Sensitive determination of three arsenic species in water by ion exclusion chromatography-hydride generation-inductively coupled plasma mass spectrometry

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A sensitive and robust speciation method for arsenic in water is described. The separation of arsenate (As^V), arsenite (As^{III}), and monomethylarsonic acid (MMA) was performed using an ion exclusion column packed with a sulfonated polystyrene resin and using dilute trifluoroacetic acid at pH 2.1 as the mobile phase. The hydride generation method was used to improve sensitivity and to eliminate interference from chloride ions. The analysis time per sample was 18 min but could be shortened to 9 min by using a column switching method. The detection limits for the arsenic species were 1.1 pg ml^{-1} for As^V, 0.5 pg ml^{-1} for As^{III}, and 0.5 pg ml^{-1} for MMA, with an injection volume of 50 μl. The relative standard deviations of five replicates of a standard containing 1 ng ml^{-1} As of each species ranged from 0.8 to 2.8%. The method was validated by analyzing reference water samples.

Introduction

Since the toxicity of an element depends on its chemical form, it is important to determine the concentration of individual chemical species in order to evaluate environmental risk. For arsenic and derivatives thereof, the toxicity decreases in the order arsenite (As^{III})>arsenate (As^V)>[dimethylarsinic acid (DMA), monomethylarsonic acid (MMA)]>[arsenobetaine (AsB), arsenocholine (AsC), tetramethylarsonium ion (TMA)]. As a result, the biological methylation of arsenic is generally thought to represent a detoxification process. However, reports have appeared concerning the toxicity of DMA, which includes DNA modification and mutagenicity.[1,2] Arsenic in water occurs mainly in inorganic forms, such as As^V and As^{III}, but also occurs in methylated forms, such as MMA and DMA, at very low concentration levels.[3,4] The levels of other organoarsenic species found in biological tissues, such as AsB, AsC, TMA, and arsenosugars, are negligible in water.

A variety of methods for the speciation of arsenic have been developed thus far,[5–8] and hyphenated methods, such as liquid chromatography-inductively coupled plasma mass spectrometry (LC-ICP-MS) and capillary electrophoresis (CE)-ICP-MS,[9] are currently popular and in common use. However, most of these methods are not applicable to the direct determination of MMA and DMA in water because these species are present at low concentrations. It has also been difficult to apply these methods to sea-water samples because of the high level of polyatomic interference from $^{40}Ar^{35}Cl$ on ^{75}As. The purpose of the present investigation was to develop a sensitive and robust method for the determination of these species in water. As the analytes, four arsenic species, *viz.*, As^{III}, As^V, MMA and DMA, were investigated because of their high level of toxicity. Another reason for selecting these species is that they form volatile hydrides. It is also possible to generate volatile hydrides from non-hydride forming species, such as AsB and AsC, provided that they are decomposed into inorganic forms by microwave digestion[10,11] or photo-oxidation.[12,13] However, these techniques were not investigated in the present study.

In order to increase the sensitivity, a variety of sample introduction methods, such as high-efficiency nebulizers,[14] ultrasonic nebulizers,[15] thermospray nebulizers,[16] direct injection nebulizers[17] and hydride generation,[3,4,9] have been used. Among these, hydride generation (HG) resulted in the highest sensitivity for arsenic species. Furthermore, since only gaseous species were introduced into the ICP *via* HG, polyatomic ion spectral interference from $^{40}Ar^{35}Cl$ on ^{75}As was not a factor. Clogging of the sampling cone and non-spectral interference, such as space charge effects, were also eliminated. It is necessary not only to increase the sensitivity but also to decrease the background signal in order to improve the detection limit. The detection limits for arsenic with LC-ICP-MS are often determined by the high background signal arising from arsenic impurities in the LC eluent. In particular, when a phosphate buffer[4,10,16–19] was used as the eluent, this phenomenon was pronounced because reagents derived from phosphorus, which belongs to the same periodic group as arsenic, generally contain significant arsenic impurities. Therefore, it is desirable to perform a chromatographic separation of arsenic species *via* the use of only a high-purity acid solution as the eluent. The LC modes investigated thus far for arsenic speciation include reversed-phase,[14] ion-pair reversed-phase,[3,14,17–21] size exclusion,[20] micellar[22] and ion-exchange chromatography.[4,16,23–25] However, in so far as we are aware, there is no example in which the separation of arsenic species was performed based on ion exclusion. In the present study, ion exclusion LC was examined for the separation of such species. Our data show that three arsenic species, *viz.*, As^{III}, As^V and MMA, can be separated using only a dilute acid solution, but that DMA cannot be eluted. The detection limits obtained with the present method were more than 20 times lower than those reported previously.[3,4] This appears to be largely due to the use of dilute acid as the eluent, which can easily be obtained in high purity, compared with salts. Although deviations in retention times and background signal fluctuation

due to co-existing ions were reported for ion-pair reversed-phase LC and ion-exchange LC,[4,18] these interferences were not observed in the experiments reported herein, suggesting that the method is of superior robustness. Because of this, the present method is directly applicable to the analysis of sea-water samples.

Experimental

Reagents

A stock solution of arsenate (As^V) at 1000 μg ml^{-1} As was prepared by dissolving sodium arsenate dibasic heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$) (reagent grade, >99%, Wako, Osaka, Japan) in water. A stock solution of arsenite (As^{III}) at 1000 μg ml^{-1} As was purchased from Wako (atomic absorption spectrometry grade). According to the manufacturer, the solution was prepared by dissolving As_2O_3 in a small portion of NaOH solution which was then neutralized with HCl solution to pH 5.0. Stock solutions of MMA and DMA at 1000 μg ml^{-1} As were prepared by dissolving monomethylarsonic acid [$CH_3AsO(OH)_2$] (Tri Chemical Laboratory, Yamanashi, Japan) and dimethylarsinic acid [$(CH_3)_2AsO(OH)$] (Tri Chemical Laboratory) in water, respectively. A 1% sodium tetrahydroborate solution was prepared by dissolving high-purity grade $NaBH_4$ (>95%, Merck, Darmstadt, Germany, or >98%, atomic absorption spectrometry grade, Kanto Kagaku, Tokyo, Japan) in a 0.1 mol l^{-1} NaOH solution immediately prior to the experiment. Sodium hydroxide (analytical-reagent grade) and nitric acid (ultrapure grade) were purchased from Merck. Trifluoroacetic acid (>99%, protein sequencing grade) and sodium sulfate (anhydrous, analytical-reagent grade) were purchased from Wako. Ultrapure water from a Milli-Q Low TOC system (Millipore, Milford, MA, USA) was used throughout.

Instrumentation

A schematic diagram of the LC-ICP-MS instrumentation with hydride generation is described in Fig. 1. An LC-6A liquid chromatograph (Shimadzu, Kyoto, Japan), equipped with a Shimadzu LC-6A pump and a sample injection valve (9725i, Rheodyne, Cotati, CA, USA) with injection volumes of 50 or 200 μl, was used. The ion exclusion column was a sulfonated polystyrene type, Shim-pack SCR-102H (30 cm long, Shimadzu). A 5 cm guard column with the same packing material was also used in a column switching method. The mobile phase was dilute trifluoroacetic acid adjusted to pH 2.1 and a flow rate of 1.5 ml min^{-1} was used. The eluate from the liquid chromatograph was first mixed with 1.5 mol l^{-1} HNO_3 (flow rate, 2.3 ml min^{-1}) and then with a 1% $NaBH_4$ solution (flow rate, 1.8 ml min^{-1}) to generate the hydrides. The mixture was then transferred to a gas–liquid separator (fabricated in our laboratory) through a poly(tetrafluoroethylene) tube (50 cm long, 3 mm id). The details of the gas–liquid separator have been described in a previous paper.[26] The waste liquid was removed immediately after the reaction from the phase separator by means of a peristaltic pump to prevent the excess of hydrogen from entering the plasma and to prevent the chromatographic peak from broadening as a result of memory effects. An ICPM-8500 inductively coupled plasma mass spectrometer (Shimadzu), equipped with a miniaturized torch, was used. Operating conditions are listed in Table 1. The data from the ICP-MS instrument were converted into ASCII format and handled with an Excel spreadsheet (Microsoft, Cambridge, MA, USA) for further processing.

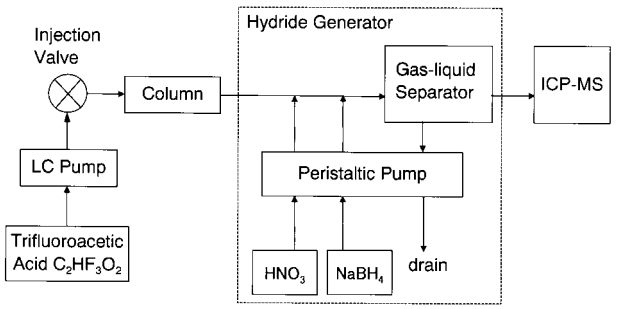

Fig. 1 Schematic diagram of the LC-ICP-MS instrumentation with hydride generation.

Results and discussion

Effect of Na_2SO_4 concentration on the As^V peak shape

Preliminary experiments revealed that a sea-water sample of As^V gave a sharp peak but that As^V, when added to pure water, gave only a small and broad peak. It was speculated that some components contained in sea-water played an important role in the generation of the sharp peak for As^V. As a result, the effect of adding NaCl or Na_2SO_4 to pure water containing 1 ng ml^{-1} of As^V was investigated. The addition of NaCl had no effect, but added Na_2SO_4 produced a marked improvement in the peak shape, although the reason for this was not apparent. The effect of Na_2SO_4 concentration on As^V and As^{III} peak shapes is shown in Fig. 2. The addition of Na_2SO_4 at 400 μg ml^{-1} as the final concentration was found to be sufficient and this concentration had no effect on the equilibrium between As^V and As^{III}. The added Na_2SO_4 did not increase the blank level due to the presence of low levels of arsenic as impurities.

Effect of $NaBH_4$ concentration

The effects of $NaBH_4$ concentration on the signal peak heights and the background equivalent concentrations (BECs) for As^V, As^{III}, and MMA are shown in Fig. 3. The BECs are defined as the concentrations that would give the equivalent peak height to the continuous background signal. Although the signal peak heights increased with increasing $NaBH_4$ concentration, the BECs became worse because of the increased background levels arising from impurities present in the $NaBH_4$ solution. In order to obtain both considerable peak heights and better BECs, 1% $NaBH_4$ was chosen as a compromise concentration. Peak broadening by incorporating a hydride generation reaction between the LC and ICP-MS steps was negligible, compared with the peak widths obtained by LC-ICP-MS without hydride generation. This is probably

Table 1 Optimum operating conditions for LC-HG-ICP-MS

ICP-MS parameters—	
Forward power/kW	1.2
Ar plasma gas/l min^{-1}	7
Ar auxiliary gas/l min^{-1}	1.5
Ar carrier gas/l min^{-1}	0.64
Sampling depth/mm	5
Measured *m*/*z*	75
Dwell time/ms	20
Hydride generation parameters—	
$NaBH_4$ concentration (%)	1
$NaBH_4$ flow rate/ml min^{-1}	1.8
HNO_3 concentration/mol l^{-1}	1.5
HNO_3 flow rate/ml min^{-1}	2.3
LC parameters—	
Column	Shim-pack SCR-102H
Mobile phase	Trifluoroacetic acid (pH 2.1)
Flow rate of mobile phase/ml min^{-1}	1.5
Sample injection volume/μl	50 or 200

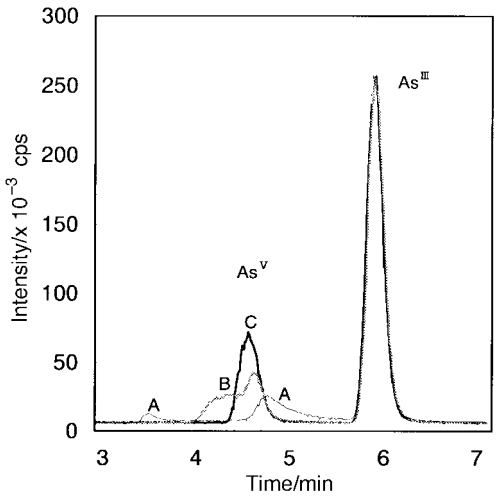

Fig. 2 Effect of Na_2SO_4 concentration on peak shapes of As^V and As^{III}. A, 0 μg ml^{-1} Na_2SO_4; B, 40 μg ml^{-1} Na_2SO_4; C, 400 μg ml^{-1} Na_2SO_4.

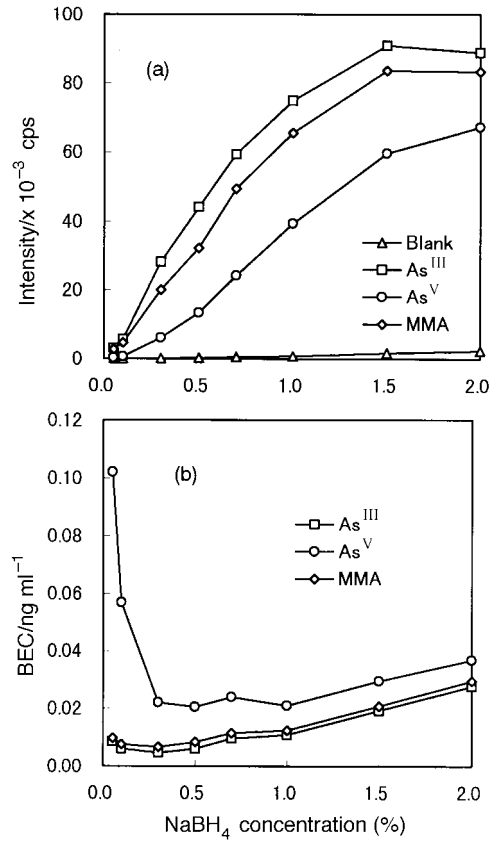

Fig. 3 Effects of $NaBH_4$ concentration on: (a) signal peak heights and (b) background equivalent concentrations (BECs).

because the transportation of gaseous hydrides from the gas–liquid separator was fairly rapid and the unreacted arsenic species in solution were rapidly removed from the gas–liquid separator by the peristaltic pump.

Retention behavior

The column used was a sulfonated polystyrene type. The mobile phase was dilute trifluoroacetic acid, adjusted to pH 2.1. Since the pK_1 values are reported to be 2.25,[27] 2.6,[28] 6.3,[28] and 9.23[27] for As^V, MMA, DMA, and As^{III}, respectively, and the protonation of DMA is reported to occur at pH 3.85,[29] As^V partly exists as an anionic form, while MMA and As^{III} predominantly exist as neutral forms, and DMA exists as a cationic form, respectively, at pH 2.1. A chromatogram of As^V, As^{III}, and MMA is shown in Fig. 4. The separation between As^V and As^{III} appears to be based on an ion exclusion mechanism. However, the separation between As^{III} and MMA is thought to be based on hydrophobic adsorption by the polymeric resin. DMA is thought to be retained on the column by electrostatic attraction and hydrophobic adsorption. This retention behavior of As^V, As^{III}, and MMA is unique compared with that reported thus far, in which the elution of As^{III} is usually earlier than As^V. Attempts to elute MMA and DMA more rapidly by using a higher pH eluent and by adding methanol to the eluent were not successful.

Calibration graphs, detection limits and repeatability

Six-point calibration graphs for As^V, As^{III}, and MMA were obtained by plotting the peak areas against the concentration of arsenic for each species in the range 0–10 ng ml^{-1}. The calibration graphs were linear within this range. The slopes and regression coefficients of the calibration graphs are given in Table 2. The detection limits, defined as three times the standard deviation of the peak areas for seven replicates of the blank, are also listed in Table 2. These values are more than 20 times lower than those reported to date.[3,4] The use of a high-purity acid as the mobile phase is thought to contribute to this improvement in the detection limits. The repeatability for the three arsenic species was evaluated from five replicates using a standard containing 1 ng ml^{-1} As of each species. The relative standard deviations are given in Table 2.

Recovery test

In order to verify the reliability of the present method, recovery tests were carried out with different types of water, such as riverine water, sea-water, and tap water, by adding standards. JAC0031 and SLRS-1 are riverine reference water samples of the Japanese Society for Analytical Chemistry (JSAC) and of The National Research Council of Canada (NRCC), respectively. CASS-3 is a reference sea-water sample of the NRCC. Each arsenic species standard was added to the reference water samples to increase the concentrations by 1 ng ml^{-1} As per species. The averages and standard deviations of four recovery tests are given in Table 3. Since the tap water is chlorinated, As^{III} added to it is rapidly oxidized to As^V by hypochlorite. Therefore, the tap water used for the recovery test was boiled for 10 min to remove chlorine species. Recoveries of the three arsenic species, which ranged from 94 to 108%, are thought to be acceptable.

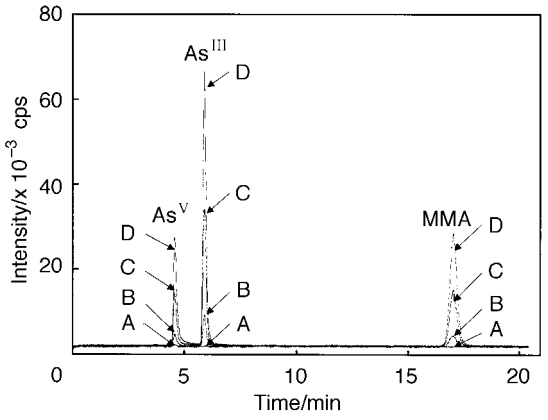

Fig. 4 Chromatograms for As^V, As^{III}, and MMA. A, Blank; B, 0.1 ng ml^{-1} As; C, 0.5 ng ml^{-1} As; D, 1.0 ng ml^{-1} As of each species.

Table 2 Calibration graphs, detection limits and repeatability

	As^{V}	As^{III}	MMA
Slope/counts per pg ml^{-1} As	349	966	877
Regression coefficient (R^2)	0.9993	0.9998	0.9999
Detection limit/pg ml^{-1} As	1.1	0.5	0.5
Repeatability ($n=5$) at 1 ng ml^{-1} As (%)	0.8	2.5	2.8

Table 3 Recovery of added As^{V}, As^{III}, and MMA from water samples (%) ($n=4$: at 1 ng ml^{-1} As)[a]

	As^{V}	As^{III}	MMA
JAC0031 riverine water	106.3±7.7	95.7±4.6	94.3±1.9
SLRS-1 riverine water	105.0±4.0	95.0±0.5	96.7±1.5
CASS-3 sea-water	108.0±5.3	96.3±2.3	101.0±0.5
Tap water	107.5±6.3	99.5±3.5	97.5±0.7

[a] ±values are standard deviations.

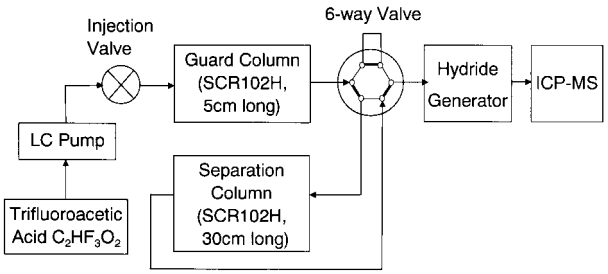

Fig. 5 Schematic diagram of LC-HG-ICP-MS with a column switching system.

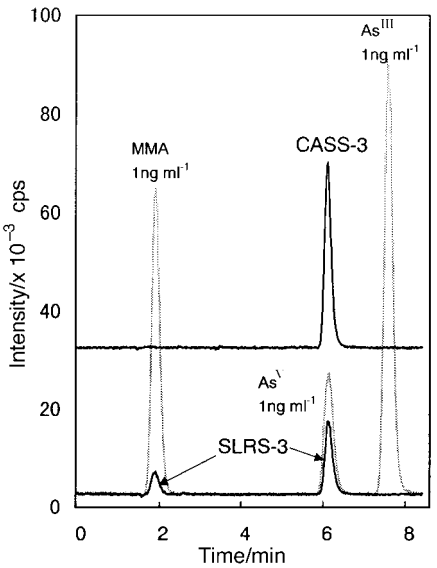

Fig. 6 Top: chromatogram of reference sea-water CASS-3; bottom: chromatograms of a standard solution containing 1 ng ml^{-1} As of each species and riverine reference water SLRS-3. The baseline for the chromatogram of CASS-3 has been shifted so that the peak can be compared readily. The backgrounds of the three chromatograms were nearly identical.

Column switching method to shorten analysis time

Approximately 18 min was required to complete one analysis, because of the long retention time of MMA. In order to shorten the analysis time, a column switching method was applied. A guard column (SCR-102H, 5 cm long) and a six-way motorized valve (Rheodyne, Model 9750) were inserted before the separation column (SCR-102H, 30 cm) as shown in Fig. 5. Initially, the valve was positioned so that As^{V} and As^{III}, eluted from the guard column, were introduced into the separation column. The valve position was then changed at 1.2 min so that MMA eluted from the guard column could be introduced directly into the hydride generator. Finally, after the detection of MMA by ICP-MS, the valve was returned to the original position at 2.6 min to complete the separation of As^{V} and As^{III} by the separation column. Peak broadening of As^{V} and As^{III} as a result of stopping the flow in the separation column from 1.2 to 2.6 min was negligible. A better separation was obtained for As^{V} and As^{III} because of the longer total column length (35 cm), compared with the result shown in Fig. 4. These modifications permitted the analysis time to be shortened to 9 min. Chromatograms for SLRS-3 and CASS-3, obtained using an injection volume of 200 µl, are shown in Fig. 6, along with the standard containing each species at 1 ng ml^{-1} As. The As^{III} peak was not observed in either of the reference water samples because of acidification with HNO_3 for sample storage. It was confirmed that As^{III} was rapidly converted to As^{V} at low concentrations by adding small portions of concentrated HNO_3 to the As^{III} standard solution at 1 ng ml^{-1} (final HNO_3 concentration, 0.1 mol l^{-1}). Therefore, it is not recommended that HNO_3 is added to the sample solutions when the speciation of arsenic is required. The peak of MMA for SLRS-3 was easily distinguishable and the fluctuation of the background for CASS-3 was much smaller, compared with the chromatograms reported previously.[3,4] Although care must be exercised in comparing the chromatograms obtained with the different ICP-MS instruments, it appears that the smaller fluctuations and the less noisy background observed here are due to the robustness of the ion exclusion column and the high purity of the mobile phase. It has also been reported that, since the high chloride concentration of a reference sea-water sample (NASS-4 of the NRCC, salinity 31.3‰) causes peak splitting for MMA, the sample must be diluted 1+3 with distilled water, in order to be analyzed accurately with an anion exchange column.[4] No such problems were encountered with the present method.

Table 4 Analytical results for various reference waters and tap water (ng ml^{-1} As) ($n=3$)

	As^{V}	As^{III}	MMA	Certified value
JAC0031 riverine water	0.22±0.014[a]	<d.l.[b]	<d.l.	0.28±0.04[c]
SLRS-1 riverine water	0.30±0.014	<d.l.	0.05±0.008	0.55±0.08
SLRS-3 riverine water	0.49±0.031	<d.l.	0.08±0.010	0.72±0.05
SLEW-2 estuarine water	0.80±0.065	<d.l.	0.03±0.005	0.792±0.082
CASS-3 sea-water	1.11±0.07	<d.l.	0.01±0.005	1.09±0.07
Tap water	0.10±0.010	<d.l.	0.06±0.012	—

[a]Precision expressed as the standard deviation. [b]Below detection limit. [c]Uncertainties for the certified values are 95% confidence intervals.

Since DMA could not be eluted from the 5 cm guard column, DMA seemed to be retained strongly on the column. Neither a deterioration of the column performance nor elevated background signals due to the retained DMA were observed during the experimental period, *viz.*, about 5 months, but the guard column should be replaced if such phenomena are observed.

Analysis of reference water samples

In order to validate the present method, three riverine reference water samples (JAC0031, SLRS-1, and SLRS-3), one estuarine reference water sample (SLEW-2, salinity 11.6‰) and one reference sea-water sample (CASS-3, salinity 30.2‰) were analyzed. Analytical results are shown in Table 4, along with the certified values. Arsenite (As^{III}) was not detected in any of the samples because of the acidification with HNO_3, as mentioned above. The sum of the concentrations of As^{V} and MMA for CASS-3 and SLEW-2 showed good agreement with the certified values. In contrast, those for riverine waters were out of the range of the certified values. In particular, the deviations from the certified values were large for SLRS-1 and SLRS-3. The reason for this is not clear at present, but one possible reason might be the existence of other species, such as DMA, which cannot be detected with the present method. A relatively large peak of DMA, as large as that of As^{V}, was observed in the SLRS-2 riverine reference water sample (NRCC).[3]

Conclusions

A highly sensitive and robust method for the speciation of arsenic in water was developed by coupling ion exclusion chromatography to ICP-MS with hydride generation as the sample introduction technique. The separation, based on ion exclusion and hydrophobic adsorption, permitted a unique elution order of $As^{V} > As^{III} \gg$ MMA by using only a dilute acid as the eluent. The use of a high-purity acid decreased the background level and improved the detection limit. The retention times of the three species were not affected by the sea-water matrix. The method was free from interference from chloride ions and was easily applied to sea-water samples. The main disadvantage of the present method is its failure to elute DMA. This is probably because DMA is retained on the column *via* hydrophobic adsorption on the polystyrene resin. The use of a more hydrophilic resin should help to decrease this effect. Methods for the purification of sodium tetrahydroborate should be pursued, to achieve a better detection limit, since the detection limit was determined by impurities in this reagent.

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