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NON-SUPPRESSED ION CHROMATOGRAPHY OF ARSENIC ANIONS WITH POTASSIUM HYDROXIDE–AROMATIC SALT MIXED ELUENTS

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SUMMARY

The efficiency of mixed potassium hydroxide–aromatic salt solutions as eluents in non-suppressed ion chromatography of arsenic anions was investigated. It was demonstrated that potassium hydroxide–sodium salicylate is the optimum eluent to separate and to detect these arsenic anions because of the formation of internal hydrogen bonding involving the salicylate anion.

INTRODUCTION

Analytical techniques for the separation and the detection of inorganic and organic arsenic compounds have been developed. In one of these methods arsenic species are transferred into volatile arsine compounds[1–4] which can then be separated by gas chromatography[1,3] or thermal volatilization[2,4], and determined mainly by spectroscopic detection.

On the other hand, most other direct methods involve liquid chromatography, which is used for the separation of arsenic compounds[5,6], and voltammetry[5] or absorption spectrometry[6]. Suppressed ion chromatography[7] (IC) was recently used to separate some arsenic compounds[8–16] and conductivity[8,13,14,16], pulse polarography[9], atomic absorption[10–12], inductively coupled argon plasma-atomic emission spectrometry[15] and electrochemical detection[16] are used for their determination.

Suppressed IC with conductivity detection is not able to detect ions having $\mathrm{p}K_a > 7$ because the conductance is measured under neutral or acidic conditions[17]. Conversely, it was suggested that non-suppressed IC[18,19] using a basic solution as an eluent[20,21] is able to determine weak acids[20] such as arsenite[21]. However, the analyses of oxysalts such as arsenic salts have not been examined thoroughly.

For these reasons, the efficiency of alkaline eluents such as potassium hydroxide and potassium hydroxide mixed with aromatic salts has been examined for the separation and determination of arsenic anions using non-suppressed IC. It was found that a suitable eluent for the elution of the arsenic compounds is a mixture of potassium hydroxide and sodium salicylate.

EXPERIMENTAL

Standard solutions

The stock solutions of 1000 μg/ml (as As) sodium arsenite [As(III)], potassium arsenate [As(V)], dimethylarsinic acid (DMA), *o*-aminophenylarsonic acid (o-APA), *p*-aminophenylarsonic acid (p-APA) and phenylarsonic acid (PA) were prepared by dissolving analytical grade salts or acids, respectively. Working standard solutions were obtained by diluting the stock solutions in distilled water. The dissociation constants of the acids are shown in Table I[22,23].

Eluents

The eluents were prepared by dissolving, in distilled water, analytical grade potassium hydroxide and sodium benzoate (pK_{a1} = 4.204[22]), potassium biphthalate (pK_{a1} = 2.950, pK_{a2} = 5.408[22]), sodium salicylate (pK_{a1} = 2.98, pK_{a2} = 12.38[22]), sodium *m*-hydroxybenzoate (pK_{a1} = 4.076, pK_{a2} = 9.85[22]) or sodium *p*-hydroxybenzoate (pK_{a1} = 4.582, pK_{a2} = 9.23[22]). After deaeration, the pH was kept above 11.8.

Apparatus

A Toyo Soda Model HLC-601 non-suppressed ion chromatograph equipped with an anion-exchange column (50 mm × 4.6 mm I.D.) packed with TSKgel IC-Anion-PW (0.03 ± 0.003 mequiv./g) was used, comprising a computer-controlled pump, a conductivity detector, a sample injector (100 μl) and an oven. The flow-rate was maintained at 1.0 ml/min under pressures of 15–30 kg/cm^2. The separator column and the conductivity detector were placed in an oven regulated at 30°C.

RESULTS AND DISCUSSION

Potassium hydroxide eluent

For anion chromatography, the following equation was derived by Gjerde *et al.*[18]

$$\log t_s = (-y/x)\log [\mathrm{E}] - \mathrm{constant} \qquad (1)$$

TABLE I

DISSOCIATION CONSTANTS OF ARSENIC COMPOUNDS (25°C)[22]

Anion	pK_{a1}	pK_{a2}	pK_{a3}
(1) Arsenite [As(III)]	9.18		
(2) Arsenate [As(V)]	2.22	6.98	11.50
(3) Dimethylarsinate (DMA)	6.273		
(4) *o*-Aminophenylarsonate (o-APA)	~2*	3.77**	8.66***
(5) *p*-Aminophenylarsonate (p-APA)	~2*	4.02**	8.92***
(6) Phenylarsonate (PA)	3.47§	8.48	

*,**,*** pK_a for $NH_3^+C_6H_4AsO_3H_2 \rightleftharpoons NH_3^+C_6H_4AsO_3H^- + H^+$, $NH_3^+C_6H_4AsO_3H^- \rightleftharpoons NH_2C_6H_4AsO_3H^- + H^+$ and $NH_2C_6H_4AsO_3H^- \rightleftharpoons NH_2C_6H_4AsO_3^{2-} + H^+$, respectively[23].

§ Ref. 23.

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 log t_s *vs.* log [E]. Therefore, by making x small or y large, the retention time is shortened upon increasing the concentration of the eluent anion.

Fig. 1 shows an ion chromatogram of five arsenic anions obtained with 6 m*M* potassium hydroxide as the eluent, which was the optimum concentration. The anion of PA was first removed from the sample because it exhibits about the same retention time as that of the anion of p-APA. In this case, the retention times of the sample anions were remarkably different, and the peaks of strongly retained anions such as those of p-APA, o-APA and As(V) were extremely broad.

Moreover, it was found that the retention time of the As(V) anion changed with its concentration; nevertheless the other arsenic anions had constant retention times.

Therefore, it was concluded that the use of potassium hydroxide solution is unsuitable for the elution of arsenic compounds.

Potassium hydroxide and aromatic salts as eluents

From above results, mixtures of 6 m*M* (pH 11.8) potassium hydroxide and aromatic salts were investigated as eluents. At this pH, the "charge" numbers of benzoate and salicylate anions are -1, and those of the other anions are -2.

The relationships between the retention times of the sample anions and the concentrations of aromatic compounds in the mixed eluents are shown in Fig. 2a–d, and can be expressed as

$$a'(\mathrm{DMA}):a'[\mathrm{As(III)}]:a'(\text{p-APA}):a'(\mathrm{PA}):a'(\text{o-APA}):a'[\mathrm{As(V)}] = 1:1:2:2:2:3 \qquad (2)$$

where $a'(\mathrm{A}) = -\mathrm{d} \log t_R(\mathrm{A})/\mathrm{d} \log C$, $t_R(\mathrm{A})$ is the retention time of the anion of A and C is the concentration of the organic eluent anion. This ratio corresponds to the ratio of the numbers of the "charge" of the sample anions. Therefore, the concentration of the eluent organic anion is very important in the separation of the arsenic anions.

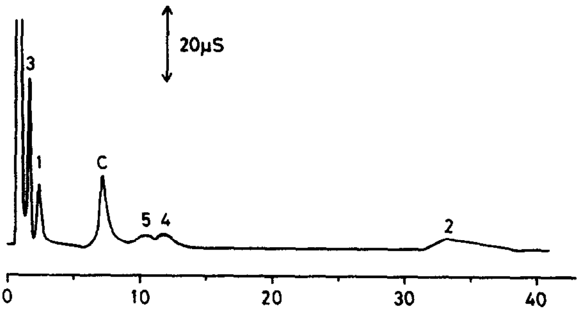


Fig. 1. Ion chromatogram of arsenic anions. Sample: 1 = As(III) (30 μg/ml as As); 2 = As(V) (30 μg/ml as As); 3 = DMA (20 μg/ml as As); 4 = o-APA (10 μg/ml as As); 5 = p-APA (10 μg/ml as As); C = carbonate. Column: TSKgel IC-Anion-PW, 0.03 mequiv./g. Eluent: 6 m*M* potassium hydroxide, pH 11.8.

Subsequently, the properties of individual aromatic anions as the eluents were examined.

Benzoate anion. The retention time of the sample anions in hydroxide–benzoate as the eluent are shown in Fig. 2a. The second dip peak[24] is close to the carbonate peak, and the peaks of the sample arsenic anions were sufficiently isolated and detected in all hydroxide–phthalate mixed eluents used. However, the retention times were little shortened and the resolution hardly improved, compared with the use of the simple hydroxide eluent.

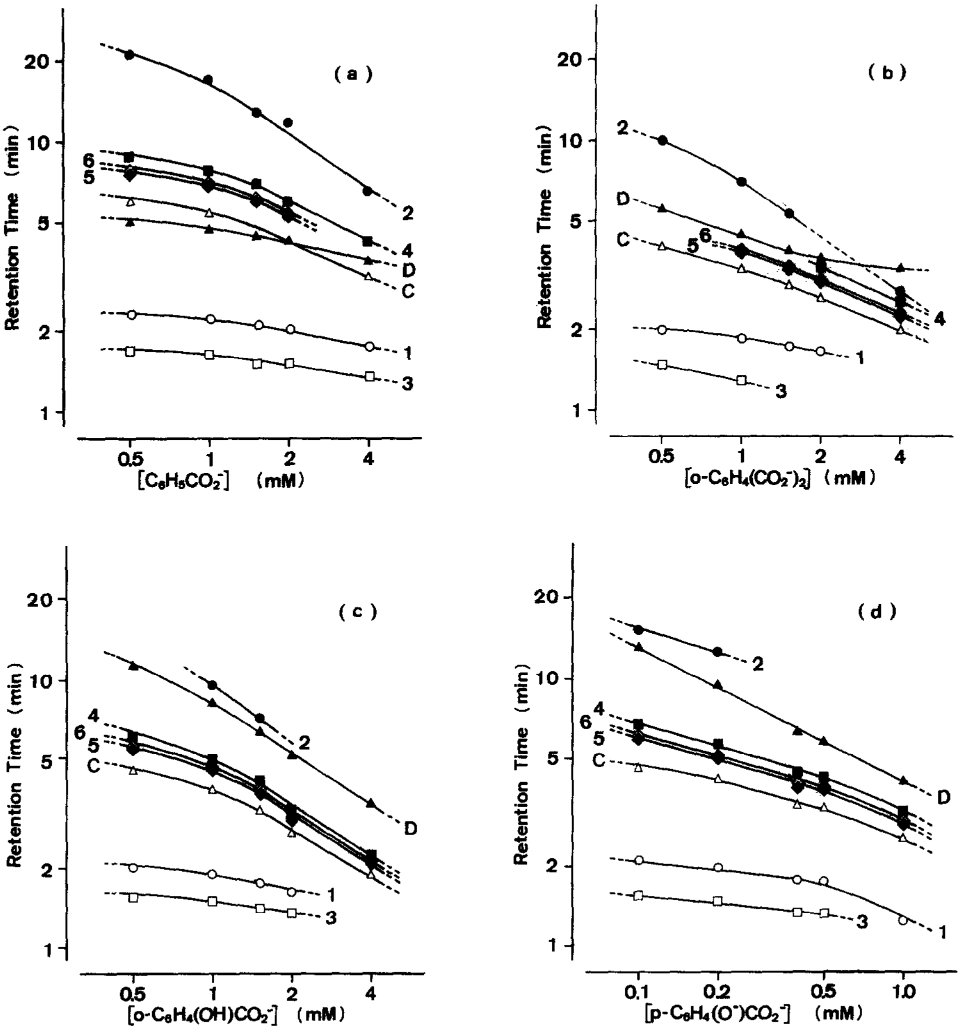


Fig. 2. Retention times of arsenic anions in mixed eluents. Sample: 1 = As(III); 2 = As(V); 3 = DMA; 4 = o-APA; 5 = p-APA; 6 = PA; C = carbonate; D = second dip peak. Column: TSKgel IC-Anion-PW, 0.03 mequiv./g. Eluents: (a) potassium hydroxide–sodium benzoate; (b) potassium hydroxide–potassium biphthalate; (c) potassium hydroxide–sodium salicylate; (d) potassium hydroxide–sodium *p*-hydroxybenzoate, pH 11.8.

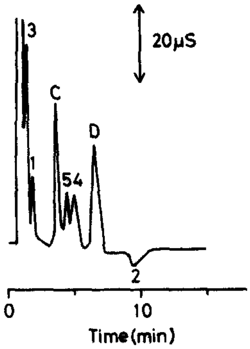


Fig. 3. Ion chromatogram of arsenic anions. Sample as in Fig. 1 except D = second dip peak. Column as in Fig. 1. Eluent: 6 m*M* potassium hydroxide–1.5 m*M* sodium salicylate, pH 11.8.

Phthalate anion. Phthalate anion has a charge of −2 and is more effective as an eluent anion than benzoate anion having a charge of −1. Therefore, as shown in Fig. 2b, the retention time of the arsenic anions is much improved by using phthalate anion as the eluent. However, since the elution behaviour of the second dip peak was so different from that of the second dip peak in the other eluents, it was impossible to detect all of the arsenic anions at once. Therefore, it was conducted that the hydroxide–phthalate mixed eluent was not effective for the separation and detection of the arsenic anions.

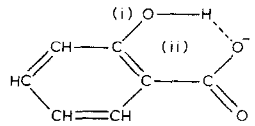
Salicylate anion. Fig. 2c shows the retention times of arsenic anions in hydroxide–salicylate mixed eluents. In this case, the useful concentration of salicylate anion was limited to the detection of the As(V) anion, because of the interference from the second dip peak. However, the retention times of the other arsenic anions were more shortened and their peaks were more sharper than in hydroxide–benzoate eluents. Therefore, this eluent is very effective for the separation and detection of the arsenic anions.

m- And p-hydroxybenzoate anions. Since the behaviours of these organic eluents are very similar, only one of them (*p*-hydroxybenzoate) is discussed. Fig. 2d shows the retention times of arsenic anions in hydroxide–*p*-hydroxybenzoate as an eluent. Assuming that the concentration of *p*-hydroxybenzoate in Fig. 2d was increased by a factor of four, the curves in Fig. 2d are similar to those in Fig. 2c.

TABLE II

QUANTITATIVE RANGES AND DETECTION LIMITS OF ARSENIC ANIONS USING 6 m*M* POTASSIUM HYDROXIDE–1.5 m*M* SODIUM SALICYLATE AS THE ELUENT

Anion	*Quantitative range (µg/ml as As)*	*Detection limit (µg/ml as As)*
(1) As(III)	5–50	3
(2) As(V)	10–50	5
(3) DMA	10–50	5
(4) o-APA	1–50	0.5
(5) p-APA	5–50	0.5
(6) PA	5–50	0.5



Accordingly, the concentration of the eluent aromatic anion should be strictly controlled in order to detect the As(V) anion rather than the salicylate anion.

It was thus found that the hydroxide–salicylate eluent is the most effective for the separation of the arsenic anions. Fig. 3 shows an ion chromatogram of an arsenic sample obtained using 6 m*M* potassium hydroxide–1.5 m*M* sodium salicylate as the eluent, *i.e.*, with the optimum salicylate concentration for 6 m*M* hydroxide (pH 11.8). The quantitative ranges and the detection limits of the arsenic anions using the same conditions are shown in Table II.

Considering the ionic structure of salicylate anion, it is estimated that the phenolic hydroxyl group bonded to benzene ring (i) accelerates the elution of sample anions. Also, because the six-membered ring (ii) is formed by hydrogen bonding between a carboxylic group and a phenolic hydroxyl group, the dissociation of the hydroxyl group is suppressed and it was supposed that the elution is delayed by a decrease in the charge number of salicylate anion.

Moreover, the sample anion peaks were not overlapped by the second dip peak produced by salicylate anion itself.

Therefore, it is concluded that good separations and detections of the arsenic anions were obtained by using hydroxide–salicylate as the eluent.

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