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Vacancy ion-exclusion chromatography of haloacetic acids on a weakly acidic cation-exchange resin

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Abstract

A new and simple approach is described for the determination of the haloacetic acids (such as mono-, di- and trichloroacetic acids) usually found in drinking water as chlorination by-products after disinfection processes and acetic acid. The new approach, termed vacancy ion-exclusion chromatography, is based on an ion-exclusion mechanism but using the sample solution as the mobile phase, pure water as the injected sample, and a weakly acidic cation-exchange resin column (TSKgel OApak-A) as the stationary phase. The addition of sulfuric acid to the mobile phase results in highly sensitive conductivity detection with sharp and well-shaped peaks, leading to excellent and efficient separations. The elution order was sulfuric acid, dichloroacetic acid, monochloroacetic acid, trichloroacetic acid, and acetic acid. The separation of these acids depends on their pK_a values. Acids with lower pK_a values were eluted earlier than those with higher pK_a, except for trichloroacetic acid due to a hydrophobic adsorption effect occurring as a side-effect of vacancy ion-exclusion chromatography. The detection limits of these acids in the present study with conductivity detection were 3.4 μ*M* for monochloroacetic acid, 0.86 μ*M* for dichloroacetic acid and 0.15 μ*M* for trichloroacetic acid.

Keywords: Vacancy ion-exclusion chromatography; Organochlorine compounds; Acetic acids; Organic acids

1. Introduction

Haloacetic acids (HAAs) have received attention over the last several years, particularly concerning the environmental problems associated with these species. Low concentrations of HAAs are also found in other fields such as drugs, dyes and chemicals [1,2], therefore it is very important to establish an effective method for their determination.

A comparative study using reversed-phase ion interaction chromatography with UV detection, and suppressed and non-suppressed anion-exchange chromatography has been reported [3]. Activated vegetal carbon was used as a sample preconcentration step. Gas chromatography coupled with ion-trap mass spectrometry has been used for the extraction and determination of HAAs such as chloroacetic acids and/or bromoacetic acids in water [4]. The method

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involved derivatization of the analyte acids to their ethyl esters using sulfuric acid and ethanol, and the developed method was applied to the analysis of tap water.

The use of ion chromatography (IC) for the determination of HAAs in water has been reported by Lopez et al. [5]. In this method, HAAs were extracted from aqueous samples with methyl *tert.*-butyl ether acidified with sulfuric acid to pH <0.5 and treated with copper sulfate pentahydrate and sodium hydrate, before being back-extracted into water and analyzed by IC with conductivity detection. Another conductivity IC method for the determination of dichloroacetic acid and trichloroacetic acid by liquid–liquid extraction has been reported and applied to real samples, again with derivatization steps [6]. Two IC methods have been described by Lackshmy et al. [7] for the determination of haloacetic acids. The first method was based on anion-exchange separation with suppressed conductivity detection; the second method used ion-exclusion separation with UV detection. However, few references on conventional ion-exclusion chromatography are available in the literature for the determination of HAAs because of the relatively poor separations obtained.

Recently, Tanaka et al. developed a new methodology called vacancy or eluent dip ion-exclusion chromatography for the separation of various groups of aliphatic or aromatic carboxylic acids on weakly acidic or strongly acidic cation-exchange resins [8–10]. In this approach the target analytes are added to the mobile phase and pure water is employed as the injected sample. Vacancy ion-exclusion chromatography has been shown to provide effective separation of various compounds which are difficult to separate using conventional ion-exclusion chromatography.

In this communication, we demonstrate the effectiveness of vacancy ion-exclusion chromatography for the separation of HAAs frequently found in treated waters, e.g. tap water. The HAAs selected for this study were monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), and acetic acid (AA) was also included. The basic principle of the new approach involves using a mixture of HAAs as the mobile phase and pure water as the injected sample, with a weakly acidic cation-exchange resin as stationary phase and highly sensitive conductivity detection. The basic mechanism for the separation of HAAs involves contributions from two sources: (1) a conventional ion-exclusion effect based on differences in pK_a values and (2) an adsorption effect. Effects of the experimental analytical conditions such as the concentration of sulfuric acid in the mixture of HAAs, the addition of an organic solvent to the mobile phase and the concentration of HAAs in the mobile phase were examined in detail to optimize the final separation conditions.

2. Experimental

2.1. Reagents and solutions

All chemicals were of analytical reagent grade and were dissolved in distilled and deionized water. Standard solutions of HAAs were prepared from the analytical reagent-grade chemicals without further purification. Standard stock solutions of HAAs were prepared as follows: 1.0 *M* sulfuric acid (SA), 0.5 *M* AA, MCAA, DCAA, and TCAA. The standard mixture used for the construction of the calibration curve was prepared from the standard stock solutions.

2.2. Instrumentation

A Dionex (Sunnyvale, CA, USA) ion chromatograph with suppressed conductivity detection (ASR-II, Auto suppression-II, used in the recycle mode) and an LC 25 enclosure system were used. The chromatographic data were processed using a Fujitsu FM-V-Biblo notebook-type personal computer. Separations were performed using a Tosoh TSKgel OApak-A column (15 cm×7.8 mm I.D.) packed with polymethacrylate-based weakly acidic cation-exchange resin in the H^+ form (particle size 5 μm, cation-exchange capacity 0.1 mequiv./ml). A mixture of SA, AA, DCAA, MCAA and TCAA was used as mobile phase at a flow-rate of 1.0 ml/min, the column temperature was maintained at 35 °C and the sample injection volume was 25 μl. The column was equilibrated for 60 min prior to use.

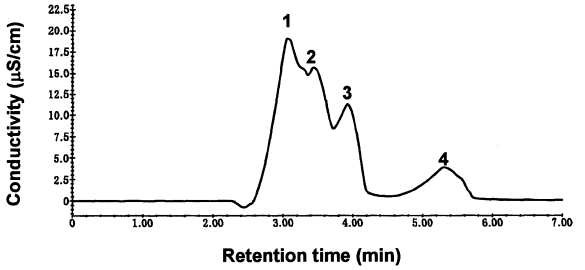

Fig. 1. Conventional ion-exclusion chromatogram of haloacetic acids obtained using pure water as mobile phase. Haloacetic acid concentrations (500 μ*M*): (1) DCAA, (2) MCAA, (3) TCAA and (4) AA. Column, TSKgel OApak-A (150 mm×7.8 mm I.D.); column temperature, 35 °C; eluent pH, 5.6; detection, conductivity detection; detection sensitivity, 100 mV=100 μS/cm; unit of retention time, min; injection volume, 0.5 ml; flow-rate, 1.0 ml/min.

3. Results and discussion

3.1. Vacancy ion-exclusion chromatographic separation of haloacetic acids

Conventional ion-exclusion chromatography using water as mobile phase gave fronted and overlapping peaks for the HAAs and AA (Fig. 1) and the separation was not improved when sulfuric acid was added to the mobile phase.

However, when a mixture of SA, AA and HAAs was used as mobile phase and pure water as the injected sample, a dramatic improvement in the separation of HAAs was obtained (Fig. 2). As can be seen from Fig. 2, a negative ''vacancy peak'' or ''eluent dip'' corresponding to each of the HAAs present in the mobile phase is present, with symmetrical and sharp peaks being observed. The identities of these peaks were confirmed using mobile phases containing each species separately.

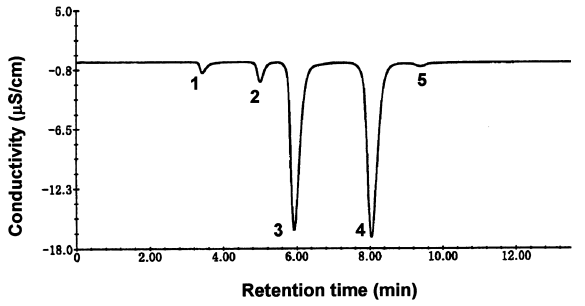

Fig. 2. Vacancy ion-exclusion chromatogram of haloacetic acids. Concentration (μ*M*) of haloacetic acids in the mobile phase (pH 3.17): (1) SA (25), (2) DCAA (500), (3) MCAA (500), (4) TCAA (500) and (5) AA (300). Sample: pure water was injected onto the column. Other chromatographic conditions as in Fig. 1.

A comparison of conventional ion-exclusion chromatography and vacancy ion-exclusion chromatography shows that the retention times of HAAs were longer in vacancy ion-exclusion chromatography, due mainly to the change in the mobile phase pH from 5.6 to 3.17. In conventional ion-exclusion chromatography, HAAs are largely deprotonated, resulting in electrostatic repulsion of the analytes from the charged surface of the column. On the other hand, in the vacancy ion-exclusion chromatographic approach, HAAs are significantly protonated when sulfuric acid is added to the mobile phase, which reduces the electrostatic repulsion and increases the adsorption of HAAs on the unfunctionalised portions of the stationary phase, leading to longer retention times.

3.2. Effect of mobile phase parameters on retention time

In a manner similar to that noted in previous studies [8–10], the retention times of the analytes tested in the vacancy ion-exclusion chromatographic system were observed to increase when increasing the concentration of the analytes in the mobile phase (Fig. 3). Increased concentrations of HAAs in the mobile phase led to a reduction of the amount of ionized HAAs, which might enhance the penetration effect of the analytes into the stationary phase. This phenomenon has been reported to be most problematic when the separation is carried out on real samples, and it would therefore be essential to control the pH of the mobile phase to a constant value [8]. One method to achieve this is by adding sulfuric acid to the mobile phase.

The effect of the concentration of sulfuric acid in the mobile phase was studied over the range 0 to 0.25 m*M*. The results, shown in Fig. 4, reveal that the retention times (t_R) of HAAs changed initially, but were virtually unaltered over the sulfuric acid concentration range 12.5 μ*M*–0.25 m*M*. Moreover, AA was not detected at >0.1 m*M* sulfuric acid since it became protonated and its conductivity response

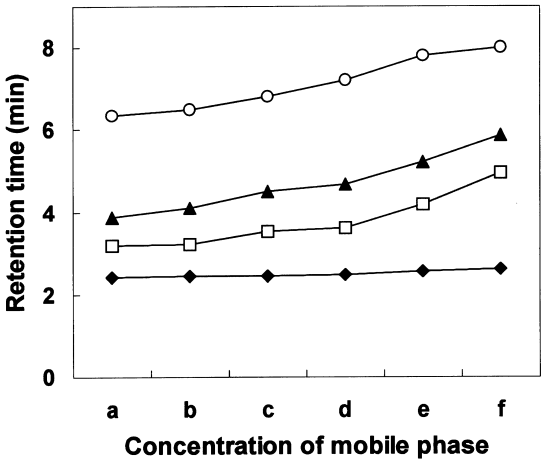

Fig. 3. Effect of concentration of haloacetic acids in the mobile phase on the retention time. Concentration of mobile phase (μM): mixture of SA—(a) 12.5, (b) 25, (c) 50, (d) 100, (e) 175 and (f) 500; DCAA—(a) 1, (b) 20, (c) 80, (d) 125, (e) 250 and (f) 500; MCAA—(a) 8, (b) 15, (c) 20, (d) 25, (e) 175 and (f) 500; TCAA—(a) 1, (b) 20, (c) 25, (d) 100, (e) 150 and (f) 500. Plot identities: (♦) SA, (▲) MCAA, (□) DCAA, and (○) TCAA. Other chromatographic conditions as in Fig. 1.

was suppressed. However, the resolution of AA was improved when small amounts of sulfuric were added to the mobile phase. A reasonable chromatogram was obtained for HAAs using 25 μM sulfuric acid (pH ~3.17) added to the mobile phase, with good peak shapes resulting from the fact that the degree of ionization remained constant across the entire sample zone. However, the sensitivity of the conductivity detection was reduced due to the increased background conductivity of the mobile phase.

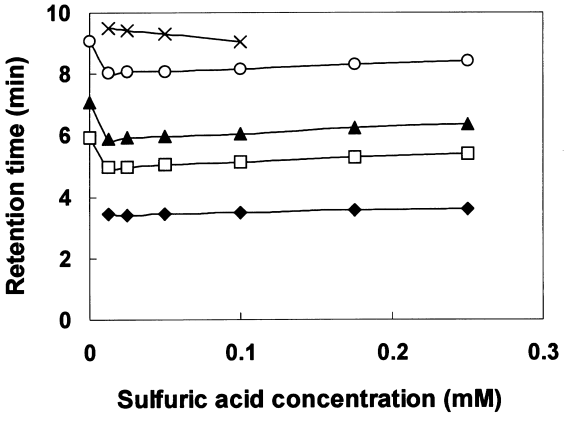

Fig. 4. Effect of sulfuric acid concentration in the mobile phase on the retention time of haloacetic acids. Mobile phase (μM): mixture of DCAA (100), MCAA (200), TCAA (300) and AA (300). Sample: pure water. Plot identities: (♦) SA, (×) AA, (▲) MCAA, (□) DCAA, and (○) TCAA. Other chromatographic conditions as in Fig. 1.

3.3. Effect of organic solvents on retention time

In many ion-exclusion chromatography systems, organic modifiers are added to the eluent in order to reduce the retention times by minimizing adsorption effects. However, the organic modifier can also be retained on the stationary phase and can be detected conductimetrically [11]. This phenomenon implies that a further vacancy peak for the organic modifier would be produced. Several organic modifiers were tested on this system and it was observed that conductimetric responses occurred for methanol (t_R = 5 min), acetonitrile (t_R = 6.53 min), *n*-propanol (t_R = 6.68 min) and butanol (t_R = 9.75 min). The methanol peak overlapped with DCAA, the acetonitrile peak was co-eluted with MCAA, the *n*-propanol peak was co-eluted with TCAA and the butanol peak was co-eluted with AA. Fig. 5 shows the vacancy ion-exclusion chromatogram obtained using 1% (v/v) butanol in the mobile phase.

In contrast, higher alcohols, such as isoamyl alcohol (t_R = 13.28 min), showed stronger retention on the resin phase and did not introduce interferences. Moreover, the addition of such organic solvents to the mobile phase had no effect on the retention times of HAAs. An interesting feature is that particularly well-shaped peaks for the analytes

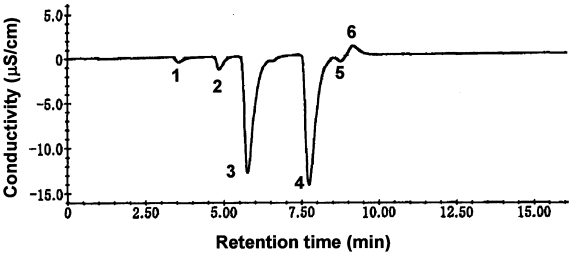

Fig. 5. Vacancy ion-exclusion chromatogram obtained using 1% (v/v) butanol in the mobile phase. Peak identifications: 1 = SA, 2 = DCAA, 3 = MCAA, 4 = TCAA, 5 = AA and 6 = butanol. Other chromatographic conditions as in Fig. 1.

were obtained by adding small amounts (1–4%) of butanol to the mobile phase, in comparison with other alcohols. However, the main obstacle of using butanol in this system is the co-elution with AA. Therefore, the addition of organic modifiers to the mobile phase or to the injected water sample was excluded in order to avoid interferences and to achieve a complete separation with high resolution for HAAs.

3.4. Retention volumes (V_R) and distribution coefficients (K_d)

In order to characterise the mode of operation of vacancy ion-exclusion chromatography on the TSKgel OApak-A column, the elution behavior of HAAs was investigated quantitatively. The retention volumes (V_R) and distribution coefficients (K_d) for HAAs together with their pK_a values are listed in Table 1. The K_d value was calculated using the following equation:

$$V_R = V_0 + V_i K_d$$

where V_R is the retention volume, V_0 is the column void volume, and V_i is the volume of liquid inside the resin in the column. V_i can be calculated from the following equation:

$$V_i = (V_0 + V_i) - V_0$$

where V_0 was taken as the V_R of a strong acid such as sulfuric acid, which was completely excluded from the resin phase, and $V_0 + V_i$ was taken as the V_R of a weak acid such as carbonate or methanol. From Table 1 it can be seen that strong acids such as sulfuric were eluted first and weak acids were eluted later, indicating that an ion-exclusion process occurred on the TSKgel OApak-A column. Analytes with K_d values between 0 (complete ion-exclusion) and 1 (complete ion permeation or penetration) are retained solely by ion-exclusion, but those with K_d greater than 1 show adsorption effects on the surface of the resin column. The K_d values for the HAAs tended to increase with increasing pK_a value, except in the case of TCAA.

Table 1
Retention volumes (V_R) and distribution coefficients (K_d) of haloacetic acids in vacancy ion-exclusion chromatography

Analyte	V_R (ml)	K_d	pK_a
Dichloroacetic acid (DCAA)	4.75	0.67	1.25
Monochloroacetic acid (MCAA)	5.88	1.20	2.87
Trichloroacetic acid (TCAA)	8.00	2.10	0.63
Acetic acid (AA)	9.28	2.60	4.76
Sulfonic acid (SA)	3.20	0.00	4.00
Methanol	5.53	1.00	15.5

Consequently, it can be concluded from Table 1 that the retention of HAAs in vacancy ion-exclusion chromatography is based mainly on two mechanisms: (1) conventional ion-exclusion chromatography such that analytes having lower pK_a values are eluted faster than those having higher pK_a; and (2) adsorption onto the resin in the column.

4. Analytical performance parameters

Under the optimum analytical chromatographic conditions (flow-rate, 1.0 ml/min; column temperature, 35 °C; injected sample volume, 0.5 ml; conductivity detection), different concentrations of HAAs were chromatographed and the conductivity detection responses were recorded. Calibration graphs, linear calibration ranges and correlation coefficients (R^2), and detection limits [calculated at a signal-to-noise ratio (S/N) of 3] for HAAs are listed in Table 2.

The reproducibility of the retention times under the optimum elution conditions was 0.16–0.5% relative standard deviation (RSD) for HAAs, as determined from five repeated chromatographic runs. The reproducibility of the chromatographic peak area was 1.36–2.37% RSD, again for five chromatographic runs. The reproducibility data are shown in Table 3.

5. Conclusion

A high-resolution and simple vacancy ion-exclusion chromatography method in which a mixture of HAAs is utilized as the mobile phase and water is the injected sample has been described. The peak shapes and conductivity detection sensitivity are superior to those observed with conventional ion-exclusion chromatography for the same analytes.

Table 2
Calibration data and detection limits for haloacetic acids in vacancy ion-exclusion chromatography

Analyte	Linear range for peak area calibration (μM)	Regression equation	Correlation coefficient (r^2) ($n=15$)	Detection limit (μM) ($S/N=3$)
SA	12.5–250	$Y=6024x-3003$	0.9981	0.64
DCAA	1–125	$Y=5471x+8093$	0.9994	0.86
MCAA	20–250	$Y=6293x+3065$	0.9980	3.40
TCAA	1–500	$Y=6210x+2006$	0.9982	0.15
AA	25–500	$Y=169.3x+667.1$	0.9990	5.10

Table 3
Reproducibility data for the retention time and peak area of haloacetic acids determined by vacancy ion-exclusion chromatography

Analyte (μM)	Reproducibility ($n=5$), RSD (%)	
	Retention time	Peak area
SA (25)	0.50	1.53
DCAA (100)	0.24	1.36
MCAA (200)	0.26	1.61
TCAA (300)	0.29	2.27
AA (300)	0.16	2.37

Separation is carried out with a TSKgel OApak-A having weakly acidic cation-exchange functional groups. The separation of HAAs is mainly based on a combination of ion-exclusion and adsorption effects.

Acknowledgements

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