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Determination of Arsenic Species by Inductively Coupled Plasma Mass Spectrometry with Ion Chromatography

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Five arsenic species, trimethylarsine oxide, dimethylarsenic acid, monomethylarsonic acid, arsenobetaine and sodium arsenite, in urine were analysed by inductively coupled plasma mass spectrometry with ion chromatography (IC ICP MS).

Since the toxicities of different arsenic compounds are different, speciation of arsenic compounds is very important in the investigation of metabolisms. In this paper, we applied ion chromatography (IC) as a separation device and inductively coupled plasma mass spectrometry (ICP MS) as a detection device. For separation of the five arsenic compounds, an anion-exchange column and, as mobile phase, tartaric acid were used. The eluent from the IC column was introduced directly into the nebulizer of the ICP MS and analysed at 75 amu. Detection limits were from 4 to 9 pg as arsenic.

Keywords: Arsenic compounds, ICP MS, IC, speciation

INTRODUCTION

Arsenic has been documented as a human carcinogen of the skin and lungs.[1] Most mammals, including human beings, are able to methylate inorganic arsenic compounds to monomethylarsonic acid (MMAs) and dimethylarsenic acid (DMAs).[2] On the other hand, arseno-betaine (AsBe), which is regarded as a non-toxic organoarsenic compound, is plentiful in seafood and is directly eliminated with the urine. Therefore, speciation analysis of arsenic compounds is required in order to study toxicity. At present, several analytical procedures have been reported. For speciation of arsenic compounds, the most commonly used technique is the application of chromatography with different detection system.[3–9] Inductively coupled plasma mass spectrometry (ICP MS) is a sensitive, accurate and precise analytical tool for ultra-trace multi-elemental and isotopic analysis. However, this method does not give any information about speciation. On the other hand, IC is a good separation method for speciation study, but lack of sensitivity is a problem for arsenic analysis. Several researchers have applied ICP MS as a detector for liquid chromatography,[7–9] but they could not demonstrate separation and detection of the five arsenic species in one injection. In this paper, we applied anion-exchange chromatography as a separation device; the eluent of IC was introduced directly into ICP MS, and the five arsenic compounds in rat urine were analysed.

MATERIALS AND METHODS

The arsenic compounds used in the experiments are listed in Table 1. These compounds were dissolved in Milli-Q water (Nihon Millipore Ltd, Tokyo, Japan). Tartaric acid was purchased from Wako Pure Chemical Industries, Osaka, Japan, and used as the mobile phase at up to 0.01 mol dm^{-3}.

The ICP MS instruments used were a model PMS2000 (for calculation of detection limits) and a model PMS200 (for rat experiments) manufactured by Yokogawa Analytical Systems Inc. (YAN), Tokyo, Japan. The operational conditions for ICP MS are represented in Table 2. Data acquisition was performed in a time chart

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Table 1 Arsenic compound used[a]

Compound	Manufacturer
Sodium arsenite (AsO_3^-)	Wako Pure Chemical, Osaka, Japan
Monomethylarsonic acid (MMAs)	Tri Chemical Lab., Kanagawa, Japan
Dimethylarsenic acid (DMAs)	Sigma, St Louis, MO, USA
Trimethylarsine oxide (TMAs)	Strem Chemicals, Newburyport, MA, USA
Arsenobetaine (AsBe)	Tri Chemical Lab., Kanagawa, Japan

[a] Used as purchased.

Table 2 ICP MS operational conditions

Instrument	PMS 2000
RF forward power	1.3 kW
RF reflected power	<5 W
Plasma gas flow	Ar, 18 L min^{-1}
Auxiliary gas flow	Ar, 1.0 L min^{-1}
Carrier gas flow	Ar, 0.88 L min^{-1}
Sampling depth	5 mm from work coil
Monitoring mass	75 amu
Dwell time	0.5 s
No. of scans	1

analysis mode at 75 amu and dwell (integration) time 500 ms for each data point.

The IC instrument and the separation column used were a model IC7000 and on Excelpak ICS-A35 anion-exchange column, respectively, which were manufactured by YAN. Excelpak ICS-A35 is polymer-based hydrophilic anion-exchange resin (ion-exchange capacity 0.15 mequiv. g^{-1} dry wt). Other operational conditions were varied to produce optimal conditions. An outlet from the separation column was directly connected to the nebulizer of the ICP MS using ETFE (ethylenetetrafluoroethylene) tube of 0.3 mm i.d. and approximately 800 mm long.

RESULTS AND DISCUSSION

In order to produce optimal operational conditions, several factors were varied as follows:

Effect of the mobile-phase pH on elution time

The pH was varied from 3 to 6 by adding NH_4OH solution to 0.001 mol L^{-1} tartaric acid. Upon increasing the pH, the elution times of organoarsenic compounds such as MMAs, DMAs and trimethylarsine (TMAs) were greatly delayed while inorganic arsenic compounds were not affected. Lower pH values produced the best separation for the five arsenic species.

Effect of the mobile-phase concentration on the elution time

The concentration of tartaric acid was varied from 0.003 to 0.01 mol L^{-1}. A constant pH was used. Higher tartaric acid concentrations greatly reduced retention of MMAs and slightly reduced retention of AsBe while DMAs was not affected. A 0.01 mol L^{-1} mobile phase produced the best separation for the five organoarsenic species.

According to these results, optimal conditions were obtained as represented in Table 3. Figure 1 is the chromatogram of a mixed standard solution. The concentration of each of the five arsenic species was 1 mg L^{-1} as arsenic. Arsenate (AsO_4^{2-}) was not added to the sample. The five

Table 3 Optimized IC operational conditions

Instrument	IC7000
Column	Excelpak ICS-A35 × 2 (150 mm × 4.6 mm i.d.—two columns in series)
Mobile phase	0.01 mol L^{-1} tartaric acid
Flow rate	1.0 mL min^{-1}
Column temperature	50 °C
Injection volume	20 μL

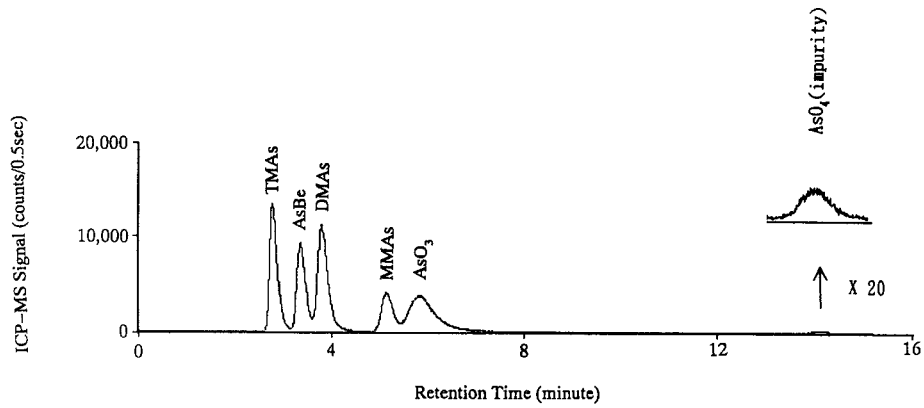

Figure 1 IC ICP MS chromatogram of mixed standard solution containing 1 mg L^{-1} as arsenic of each species except AsO_4^{3-}.

arsenic species and arsenate were completely separated within 15 min. Since the temperature of plasma is very high (over 6000 K) arsenic compounds are decomposed and turned into arsenic oxygen, hydrogen and carbon ions, which means that the sensitivity of an arsenic compound as arsenic does not depend upon the structure of the arsenic compound. When the concentration of the arsenic compounds as arsenic is the same, each compound produces the same sensitivity at 75 amu, giving the same area on a chromatogram. Good agreement was obtained for TMAs, AsBe and DMAs, but MMAs and AsO_3^- were less sensitive than was expected. When standard solutions of each arsenic compound, i.e. TMAs, AsBe and DMAs, were injected, each arsenic species gave almost the same peak area. But when these standard solutions were mixed, TMAs gave a relatively larger peak area while AsBe gave a relatively smaller peak area. We assume that AsBe was partially decomposed to TMAs in the mixed standard solution. In the case of MMAs, a lack of purity may be a main reason. Arsenite (AsO_3^-) also decomposed in the mixed standard solution. In the case of MMAs, a lack of purity may be a main reason. Arsenite (AsO_3^-) also decomposed in the mixed standard solution, giving arsenate (AsO_4^{2-}). Sampling efficiency, as for organotins, is good and is not the cause.

It must be taken into consideration that molecular-ion interference of ArCl at 75 amu may occur in ICP MS if a sample contains higher concentrations of chlorine[10] (75 amu peak can arise in ICP MS as a recombined molecular ion generated by the plasma argon gas (^{40}Ar) and ^{35}Cl). Using the optimal operational conditions, a 1000 mg L^{-1} chlorine standard solution was analysed. No peaks at 35 and 37 amu were observed within 60 min.

Detection limits

Detection limits were calculated from 10 times the square root (σ) of a blank signal (RSD 10%) and a sensitivity factor obtained by a 1 mg L^{-1} standard solution. Table 4 represents the detection limits of arsenic species and relative standard deviations.

Application

The IC ICP MS method was applied to determine organoarsenic species in rat urine (40 µL for each

Table 4 Detection limits

Arsenic compound	Detection limit (µg L^{-1})	RSD ($n=3$) (%)
Sodium arsenite (AsO_3^-)	0.39	3.9
Monomethylarsonic acid (MMAs)	0.44	4.9
Dimethylarsenic acid (DMAs)	0.28	4.1
Trimethylarsine oxide (TMAs)	0.25	4.7
Arsenobetaine (AsBe)	0.22	3.2

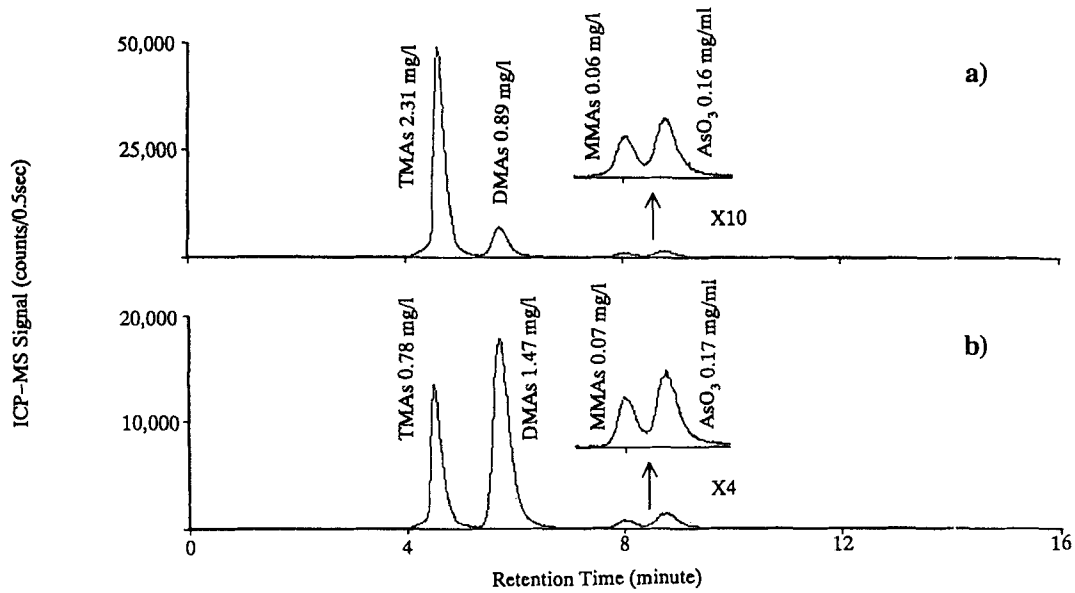

Figure 2 IC ICP MS chromatogram of urine collected from DMAs-exposed rats: (a) 50 mg L^{-1} DMA; (b) 100 mg L^{-1} DMA, in drinking water. Injection volume was 50 μL.

analysis at days 18, 22, 26 and 30). The urine was collected from male rats to which different kinds of carcinogen had first been administered and then different concentrations of DMAs had been given through the drinking water. (*N*-butyl-*N*-(4-hydroxybutyl)nitrosamine (BBN) at 0.05% in drinking water during weeks 1 and 2, followed by *N*-bis(2-hydroxypropyl)nitrosamine (BBN) at 0.05% in drinking water during weeks 3 and 4; then, after a two-week interval, 50, 100, 200 and 400 mg L^{-1} of DMA were given to the rats for four weeks. Figure 2 represents a chromatogram of rat urine diluted 10-fold after dosage with 100 and 50 mg L^{-1} DMAs in drinking water. Comparing the two chromatograms, Figs 1 and 2, retardation of the retention time from the standard solution was observed which seemed to be due to a higher salt matrix. The retentions of each peak were checked by adding corresponding standard solutions to the rat urine.

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