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Journal of Chromatography A, 671 (1994) 309–313

JOURNAL OF CHROMATOGRAPHY A

Determination of haloacetic acids by ion chromatography

Lakshmy M. Nair*, Raaidah Saari-Nordhaus, James M. Anderson, Jr.

Alltech Associates, Inc., 2051 Waukegan Road, Deerfield, IL 60015, USA

Abstract

Two ion chromatography methods for the determination of haloacetic acids are described in this paper. The first method is based on anion-exchange separation with suppressed electrical conductivity detection. The second method is based on anion-exclusion separation with UV detection. Both methods are simple and fast. The detection limits for the haloacetic acids are in the μg/l range. Applications of these methods for the determination of haloacetic acids in some real world samples are shown.

1. Introduction

Haloacetic acids are present in many samples due to their use in various industrial applications. Trace amounts of these acids are found in drinking water as chlorination by-products. Mono-, di- and trichloroacetic acids are used as base materials for colorant manufacturing, pharmaceutical synthesis and antiseptics, respectively. Trichloroacetic acid is also used as a herbicide and as an important intermediate in chemical industry. Trifluoroacetic acid is used to cleave peptides from solid-phase resins in peptide synthesis. Many haloacetic acids are toxic and having reliable methods for their determination is very important.

The standard method for determining halogenated acetic acids is by liquid–liquid extraction and gas chromatography (GC) with electron-capture detection. This method is described in US EPA method 552 [1] and is applicable to the determination of six halogenated acetic acids in drinking water, ground water and raw water. Even though the detection limits for the acids are in the low μg/l range, this method is complicated and time consuming. Determination of acetic, dichloroacetic and trichloroacetic acids by high-performance liquid chromatography (HPLC) has also been reported [2]. The method is based on ion-interaction separation with UV detection at 210 nm. Separation of mono-, di- and trichloroacetic acid by ion-exchange chromatography was reported by Houdeau *et al.* [3]. A silica-based anion exchanger was used for the separation, combined with refractive index detection.

Two ion chromatography (IC) methods are described in this paper for the determination of haloacetic acids. The first method is based on anion exchange separation with suppressed electrical conductivity detection. The second method is based on anion exclusion separation with UV detection. IC is one of the fastest growing analytical techniques for the determination of ionic species. It offers simple, reliable and inexpensive means for the simultaneous separation and determination of inorganic and organic ions in complex mixtures. Both IC methods described

* Corresponding author.

0021-9673/94/$07.00
SSDI 0021-9673(93)E1138-P

here are fast and simple. The detection limits are in the μg/l range. Sample preparation for IC analysis is less time consuming than the GC technique and the instrumentation is simple. However, the detection limits for haloacetic acids by GC method are much lower than the methods described here.

2. Experimental

Anion chromatography was performed on an Alltech (Deerfield, IL, USA) ion chromatography system that consists of a Model 325 HPLC pump, a Model 335 suppressor module, and a Model 320 conductivity detector. A Rheodyne (Cotati, CA, USA) Model 9125 injection valve was used to introduce the sample. For anion-exclusion chromatography, the same HPLC pump and injector were used along with an Alltech Model 330 column heater and a Linear (Linear Instruments, Reno, NV, USA) Model 204 UV–VIS detector. The temperature of the column heater was maintained at 35°C. All data were recorded on a Spectra-Physics (Santa Clara, CA, USA) SP 4400 Chromjet integrator.

The Alltech Universal Anion 300 Column (150 mm × 4.6 mm) was used to separate the haloacids by anion-exchange chromatography. For the ion-exclusion method, a Wescan (Alltech) Anion Exclusion Column (300 mm × 7.8 mm) was used. All reagents and standards were prepared from reagent-grade chemicals (Aldrich, Milwaukee, WI, USA) and distilled deionized water.

3. Results and discussion

3.1. Ion-exchange method

A suppressor-based IC method [4] is used for the separation of haloacetic acids by ion exchange. The haloacetic acids are separated on an anion-exchange column with a basic sodium carbonate–hydrogencarbonate eluent. The column effluent flows to a suppressor device before entering the conductivity detector. The suppressor exchanges the cations from the eluent and sample for hydronium ions forming carbonic acid (low conductivity) and fully protonated haloacetic acids (high conductivity). This results in a decrease in conductivity for the eluent and an increase in conductivity for the sample ions. Over all detection sensitivity for the anions is improved considerably [4]. Various suppressor devices are available. The method described here uses an Alltech Solid Phase Chemical Suppressor (SPCS) [5]. The SPCS consists of a suppressor module which houses a 10-port switching valve and two disposable cartridges. The cartridges are packed with specially treated sulfonated polystyrene–divinylbenzene cation-exchange resin in the hydrogen form. The SPCS is connected between the analytical column and the conductivity detector. The flow diagram of the SPCS is shown in Fig. 1. The eluent from the analytical column flows through one cartridge at a time. While one cartridge is being used, the effluent from the detector flows through the other cartridge to pre-equilibrate the cartridge. This reduces the baseline shift due to conductance change when the valve is switched.

Fig. 2 shows the anion-exchange separation of acetic, monochloroacetic (MCA), dichloroacetic (DCA) and trichloroacetic (TCA) acids. The acids are separated on a hydroxyethyl methacrylate based anion-exchange stationary phase with sodium carbonate–hydrogencarbonate eluent. Carbonate–hydrogencarbonate eluent seems to be the best counter ion for the separation since TCA has high affinity toward the stationary phase. When sodium tetraborate or

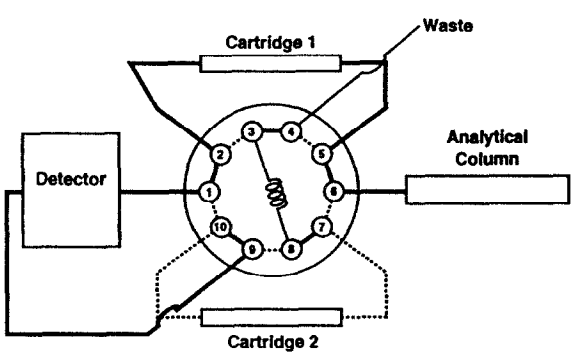

Fig. 1. Flow diagram of the SPCS system.

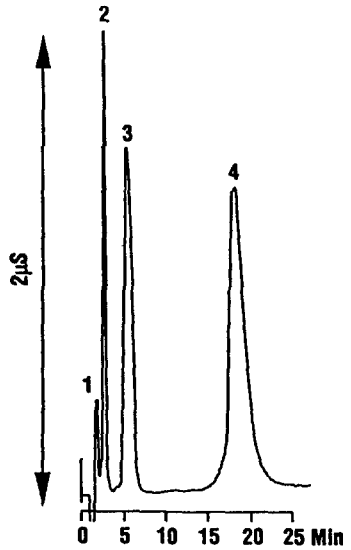

Fig. 2. Separation of chloroacetic acids by anion exchange. Peaks: 1 = acetate (10 mg/l); 2 = monochloroacetate (10 mg/l); 3 = dichloroacetate (20 mg/l); 4 = trichloroacetate (20 mg/l). Column: Universal Anion 300 (150 mm × 4.6 mm). Eluent: 2.2 m*M* sodium carbonate–2.8 m*M* sodium hydrogencarbonate. Flow-rate: 2 ml/min. Detector: conductivity. Injection volume: 100 µl.

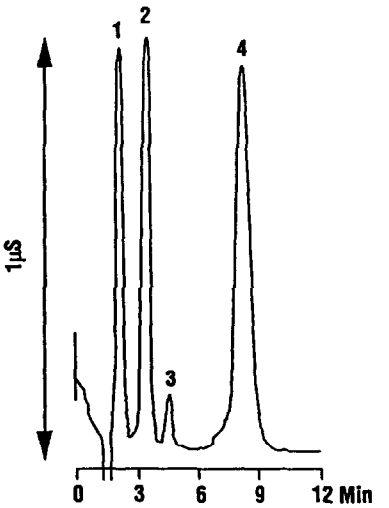

Fig. 3. Separation of bromoacetic acids by anion exchange. Peaks: 1 = acetate (10 mg/l); 2 = bromoacetate (10 mg/l); 3 = chloride; 4 = dibromoacetate (10 mg/l). Column: Universal Anion 300 (150 mm × 4.6 mm). Eluent: 2.2 m*M* sodium carbonate–2.8 m*M* sodium hydrogencarbonate. Flow-rate: 2 ml/min. Detector: conductivity. Injection volume: 100 µl.

sodium hydroxide eluent (common eluents used with suppressor-based IC) were used for this separation, DCA and TCA were retained on the column too long. Three chloroacetic acids along with acetic acid are separated within 18 min with excellent resolution and sensitivity by carbonate–hydrogencarbonate eluent. The same method can be used for the separation of acetic, monobromoacetic (MBA), dibromoacetic (DBA) acid and trifluoroacetic (TFA) acids. Fig. 3 shows the separation of monobromoacetic acid and dibromoacetic acid. If both chloro and bromo acids are present in the same sample, bromoacetic acid may co-elute with monochloroacetic acid. Other anions are well resolved from each other. The resolution can be modified easily by either changing the concentration of the eluent or the length of the column.

3.2. Ion-exclusion method

Ion exclusion is commonly used to separate weakly ionized anions such as carboxylic acids, organic acids and weak acid anions. Ion-exclusion mechanisms are based on the separation of molecular compounds by differences in partitioning between the interstitial mobile phase (usually water) and the stagnant mobile phase within the pores of the resin [6]. A strong inorganic acid eluent combined with a sulfonated cation-exchange column is normally used for the separation. Both conductivity and UV detection have been used. The method developed here uses phosphoric acid eluent with UV detection at 210 nm. UV detection was chosen due to high conductivity of the phosphoric acid eluent. The sample acids are detected with lower sensitivity with conductivity detection. Other eluents such as dilute sulfuric acid or nitric acid were also tried for the separation. These eluents are found to be inappropriate for haloacetic acid separation because of the poor sensitivity and bad resolution.

Fig. 4 shows a separation of TCA, DCA, acetic acid and MCA by the anion-exclusion method. TCA is more ionized than the other anions, and elutes rapidly from the column, followed by DCA, acetic acid and MCA. Other haloacids such as bromo, dibromo and trifluoro acetic acids can be separated by the same meth-

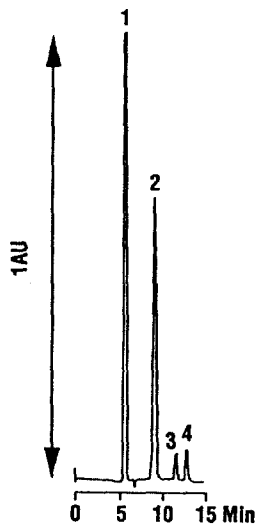

Fig. 4. Separation of chloroacetic acids by anion exclusion. Peaks: 1 = trichloroacetic acid (10 mg/l); 2 = dichloroacetic acid (10 mg/l); 3 = acetic acid (10 mg/l); 4 = monochloroacetic acid (10 mg/l). Column: Anion exclusion (300 mm × 7.8 mm). Eluent: 1% phosphoric acid. Flow-rate: 0.8 ml/min. Detector: UV, 210 nm. Injection volume: 100 μl.

ods, but may co-elute with other haloacids if they are present in the sample.

The anion-exchange separation is suitable for MCA, TFA and bromoacetic acid separation because sensitivity for these acids is better than with the ion-exclusion method. The ion-exclusion method is more advantageous to trichloro, dichloro and dibromo acetic acids separation because of higher sensitivity. Both methods have some co-elution problems, but depending on the nature of the analytes, either method can be used for the analysis.

3.3. Method detection limits

The detection limits calculated as 3× signal-to-noise ratio based on 100 μl injection volume using both methods are summarized in Table 1. The detection limits vary from 5 to 130 μg/l. These values are higher than the values reported in US EPA method 552 as shown in Table 1, however IC methods are simpler and require less sample preparation. The GC method requires liquid–liquid or micro-extraction which can be time consuming. Sample preparation for IC analyses requires simple dilution and filtration. The GC method is more sensitive than IC, hence the method described here are not suitable for monitoring haloacetic acids in drinking water, raw water and ground water. The detection limits by IC may be improved by pre-concentration of the sample.

3.4. Applications

The application of these methods for real samples are shown in Fig. 5. Fig. 5a, b and c show separations of peptide, antiseptic and drinking water samples using the ion-exchange method. The peptide sample was dissolved in deionized water and filtered through a 0.2-μm

Table 1
Method detection limits for haloacetic acids

Haloacetic acid	Method detection limit (μg/l)[a]		
	Ion exchange	Ion exclusion	Method 552[b]
Acetic acid	12.0	130.0	–
Monochloroacetic acid	8.0	70.0	0.10
Dichloroacetic acid	16.0	8.0	0.09
Trichloroacetic acid	80.0	5.1	0.06
Trifluoroacetic acid	12.0	65.0	–
Bromoacetic acid	21.0	85.0	0.08
Dibromoacetic acid	30.0	90.0	0.05

[a] 100 μl Injection volume, calculated as 3× signal-to-noise ratio.
[b] Method detection limits in reagent water reported in US EPA method 552.

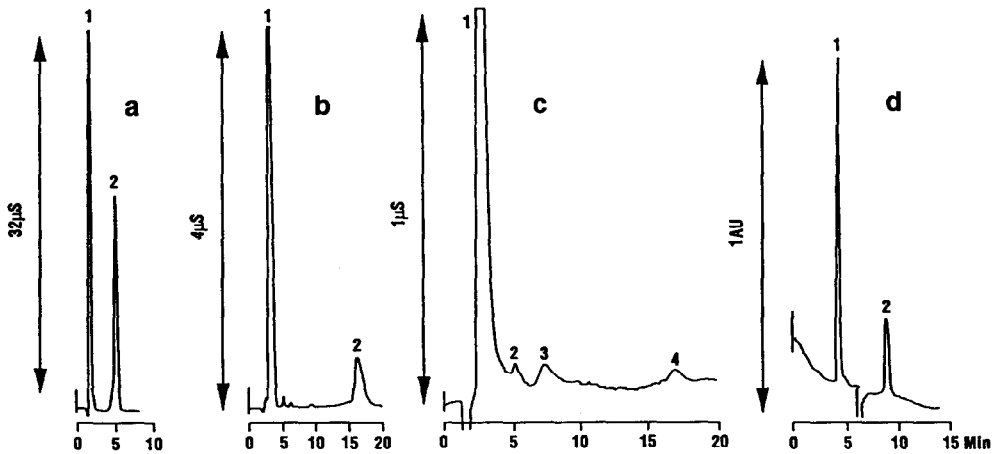

Fig. 5. Separations using ion-exchange (a, b, c) and ion exclusion methods (d). Columns: (a, b, c) Universal Anion 300 (150 mm × 4.6 mm). Eluent: 2.2 m*M* sodium carbonate–2.8 m*M* sodium bicarbonate. Flow-rate 2 ml/min. Detector: Conductivity. Injection volume: 100 µl: (d) Anion exclusion (300 mm × 7.8 mm). Eluent: 1% Phosporic acid. Flow-rate 0.8 ml/min. Detection: UV at 210 nm. Injection volume: 100 µl. Samples: (a) Peptide sample. Peaks: 1 = acetate; 2 = trifluoroacetate. (b) Antiseptic solution. Peaks: 1 = chloride; 2 = trichloroacetate. (c) Water spiked with haloacetic acids. Peaks: 1 = chloride; 2 = dichloroacetate (30 µg/l); 3 = dibromoacetate (60 µg/l); 4 = trichloroacetate (160 µg/l). (d) Herbicide. Peaks: 1 = trichloroacetic acid; 2 = dichloroacetic acid.

syringe filter before injection. The antiseptic solution was diluted 20-fold in deionized water and injected. The water sample was spiked with 30 µg/l DCA, 60 µg/l DBA and 160 µg/l TCA, respectively. Fig. 5d shows the analysis of herbicide using the ion-exclusion method. The sample was diluted in deionized water before injection.

4. Conclusions

IC provides a simple and sensitive method for the analysis of haloacetic acids. Either ion exchange with suppressed conductivity detection or ion exclusion with UV detection methods may be used for the determination. Compared to the GC method, IC is easier for routine analyses of haloacetic acids. The detection limits by both IC methods are in the ppb range. Because GC method is more sensitive, the IC methods described here are not suitable for US EPA work. Studies to improve the detection limits are under investigation. Some co-elution problems may occur depending on the analytes of interest, but can be avoided by choosing either one of the methods.

5. References

[1] *Method 552, The Determination of haloacetic acids in Drinking Water by Liquid/Liquid Extraction and Gas Chromatography with Electron Capture Detection*, US Environmental Protection Agency, Cincinnati, OH, 1989.
[2] S. Husain, R. Narsimha, S.N. Alvi and R.N. Rao, *J. Chromatogr.*, 600 (1992) 316–319.
[3] M. Houdeau, M. Thibert and M. Caude, *Analusis*, 5 (1977) 286–290.
[4] D.T. Gjerde and J.S. Fritz, *Ion Chromatography*, Hüthig, New York, 2nd ed., 1987, Ch. 6.
[5] R. Saari-Nordhaus and J.M. Anderson, Jr., *Am. Lab*, (1994) in press.
[6] J. Morris and J.S. Fritz, *LC·GC*, 11 (1993) 513.