium did not compensate for As signal variations for solutions containing higher concentrations of organic solvents. This was further observed when 20 μl samples were injected. These samples gave 135–474% enhancements for As signals when Y was used as the internal standard.

Indium, one of the most commonly used internal standards in ICP-MS, compensated adequately for As signal fluctuations when 0.2 or 0.5 μl solutions containing up to approximately 20.8% v/v isopropyl alcohol or 20% v/v methanol were injected. However, for solutions containing higher amounts of organics severe interferences were observed. When 20 μl samples were injected, enhancements ranging from 132 to 403% were observed, indicating that as little as 5% v/v methanol causes considerable As signal enhancement when using a conventional FI system. Similar observations were made for Sb (Table 3).

Determination of arsenic in solutions containing organic solvents

Solutions containing Se (300 pg μl^{-1}), Y (10 pg μl^{-1}) and In (10 pg μl^{-1}), and 0.05% HNO_3, along with various amounts of methanol and isopropyl alcohol, were spiked with As and subsequently analysed for their As content. External calibrations were applied in order to quantify As and determine As recoveries. No organics were added to the calibration standards used for the external calibration. The results obtained from this experiment are summarised in Table 4. The average As recovery determined using μFI-ICP-MS with the Se internal standard was 105 ± 4%, whereas the As recoveries obtained using Y or In as internal standard were 114 ± 3 and 109 ± 2%, respectively. Arsenic recoveries obtained using Se as the internal standard reached 119% when 20 μl samples were injected. Samples were subsequently diluted 40-fold so that a 20 μl sample contained the same absolute amount of carbon as a 0.5 μl non-diluted sample. Arsenic recoveries obtained for the diluted samples were determined to be 98 ± 2%, with Se as the internal standard. These findings suggest that sample dilution and subsequent injection *via* a conventional 20 μl injection loop give results similar to those obtained when analysing non-diluted samples *via* a 0.5 μl injector. This means that both approaches can be used with similar results. However, the μFI procedure offers superior aLOD (Table 2), higher sample throughput, and, most importantly, can handle samples with a high organic content without the need for sample dilution.

In almost all cases, the In internal standard also provided acceptable recoveries for As when non-diluted 0.5 μl samples were analysed. High recoveries, however, were observed when solutions containing elevated levels of isopropyl alcohol were analysed. Although this finding is not fully understood, it may relate to differences in the washout characteristics of methanol and isopropyl alcohol, which may relate to differences in their viscosity and/or vapour pressure.

Determination of arsenic in diluted wine samples

According to Baluja-Santos and Gonzalez-Portal,[21] the concentration of As in wines depends on a variety of factors such as soil composition, grape variety, climatic conditions, use of pesticides, vinification process and storage conditions. The Officer Internationale de la Vigne et du Vin has set the maximum limit of As in wines at 200 pg μl^{-1}. Although very little data regarding As concentrations in wine has been published, it is accepted that uncontaminated wines contain only a few pg μl^{-1} of As.[21–24] In the past, the classical Gutzeit method was used for determining As in wine. The method is based on the generation of volatile arsines, followed by their reaction with silver diethyldithiocarbamate and subsequent measurement of the As-containing complex using molecular absorption.[25] The LOD for this method, estimated at 10 pg μl^{-1}, is probably insufficient for the analysis of most wines. Hydride generation atomic absorption spectrometry has been used for the determination of several hydride-forming elements, including As, in wine and beverages.[21] The technique normally requires sample decomposition, a time consuming procedure which may result in sample contamination or analyte loss. Also, when electrothermal atomic absorption spectrometry is used it is preferred that the wine sample is decomposed prior to the analysis, especially when As concentrations are close to the method's LOD, which was reported to be 1.8 pg μl^{-1} for untreated wine.[22] Following wine decomposition, the cLOD was determined to be 0.5 pg μl^{-1}. The main difficulties encountered when analysing wines are caused by their complex matrix. Wines contain ethanol in addition to a variety of inorganic and other organic substances sometimes at concentration levels of up to 1%. The main inorganic ions, present at about 1 g l^{-1}, are K^+, Na^+, Mg^{2+} and Ca^{2+}. The organic substances are mainly citric acid, glycerol, polyphenols, various proteins, amino acids and polysaccharides. White wines are less abundant in dissolved substances than red wines, particularly with respect to polyphenols.[26]

The μFI-ICP-MS system developed in this work was tested for determining As recoveries in wine samples spiked with As. The average As recoveries were determined to be 76 ± 7 and 100 ± 2% when using Se and In as internal standards, respectively (Table 5). These findings suggest that Se does not compensate adequately for As signal variations in wine samples. This is probably due to the effects caused by the elevated

Table 4 Arsenic recoveries from de-ionised water solutions containing various amounts of organic solvents (mean $\pm s$; $n = 3$). MeOH = Methanol; i-PrOH = isopropyl alcohol

	% Recovery of As from de-ionised water spiked with organic solvents						
Internal standard	5% MeOH +5% i-PrOH	10% MeOH +5% i-PrOH	20% MeOH +5% i-PrOH	30% MeOH +5% i-PrOH	5% MeOH +10% i-PrOH	5% MeOH +20% i-PrOH	5% MeOH +30% i-PrOH
Se[a]	102 ± 2	104 ± 2	106 ± 3	107 ± 5	107 ± 6	109 ± 2	102 ± 6
Se[b]	99 ± 2	102 ± 1	111 ± 1	119 ± 3	105 ± 1	117 ± 1	112 ± 2
Se[c]	98 ± 2	100 ± 1	96 ± 5	100 ± 5	96 ± 2	100 ± 3	100 ± 6
Y[a]	105 ± 4	104 ± 2	110 ± 1	116 ± 3	114 ± 5	121 ± 4	132 ± 3
Y[b]	183 ± 5	199 ± 5	242 ± 5	308 ± 9	232 ± 1	315 ± 4	364 ± 18
Y[c]	78 ± 1	88 ± 3	92 ± 4	90 ± 8	86 ± 2	94 ± 3	102 ± 5
In[a]	102 ± 2	101 ± 2	106 ± 2	110 ± 5	107 ± 3	114 ± 3	122 ± 7
In[b]	184 ± 2	206 ± 3	255 ± 4	315 ± 12	233 ± 2	320 ± 5	300 ± 15

[a]Sample chamber 0.5 μl, carrier flow 200 μl min^{-1}. [b]Conventional loop 20 μl, carrier flow 200 μl min^{-1}. [c]Conventional loop 20 μl, carrier flow 200 μl min^{-1} and diluted sample.

Table 5 Arsenic recoveries from spiked wine samples (mean $\pm s$; $n=3$)

Type of wine	Spiked As (ppb)	As recovery (%)	
		Se internal standard	In internal standard
Vin de Pays Des Cotes de Gascogne, France (white)	10	67 $\pm$ 11	95 $\pm$ 3
	20	75 $\pm$ 10	103 $\pm$ 1
Vin de Pays de l'Herault, France (red)	10	81 $\pm$ 7	98 $\pm$ 1
	20	84 $\pm$ 7	103 $\pm$ 1
Vino de la Tierra, Spanish (white)	10	76 $\pm$ 4	92 $\pm$ 1
	20	77 $\pm$ 1	103 $\pm$ 3
Maureillera Cotes de Provence, France (rosé)	10	74 $\pm$ 9	103 $\pm$ 4
	20	78 $\pm$ 6	102 $\pm$ 1

Table 6 Concentration of As in wines[a] (mean $\pm s$; $n=3$)

Type of wine	Concentration of As/pg μl^{-1}	
	External calibration	Standard additions
Vin de Pays Des Cotes de Gascogne, France (white)	10.4 $\pm$ 1.3	9.7 $\pm$ 1.1
Vin de Pays de l'Herault, France (red)	13.2 $\pm$ 1.0	12.6 $\pm$ 0.7
Vino de la Tierra, Spanish (white)	7.7 $\pm$ 0.2	7.2 $\pm$ 0.2
Maureillera Cotes de Provence, France (rosé)	8.3 $\pm$ 0.6	8.3 $\pm$ 0.2

[a]In internal standard used in all determinations.

concentrations of other matrix elements (Ca, Na, K or Mg).[12,26] Indium, on the other hand, seems to be a suitable internal standard for determining As in wine.

Four different wines, diluted 1+1 with de-ionised water, were analysed for their As content. Indium was used as the internal standard during the analysis. External calibrations were constructed by using aqueous standards containing As at a range of concentrations and 5 pg μl^{-1} In in 0.1% nitric acid. The concentration of As in these wines, as determined using external calibration and standard additions methods, is reported in Table 6. It was observed that both methods found As to be present in the wines at approximately 10 pg μl^{-1}. It should also be mentioned that the slopes of the calibration plots obtained using external calibration (0.0191 ± 0.0003) and standard additions (0.0195 ± 0.0004) were almost identical, indicating that the In internal standard compensated adequately for the matrix effects caused by the wine sample. These findings also indicate that the external calibration procedure is equally suited to determining As in wines by μFI-ICP-MS, and thus the time consuming and tedious standard additions methodology is not necessary. Although the As concentrations found in the wines analysed are in the same range as those determined by other workers[21–24] for other types of wines, it was extremely difficult to establish the accuracy of the present μFI-ICP-MS method for quantifying As in wines, especially since no wine reference material with certified concentrations of As is currently available. However, the fact that the external calibration and standard additions methodologies gave almost identical results supports the validity of the method. It should also be mentioned that when monitoring m/z 77 we did not observe any evidence for the presence of $^{40}Ar^{37}Cl^+$, which can cause interference at m/z 75 ($^{40}Ar^{35}Cl^+$ on As^+). Because wines contain chloride at about 100 μg ml^{-1}, it is essential to check for any chloride interferences when using μFI-ICP-MS for their analysis.

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References

1 A. Lasztity, A. Krushevska, M. Kotrebai, R. M. Barnes and D. Amarasiriwardena, *J. Anal. At. Spectrom.*, 1995, **10**, 505.
2 E. H. Larsen, G. Pritzl and S. H. Hansen, *J. Anal. At. Spectrom.*, 1993, **8**, 1075.
3 W. R. Cullen and K. J. Reimer, *Chem. Rev.*, 1989, **89**, 713.
4 K. Ogoshi, I. Mori, K. Gotoh and K. Ogawa, *Appl. Organomet. Chem.*, 1996, **10**, 757.
5 S. A. Pergantis, E. M. Heithmar and T. A. Hinners, *Anal. Chem.*, 1995, **67**, 4530.
6 B. S. Sheppard, J. A. Caruso, D. T. Heitkemper and K. A. Wolnik, *Analyst*, 1992, **117**, 971.
7 M. Ma and X. C. Le, *Clin. Chem.*, 1998, **44**, 539.
8 J. Goossens, F. Vanhaeche, L. Moens and R. Dams, *Anal. Chim. Acta*, 1993, **280**, 137.
9 E. H. Larsen and S. Stürup, *J. Anal. At. Spectrom.*, 1994, **9**, 1099.
10 S. H. Tan and G. Horlick, *Appl. Spectrosc.*, 1986, **40**, 445.
11 P. Allain, L. Jaunault, Y. Mauras, J.-M. Mermet and T. Delaporte, *Anal. Chem.*, 1991, **63**, 1497.
12 S. A. Pergantis, G.-M. Momplaisir, E. M. Heithmar and T. A. Hinners, in *Proceedings of the 44th ASMS Conference on Mass Spectrometry and Allied Topics, Portland, Oregon, 1996*, American Society for Mass Spectrometry, 1996, p. 21.
13 S. Saverwyns, X. Zhang, F. Vanhaecke, R. Cornelis, L. Moens and R. Dams, *J. Anal. At. Spectrom.*, 1997, **12**, 1047.
14 B. Magyar, P. Lienemann and H. Vonmont, *Spectrochim. Acta, Part B*, 1986, **41**, 27.
15 D. W. Hausler and L. T. Taylor, *Anal. Chem.*, 1981, **53**, 1223.
16 T. J. Brotherton, P. E. Pfannerstill, J. T. Creed, D. T. Heitkemper, J. A. Caruso and S. E. Pratsinis, *J. Anal. At. Spectrom.*, 1989, **4**, 341.
17 F. Vanhaecke, M. van Holderbeke, L. Moens and R. Dams, *J. Anal. At. Spectrom.*, 1996, **11**, 543.
18 S. D. Lofthouse, G. M. Greenway and S. C. Stephen, *J. Anal. At. Spectrom.*, 1997, **12**, 1373.
19 J. A. McLean, H. Zhang and A. Montaser, *Anal. Chem.*, 1998, **70**, 1012.
20 S. A. Pergantis, E. M. Heithmar and T. A. Hinners, *Analyst*, 1997, **122**, 1063.
21 C. Baluja-Santos and A. Gonzalez-Portal, *Talanta*, 1992, **39**, 329.
22 B. T. Kildahl and W. Lund, *Fresenius' J. Anal. Chem.*, 1996, **354**, 93.
23 S. N. F. Bruno, R. C. Campos and A. J. Curtius, *J. Anal. At. Spectrom.*, 1994, **9**, 341.
24 G. A. Pedersen, G. K. Mortesen and E. H Larsen, *Food Addit. Contam.*, 1994, **11**, 351.
25 P. D. Handson, *J. Sci. Food Agric.*, 1984, **35**, 215.
26 S. Augagneur and B. Medina, *J. Anal. At. Spectrom.*, 1996, **11**, 713.

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