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## Note

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### Non-suppressed ion chromatography of arsenic anions using sodium nitrite solutions as eluents

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One analytical technique for the separation and the detection of inorganic and organic arsenic compounds is a reduction method, by which arsenic species are reduced to volatile arsine compounds<sup>1–4</sup> and separated by gas chromatography<sup>1,3</sup> or thermal volatilization<sup>2,4</sup> and determined spectroscopically. On the other hand, most direct methods involve liquid chromatography<sup>5,6</sup> equipped with voltammetric<sup>5</sup> or absorption spectrometric<sup>6</sup> detectors. Suppressed ion chromatography (IC)<sup>7</sup> has recently been used to separate and to determine some arsenic compounds<sup>8–16</sup> with conductivity detection<sup>8,13,14,16</sup>, pulse polarography<sup>9</sup>, atomic absorption<sup>10–12</sup>, inductively coupled argon plasma–atomic emission spectrometry<sup>15</sup> or electrochemical detection<sup>16</sup>.

Non-suppressed IC<sup>17,18</sup> is a very useful system with various kinds of eluents. We have previously reported on the analysis of inorganic or organic arsenic anions using potassium hydroxide eluents and potassium hydroxide–aromatic salts mixed eluents<sup>19,20</sup>, but the effect of neutral eluent solutions on the chromatography has not been examined in spite of the fact that the charge of these arsenic anions decreases and that the burden of the IC system is relieved.

For these reasons, the efficiency of neutral eluents such as sodium chloride, sodium sulphate, sodium nitrite and sodium nitrate in the separation and determination of arsenic anions by non-suppressed IC has been studied. It was found that the most suitable eluent for the elution of the arsenic compounds is sodium nitrite solution.

## EXPERIMENTAL

### *Standard solutions*

The stock solutions of 1000 µg/ml (as As) potassium arsenate [As(V)], dimethylarsinic acid (DMA), *o*-aminophenylarsonic acid (*o*-APA), *p*-aminophenylarsonic acid (*p*-APA), phenylarsonic acid (PA) and *o*-nitrophenylarsonic acid (*o*-NPA) were prepared by dissolving analytical grade salts or acids in distilled water, respectively. The stock solution of 1000 µg/ml (as As) sodium methylarsonate (MMA) was prepared by dissolving the salt, synthesized according to method of Quick and Adams<sup>21</sup>, in distilled water. Working standard solutions were obtained by diluting the stock solutions in

TABLE I  
DISSOCIATION CONSTANTS OF ARSENIC COMPOUNDS AT 25°C<sup>22</sup>

Compound	$pK_{a1}$	$pK_{a2}$	$pK_{a3}$
1 Arsenic acid [As(V)]	2.22	6.98	11.50
2 Methylarsonic acid (MMA)	3.41	8.18	
3 Dimethylarsinic acid (DMA)	6.273		
4 <i>o</i> -Aminophenylarsonic acid ( <i>o</i> -APA)*	≈ 2	3.77	8.66
5 <i>p</i> -Aminophenylarsonic acid ( <i>p</i> -APA)*	≈ 2	4.02	8.92
6 Phenylarsonic acid (PA)	3.47**	8.48	
7 <i>o</i> -Nitrophenylarsonic acid ( <i>o</i> -NPA)	3.37	8.54	

\* Values are  $pK_a$  of  $NH_3^+C_6H_4AsO_3H_2 \rightleftharpoons NH_3^+C_6H_4AsO_3H^- + H^+$ ,  $NH_3^+C_6H_4AsO_3H^- \rightleftharpoons NH_2C_6H_4AsO_3H^- + H^+$  and  $NH_2C_6H_4AsO_3H^- \rightleftharpoons NH_2C_6H_4AsO_3^{2-} + H^+$ , respectively<sup>23</sup>.

\*\* From ref. 23.

distilled water. The dissociation constants of sample arsenic acids are shown in Table I<sup>22,23</sup>.

#### River-water

As an example of an application, river-water collected at the Kamo river (Kyoto, Japan) was used after filtration through a 0.45- $\mu$ m millipore filter.

#### Eluents

The eluents were prepared by dissolving analytical grade sodium chloride, sodium sulphate, sodium nitrate and sodium nitrite ( $pK_a = 3.14^{22}$ ), respectively, and then deaerated.

#### Apparatus

A Tosoh Model non-suppressed ion chromatograph HLC-601 equipped with an anion-exchange column (50 mm  $\times$  4.6 mm I.D.) packed with TSKgel IC-Anion-PW (particle size  $10 \pm 0.005 \mu$ m, capacity  $0.03 \pm 0.003$  mequiv./g) was used. It consisted of a computer-controlled pump, a conductivity detector, a sample injector (100  $\mu$ l) and an oven. The flow-rate was maintained at 1.0 ml/min under a pressure of 15–30 kg/cm<sup>2</sup>. The separator column and the conductivity detector were placed in an oven regulated at 30°C. The data were recorded by a Shimadzu Model Chromatopack C-R1A.

## RESULTS AND DISCUSSION

#### Sodium chloride, sulphate and nitrate eluents

The elution power of these eluents was observed to lie in the order sulphate > nitrate > chloride for the elution of the sample anions, but the differences were small.

In unbuffered solution, the pH of these solutions is theoretically 7.0, but it is difficult to maintain their pH constant. In this case, the elution behaviour of arsenic (V) anion was significantly affected by a small change in the eluent pH, since the charge of the anion is changed. At pH < 7, the peak of As(V) is slightly overlapped by that of *o*-APA anion and at pH > 7 the retention time of As(V) depends on the eluent

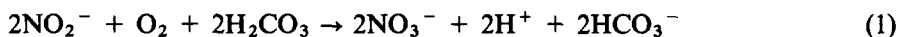
pH. As seen in Table I<sup>22,23</sup>, the eluent pH has to be controlled to 7.0–8.1, at which the charge of As(V) is  $-2$ , for the effective separation and determination of arsenic anions.

Even when the buffer solution is used to control the pH, the eluent containing buffer is unsuitable for ion chromatography with conductivity detection due to acting as eluent of the buffer anion itself. For this reason, solutions of these salts cannot be used as eluents for the separation and the determination of arsenic anions.

#### *Sodium nitrite eluent*

**Characteristics.** The elution behaviour of the sodium nitrite eluent was similar to that of the solutions mentioned above. The elution power of these four eluents followed the order of sulphate > nitrate > nitrite > chloride. Nitrous acid (HNO<sub>2</sub>) is a weak acid ( $pK_a = 3.14^{22}$ ), and these solutions are buffered with strong bases. Their pH is effectively controlled so that the charge of As(V) is probably regulated to  $-2$ .

**Prevention of the oxidation of nitrite anion and lowering of eluent pH.** When using sodium nitrite eluents it is important to suppress the air oxidation of nitrite anion because the eluent pH is lowered. From the reaction mechanism reported by Klemenc and Pollak<sup>24</sup> and Reinders and Vles<sup>25</sup>, the overall reaction is as follows:



The oxidation is prevented by the depression of the absorption of carbon dioxide. Thus, for the prevention of absorption of carbon dioxide in air, a bottle filled with 100 mM potassium hydroxide solution is placed before the eluent bottle.

Moreover, in anion chromatography, the following relationship was given by Gjerde *et al.*<sup>17</sup>.

$$\log t_s = (-y/x)\log [E] - \text{constant} \quad (2)$$

where  $t_s$  is the retention time of the sample anion,  $x$  and  $y$  are the charge numbers of the eluent anion and the sample anion, respectively, and  $[E]$  is the concentration of the eluent anion. The ratio  $(y/x)$  is given by the slope of a plot of  $\log t_s$  vs.  $\log [E]$ . The charge of the sample anion can be estimated from this ratio.

Fig. 1 shows the retention times of sample arsenic anions obtained by using sodium nitrite solutions as eluents. From the slope and the concentration of the eluent, it was estimated that the charge of As(V) is  $-2$  and that carbon dioxide is hardly absorbed.

#### *The use of sodium nitrite eluent*

**Optimum chromatographic condition.** As shown in Fig. 1, the separation of arsenic(V) anion from other sample arsenic anions is possible by using concentrations lower than 3 mM, and if the concentration of eluent anion is increased the time required for separation and determination of sample anions becomes short. The concentration of the salt chosen was 2 mM and the eluent pH was regulated at 7.3.

The oven, in which the column and detector are placed, was regulated at 30°C because the oven temperature hardly influences the separation of the arsenic anions,

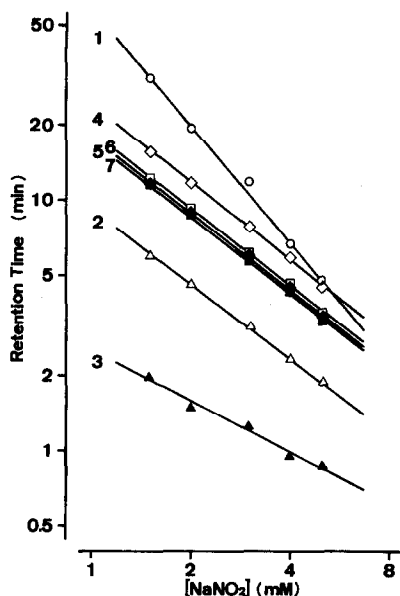


Fig. 1. Retention times of arsenic anions. Samples: 1 = As(V) (slope 1.55); 2 = MMA (slope 0.99); 3 = DMA (slope 0.69); 4 = *o*-APA (slope 0.94); 5 = *p*-APA (slope 1.01); 6 = PA (slope 1.01); 7 = *o*-NPA (slope 1.01). Column TSKgel IC-Anion-PW, 0.03 mequiv./g. Eluent: sodium nitrite.

and the eluent flow-rate was maintained at 1.0 ml/min after consideration of the separation of these anions and the time required.

Fig. 2 shows an ion chromatogram of an arsenic sample obtained under the above conditions.

*Quantitative ranges and detection limits of arsenic anions.* The quantitative ranges and the detection limits of the arsenic anions obtained by using the conditions shown in Fig. 2 are given in Table II. Better result was not obtained on the determination of As(V), because the separation of As(V) from other organoarsenic anions was prior to the determination of As(V) and the concentration of the eluent had to be lowered.

*Separation of aromatic organoarsenic anions.* The peaks of *o*-NPA, *p*-APA and PA anions were not separated and only the total concentration of these three arsenic anions was measured because these anions have very similar limiting equivalent ionic conductances.

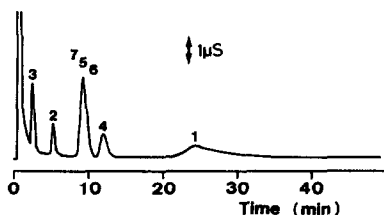


Fig. 2. Ion chromatogram of arsenic anions. Sample: 1 = As(V) (30  $\mu\text{g/ml}$  as As); 2 = MMA (10  $\mu\text{g/ml}$  as As); 3 = DMA (20  $\mu\text{g/ml}$  as As); 4 = *o*-APA (10  $\mu\text{g/ml}$  as As); 5 = *p*-APA (10  $\mu\text{g/ml}$  as As); 6 = PA (10  $\mu\text{g/ml}$  as As); 7 = *o*-NPA (10  $\mu\text{g/ml}$  as As). Column: TSKgel IC-Anion-PW, 0.03 mequiv./g. Eluent: 2 mM sodium nitrite, pH 7.3

TABLE II

QUANTITATIVE RANGES AND DETECTION LIMITS OF ARSENIC ANIONS USING 2 mM SODIUM NITRITE AS THE ELUENT

Anion	Quantitative range ( $\mu\text{g/ml}$ as As)	Detection limit ( $\mu\text{g/ml}$ as As)
1 As(V)	20-50	5
2 MMA	1-50	0.3
3 DMA	3-50	0.3
4 <i>o</i> -APA	1-50	0.3
5 <i>p</i> -APA	1-50	0.3
6 PA	1-50	0.3
7 <i>o</i> -NPA	1-50	0.3

On the other hand, the peak of *o*-APA anion was separated from those of the three anions, because *o*-APA anion has a different structure, involving hydrogen bonding between an hydrogen atom of the amino-group and an oxygen atom of the arsonate-group.

*Comparison between sodium nitrite eluent and basic eluent.* Previously, we reported that potassium hydroxide-sodium salicylate is the preferred basic eluent in non-suppressed IC of arsenic anions<sup>20</sup>.

For the separation of and the sensitivity towards these arsenic anions, sodium nitrite is slightly better than the mixed eluent. Moreover, the lifetime of the separator column is extended because the column is used under mild conditions.

However, in the separation of arsenic anions including arsenite [As(III)] or its derivatives, sodium nitrite is unsuitable as an eluent because these arsenic species have no charge under conditions of neutral pH.

*Application to the synthetic arsenic samples.* Standard solutions containing 1-20  $\mu\text{g/ml}$  (as As) arsenic anions in river-water were prepared in order to evaluate the method. The recovery results are shown in Table III. Although the river-water includes many inorganic and organic anions, there was no interference with the deter-

TABLE III

RECOVERY OF ARSENIC ANIONS ADDED TO RIVER-WATER

Anion	Recovery (%)
1 As(V)	—*
2 MMA	100.8 $\pm$ 0.8
3 DMA	99.9 $\pm$ 2.2
4 <i>o</i> -APA	101.7 $\pm$ 2.0
5 <i>p</i> -APA	92.6 $\pm$ 1.4
6 PA	87.8 $\pm$ 0.5
7 <i>o</i> -NPA	95.8 $\pm$ 1.5

\* Unsuitable for determination.

mination of the arsenic anions. It was found that sodium nitrite as the eluent is effective in controlling the pH and in separating these arsenic anions from one another and from other anions.

Thus, sodium nitrite as the eluent is effective for the separation of arsenic compounds and this chromatographic method is applicable to practical samples.

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