AccuTOF™

Determination of Haloacetic Acids in Water by LC/MS

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Introduction

Haloacetic acids (HAAs) are disinfection byproducts (DBPs) of the chlorination of drinking water. Dichloroacetic acid and trichloroacetic acid are animal carcinogens. We present an ion-pair HPLC and negative electrospray ionization mass spectrometry (ESI-MS) method with a "function-switching" feature for analysis of all 9 haloacetic acids, monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), monobromoacetic acid (MBAA), bromochloroacetic acid (BCAA), dibromoacetic acid (DBAA), bromodichloroacetic acid (BDCAA), trichloroacetic acid (TCAA), chlorodibromoacetic acid (CDBAA), and tribromoacetic acid (TBAA). JEOL MassCenter™ software can switch different MS settings by the time course. This "function-switching" feature enables each HAA to be analyzed under its optimized MS conditions so that the highest sensitivity can be achieved. Using triethylamine (TEA) as an ion-pairing reagent, a good HPLC separation of all 9 HAAs has been achieved. The optimized MS conditions for each HAA were evaluated.

Experimental

The system included a JEOL AccuTOF™ time-of-flight mass spectrometry system and an Agilent 1100 HPLC. Complete system control and data evaluation were carried out using a JEOL MassCenter™ workstation.

All solvents used were of HPLC grade. The standard solutions were prepared by mixing 9 HAAs in water with the concentration ranging from 0.1 µg/mL to 100 µg/mL.

Table 1. Chromatographic conditions

Column:	Luna C_{18} (2), 5µm, 2.0 x 150-mm	Gradient:	Start from 100% A for 3 min to 50% B in 15 min
Mobile phase:	A = 0.05% TEA and 0.15% formic acid in Water	Flow rate:	0.2 mL/min
	B = 0.05% TEA and 0.15% formic acid in acetonitrile	Injection volume:	10 µL

Table 2. MS Conditions

MS Functions	Needle Voltage (V)	Orifice1 Voltage (V)	Orifice2 Voltage (V)	RingLens Voltage (V)	Ion Guide Voltage (V)	Desolva-ting T (°C)	Orifice1 T(°C)	Desolvat-ing gas (L/min)	Nebulizing gas (L/min)
Function1	-2000	-30	-3	-3	400	250	100	2.0	5.0
Function2		-29	-4	-4	925				
Function3		-30	-4	-4	1225				
Function4		-40	-5	-4	1350				
Function5		-40	-3	-2	800				

Results and Discussion

For mono and di-HAAs, the protonated ions were observed as the base peak when the orifice 1 voltage was set around 30V and presented maximum sensitivities. On the other hand, for tri-HAAs, the sensitivities of the deprotonated ions were very low and the decarboxylated ions were observed as the base peak. Thus, the protonated ions for mono and di-HAAs and decarboxylated ions for tri-HAAs were selected to construct mass chromatograms for analysis. Figure 1 shows the mass chromatograms for each HAA with the injective amount of 100 ng.

The optimized MS conditions were evaluated by using a syringe pump to infuse a 9 HAA mixture with a concentration of 50 µg/mL. Each parameter in Table 2 was fine tuned until the highest intensity for selected ions was achieved. The results are listed in Table 2.

Each individual HAA was detected under its optimized MS conditions by using the "function-switching" feature in JEOL MassCenter™ software. Five MS settings were switched during the data acquisition procedure according to the retention times of the HAAs. The MS settings for each function are listed on Table 2. The selected ions for mass chromatograms and the "functions" for each HAA detection are listed on Table 3.

Table 3 Selected ions for mass chromatograms and "function-switching"

HAA	MCAA	DCAA	MBAA	BCAA	DBAA	BDCAA	TCAA	CDBAA	TBAA
$[M-H]^-$	92.9743	126.9354	136.9238	172.8826	216.8323				
$[M-COOH]^{1-}$						162.8536	116.9066	206.8034	250.753
Function	1	2	2	3	3	4	5	4	4
R^2	0.998	0.9885	0.9979	0.9973	0.9994	0.9981	0.9981	0.9984	0.9986

The calibration curves were determined by external calibration in the concentration range 0.1 – 100 µg/mL. As shown in Table 3, the linearity was very good for all HAAs with correlation coefficients (R^2) greater than 0.99.

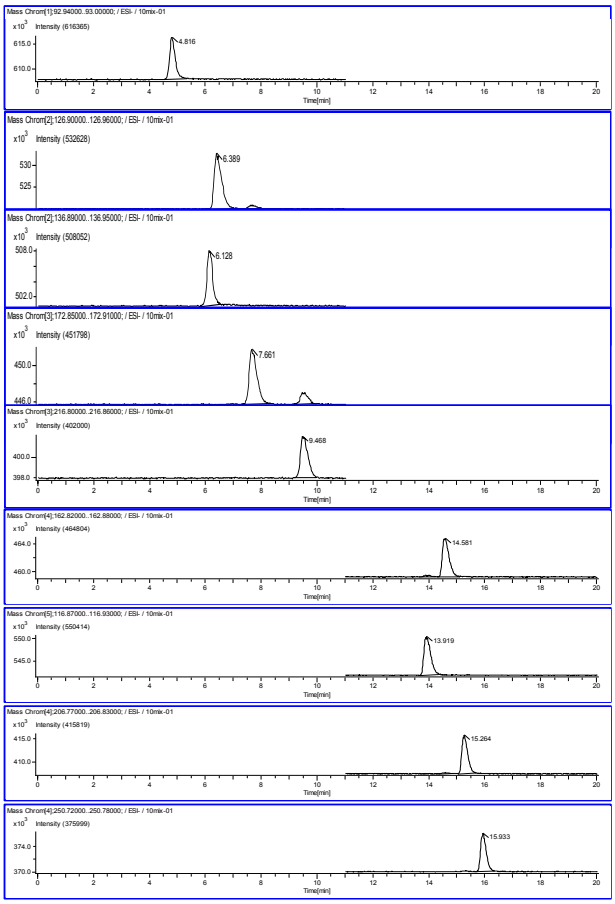

Fig 1. Mass Chromatograms of HAAs.

Conclusions

All 9 HAAs can be separated by reverse-phase HPLC with TEA as the ion-pairing reagent. A "function-switching" feature in JEOL MassCenter™ software enables each HAA be detected under its optimized MS conditions so that the highest sensitivity can be obtained.

References

1. Magnuson, ML and Kelty CA, *Microextraction of nine haloacetic acids in drinking water at microgram per liter levels with electrospray-mass spectrometry of stable association complexes*, Anal. Chem. 2000, 72, 2308-12.
2. Loos, R and Barcelo D, *Determination of haloacetic acids in aqueous environments by solid-phase extraction followed by ion-pair liquid chromatography – electrospray ionization mass spectrometric detection*, J. Chrom. A, 2001, 938, 45-55.