Comparative Study of Sample Preparation Techniques Coupled to GC for the Analysis of Halogenated Acetic Acids (HAAs) Acids in Tap Water

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Abstract

Halogenated acetic acids (HAAs) are one of the most common disinfection by-products formed during chlorination of drinking water. Currently, there are three U.S. Environmental Protection Agency-approved methods for analysis of HAAs in drinking water: U.S. EPA method 552.2, Standard Method 6251, and U.S. EPA method 552.3. The current U.S.EPA-approved HAA analysis methods require tedious and time-consuming liquid–liquid extraction (LLE) and the use of hazardous chemicals. Besides U.S. EPA methods, capillary electrophoresis (CE), liquid chromatography (LC), including ion chromatography (IC), and electrospray ionization mass spectrometry (ESI-MS) have been applied in order to determine the HAAs in portable water with high detection limits. Detection limits required to analyze portable water samples can be regularly achieved only by gas chromatography–electron capture detector (ECD) and ESI-MS. In this study, improved gas chromatography–mass spectrometry (GC–MS) method was able to achieve HAAs analysis at low detection limits. Thus, a safe and rapid method is needed for the micro-determination of HAAs. A method involving solid-phase extraction (SPE) followed by GC–MS was developed to determine the HAAs in tap water. Selectivity, percent recovery, and detection limit studies were carried out on a LC–SAX (quaternary ammonium anion exchanger) SPE. Under optimized conditions, average recoveries for all nine HAAs spiked in drinking water samples ranged from 78.7% to 100%. The relative standard deviation data was found to range from 1.0% to 12.5% based upon five repeat recovery experiments, and estimated detection limit ranging between 0.16–0.009 µg/L was obtained. On this basis, SPE was studied as a possible alternative to LLE for the analysis of HAAs in water. Finally, the performance of the SPE-GC–MS with spiked drinking water samples was tested, and the results were compared with those obtained using LLE-GC–ECD. The method was applied for determination of HAAs in drinking water and water samples.

Introduction

Water chlorination has been accepted as one way of disinfecting potable water or wastewater from sewage-treatment plants. During chlorination, various chlorinated organic compounds are formed by the reaction of organic substances (such as humic material) with chlorine. Chlorination byproducts are classified as probable human carcinogens. In particular, trihalomethanes (THMs), which are considered carcinogenic, have received attention. However, total organic halide (TOX) in chlorinated water could not be accounted for by the amount of THMs formed during chlorination. Hence, increased attention has been paid to the non-volatile fraction such as haloacetic acids (HAAs) of TOX (1).

To analyze the presence of HAAs in drinking water, a reliable and accurate analytical method is needed. Currently there are three U.S. Environmental Protection Agency (U.S. EPA) approved methods, namely the U.S. EPA Method 552.2, Standard Method 6251, and U.S. EPA method 552.3 (2–4). In all the three methods, HAAs are extracted from water samples using methyl tert-butyl ether (MTBE), converted into methyl esters using diazomethane or acidic methanol, and analyzed by gas chromatography–electron capture detector (GC–ECD). The methods have since been fine-tuned by several researchers (5–7). However, all the methods have the following shortcoming: (*i*) a low sensitivity for monochloroacetic acids (MCAA), (*ii*) susceptible to chromatographic interference, and (*iii*) identification problem due to drifting in retention time. In this study, GC–MS was used to improve the identification capabilities in complex water matrix. Method involving reversed-phase ion interaction chromatography (RP-IPC), liquid chromatography–mass spectrometry (LC–MS), high performance liquid chromatography (HPLC), capillary electrophoresis (CE), and ion chromatography (IC) (8–13) are not suitable for analysis of HAAs in water due to high detection limits (DL) or sample matrix interferences. Methods using electrospray ionization mass spectrometry (ESI-MS), high field asymmetric waveform ion mobility spectrometry (FAIMS-MS), or ion chromatography–inductive coupled plasma–mass spectrometry (IC–ICP-MS) provide low DL, but these instruments are expensive and not widely available (14,15). Two MS-methods for analyzing HAAs have been reported (8,16). Method as proposed by Martinez et al. (8) was capable of analyzing five chlorinated HAAs only but having high DL (3–20 µg/L) and low recovery (18%–45%). In contrast, the method proposed by Xie (16) managed to analyze all nine HAAs components. However,

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Xie's method suffers weakness in term of having unacceptable high recovery (117–165%) for brominated species. Therefore, it is imperative that a better, more robust, and more sensitive SPE-GC–MS-based method be developed for the analysis of all nine HAAs inclusive of chlorinated and brominated species in drinking water. The developed SPE-GC–MS was used for quantification and qualification studies of halogenated acids in water.

In order to achieve detection at low ppb level, LLE and SPE are the usual off-line sample preconcentration techniques of choice. LLE is more labor-intensive as compared to SPE. However, LLE has been the most frequently used technique for the determination of HAAs compounds (3,5,8). In this case, MTBE is used as the extracting solvent, and an acidic pH is required to extract the non-dissociated acidic compounds of the sample.

New development has seen SPE becoming the extraction technique of choice for environmental samples because it overcomes some of the problems of LLE (e.g., large amount of generally toxic and inflammable organic solvents or the greater the cost and duration of concentration step) (17). Furthermore, SPE can adjust the selectivity, affinity and capacity as new materials are developed.

In this study, a SPE technique based on LC–SAX SPE cartridge is used together with GC–MS in ion selective mode (SIM) for determination of HAAs from tap water. The performance of the SPE-GC–MS-SIM method is evaluated using spiked drinking water samples and the results were compared with those obtained using the U.S. EPA Method 552.3 (i.e., the LLE-GC–ECD) and other reported methods.

Material and Methods

Chemicals and standards

Reagent-grade H_2SO_4, pesticide-grade Na_2SO_4, methanol, and MTBE were used as purchased without further purification. HAA standards (purity 99.9%) were purchased from a commercial source (Supleco, Munich, Germany). The standard contained 1000 mg/mL of each of nine HAAs.

Sample preparation

LLE

The sample preparation procedure as described in EPA Method 552.3 (U.S. EPA, 2003), was used in the study. After adding 1.5 mL of concentrated H_2SO_4, 16 g of Na_2SO_4, and the surrogate (2,3-dibromobutanoic acids), 40 mL of spiked water sample was extracted with 3 mL of MTBE spiked with the internal standard, 1,2,3-trichloropropane manually for 2 min. Then 2.5 mL of extract was methylated by adding 3.0 mL of 10% H_2SO_4 methanolic solution and kept at 50°C for 2 h. To the cooled mixture, 7 mL of sodium sulphate solution is added, mixed, and then neutralized with 1 mL of saturated $NaHCO_3$ solution. Aliquots of the extract are placed in amber vials for GC analysis.

SPE

A commercial quaternary ammonium strong anion exchanger cartridge (Siliabond, SAX) was used as SPE sorbent. Disposable 3 mL SPE cartridges with 500 mg sorbent were employed. Cartridges were activated and conditioned prior to use using 10 mL methanol followed by 10 mL deionized water. Once activated, 50 mL of spiked water sample was passed through the SPE cartridge without a vacuum system. A clean up step was performed using 10 mL of methanol to remove possible contaminants in the sorbent. Then the HAAs retained were eluted with 3 mL of 10% H_2SO_4/MeOH solution. Finally, the collected extracts were heated with (2 mL) MTBE at 50°C for 2 h in order to enhance the quantitative methylation of the analyte (HAA). After methylation, 7 mL of Na_2SO_4 solution was added to increase the extraction efficiency by means of salting out effect. Finally 1 mL MTBE extracted samples were placed in amber vials prior to GC analysis.

Instrumentation

GC–ECD

The experiments were performed with Varian CP-3800 GC–ECD. A straight split mode injection was used in the experiment. Compounds were separated using a DB 5.625 capillary column (30 m × 0.25 mm i.d, 0.25-µm film thickness). The injector and detector temperature were set at 210°C and 290°C, respectively. Nitrogen was used as the carrier gas at a flow rate of 5.0 mL/min. The GC oven temperature was started from initial temperature of 40°C, held for 5 min, and then increased at 10°C /min to 180°C, held for 3 min. The total run time was 22 min. A volume of 2.0 µL sample was injected into the GC using the 10-µL syringe. A calibration curve was plotted between GC peak areas versus concentration of each analyte (standards).

GC–MS

A Hewlett-Packard 5890 GC equipped with an HP5972 mass spectrometer and an HP7673 automatic injector was used (Palo Alto, CA). The GC system was equipped with a split/splitless injector. The fused silica capillary column DB 5.625 (30 m × 0.25 mm i.d. × 0.25-µm film thickness) fused silica was used. The column was inserted directly into the ion source of the mass spectrometer. The data were acquired with an HP Chemstation equipped with a Wiley 257 mass spectral library, which was used to compare the experimental spectra obtained. The chromatographic conditions were as follows: the initial column temperature was 40°C, which was held for 10 min. Finally it was raised to 150°C at 5°C/min. The injector was set at 210°C, and the transfer line was maintained at 280°C, respectively. A 3-µL aliquot of the sample was injected in the split mode. Helium was the carrier gas used at a flow rate of 0.4 mL/ min. The electron impact (EI) ionization conditions were: ion energy 70 eV and mass range 10 to 500 in the full-scan mode. Chromatograms were also recorded under time-scheduled selected ion monitoring (SIM). The MS was tuned to *m/z* 69, 219, and 502 with perfluorobutylamine (PFTBA).

Results and Discussion

The linearity was checked under SIM acquisition for HAAs using methylated standards over the range of 20–100 µg/L. Recoveries of HAAs using SPE extraction were checked by

spiking 50 mL of water sample with freshly prepared HAAs standards to get the final concentrations of 40 µg/L and 60 µg/L. The water samples were then extracted according to the standard procedure at the optimum conditions. Five replicate measurements were carried out for each concentration level. Similar experiments to recover HAAs from spiked drinking water samples were made using the LLE method. Total ion chromatogram (TIC) of standards solution of 60 µg/L nine HAAs using SPE-GC–MS is shown in Figure 1.

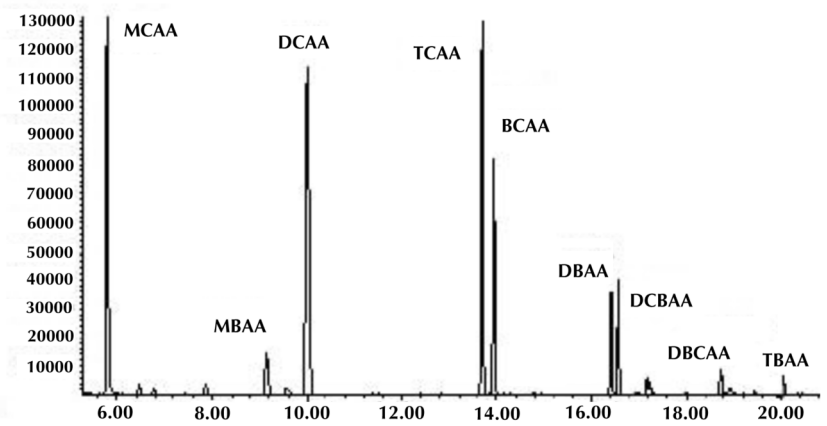

Figure 1. TIC chromatograph of a 60 µg/L of HAAs spiked in drinking water using SPE-GC–MS.

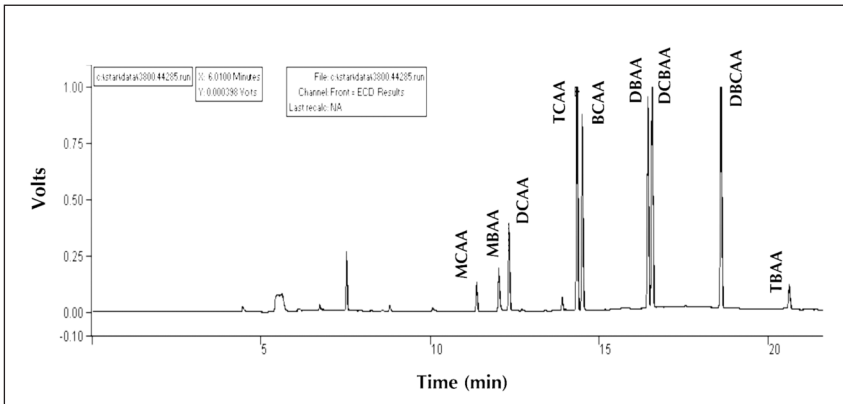

Figure 2. GC–ECD chromatogram of a haloacetic acids standard prepared in deionized water using LLE-GC–ECD method.

As can be seen from the recovery results in Table I, for the SPE-GC–MS method, the HAAs recovery were in the range of 70.4–114.6 % for spiking levels of 40 µg/L and 60 µg/L. The relative standard deviations (RSD) ranging from 2.3% to 12.5 % were obtained for the previously stated spiked concentrations. In the case of LLE-GC–ECD method, similar recovery ranges of 69–118 % were obtained with the relative standard deviation ranging from 1.8% to 3.6%. However, while the SPE technique has acceptable recoveries for all nine components tested, the LLE technique has unacceptable recovery for TBAA at both spiking levels. The poor recovery for TBAA may be due to decarboxylation with sodium bicarbonate which was used in neutralization step in LLE (18). GC–ECD chromatogram of a haloacetic acids standard prepared in de- ionized water using LLME-GC–ECD method is shown in Figure 2.

In comparison with the GC–ECD method, the GC–MS method enables all nine HAAs to be detected in chlorinated water at very low ppb level using selective ion monitoring (SIM) mode whereas the GC–ECD method has slightly poorer detection limits. The method detection limit (MDL) was calculated as 3.14 times the standard deviation of the seven replicate. The value, 3.14, is the value of t for 3–1= 2 degrees of freedom and at 99% level from the one-sided t distribution table (2). The limit of quantitation (LOQ) is 3.33 times MDL. As can be seen from the MDL results in Table II, all HAAs were detected in the range of 0.009 µg/L to 0.42 µg/L using SPE as compared to the LLE results, which were from 0.01 µg/L to 0.63 µg/L. The SPE-GC–MS method proved to be more sensitive for the determination of all HAAs tested in this study, having the lowest detection limits except for dibromochloroacetic acids (DBCAA) and tribromoacetic acids (TBAA). DL of DBCAA and TBAA were much higher with LLE-GC–ECD as well. Table II also shows the values of limit of quantitation (LOQ) together with the MDL values. In spite of those, robustness, reproducibility, linearity, specificity, and precision was tested. However, application of the ANOVA (Table III) indicate statistically no significant difference between the detection limits and recovery of SPE-GC–MS and LLE-GC–ECD methods.

Results from the SPE-GC–MS method and LLE-GC–ECD method are compared in Figure 3. In general, the results from the two methods were in good agreement. Although dichloroacetic acids (DCAA), trichloroacetic

Table I. Recovery, Relative Standard Deviation, and Correlation Coefficient (R^2) for the Nine HAAs Using SPE-GC–MS and LLE-GC–ECD

	LLE-GC–ECD			SPE-GC–MS		
Compounds	R^2	40 µg/L %R (%RSD)	60 µg/L %R (%RSD)	R^2	40 µg/L %R (%RSD)	60 µg/L %R (%RSD)
Monochloroacetic acids (MCAA)	0.996	78.5 (2.6)	80.1(3.4)	0.998	82.6 (4.1)	82.6 (7.1)
Monobromoacetic acids (MBAA)	0.995	88.3 (3.0)	85.4 (1.7)	0.992	77.4 (6.2)	70.4 (5.1)
Dichloroacetic acids (DCAA)	0.997	97.3 (1.8)	80.3 (1.0)	0.999	98.6 (5.0)	110.0 (6.0)
Trichloroacetic acids (TCAA)	0.994	93.9 (1.7)	94.6 (1.2)	0.996	94.2 (4.9)	81.4 (5.4)
Bromochloroacetic acetic acids (BCAA)	0.995	97.9 (1.8)	118.1 (3.2)	0.996	88.6 (2.3)	83.8 (4.8)
Dibromoacetic acids (DBAA)	0.990	104.0 (2.4)	115.3 (2.0)	0.997	100.0 (7.9)	114.6 (3.6)
Dichlorobromoacetic acids (DCBAA)	0.995	95.3 (2.0)	98.9 (1.4)	0.997	91.4 (6.8)	83.6 (6.6)
Dibromochloroacetic acids (DBCAA)	0.991	86.4 (2.8)	84.6 (3.0)	0.992	107.6 (6.9)	98.8 (6.5)
Tribromoacetic acids (TBAA)	0.997	65.7 (2.4)	69.0 (3.6)	0.999	76.6 (8.8)	78.7 (12.5)
Mean % Recovery	89.7	91.8		90.7	89.3	

Table II. The Estimated MDL and LOQ for the Nine HAAs Using SPE-GC–MS and LLE-GC–ECD

	LLE-GC–ECD		SPE-GC–MS	
Compounds	LOD (µg/L)	LOQ (µg/L)	LOD (µg/L)	LOQ (µg/L)
MCAA	0.28	0.84	0.21	0.65
MBAA	0.04	0.12	0.16	0.48
DCAA	0.01	0.03	0.02	0.06
TCAA	0.06	0.18	0.03	0.09
BCAA	0.05	0.15	0.009	0.02
DBAA	0.06	0.18	0.04	0.12
DCBAA	0.09	0.27	0.08	0.26
DBCAA	0.31	0.93	0.21	0.63
TBAA	0.63	1.89	0.42	1.26

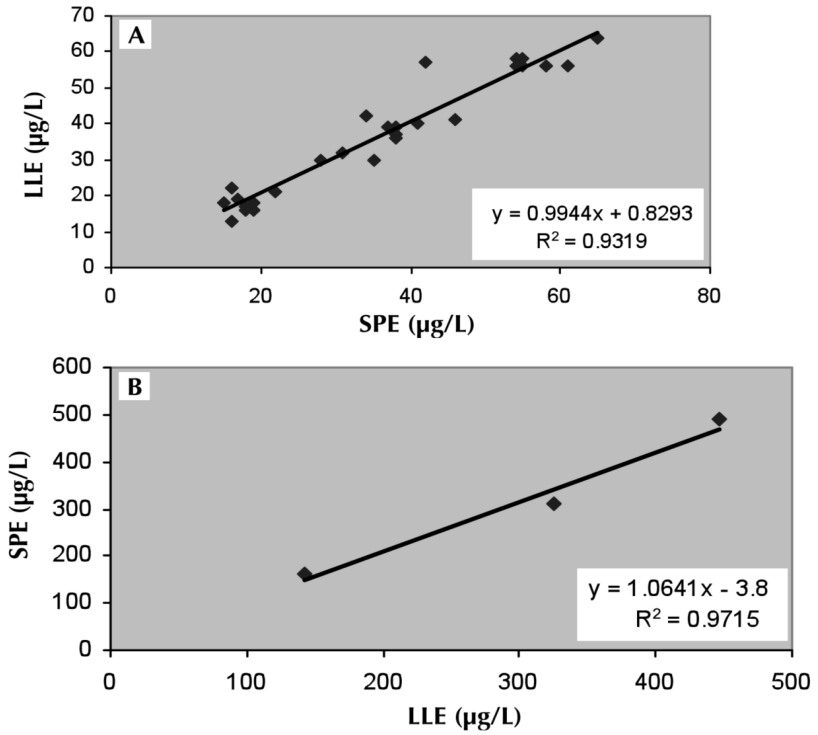

Figure 3. Comparison of results from the SPE-GC–MS and LLE-GC–ECD for analysis of (A) individual HAAs and (B) sum of 9 HAA concentrations in spiked drinking water sample.

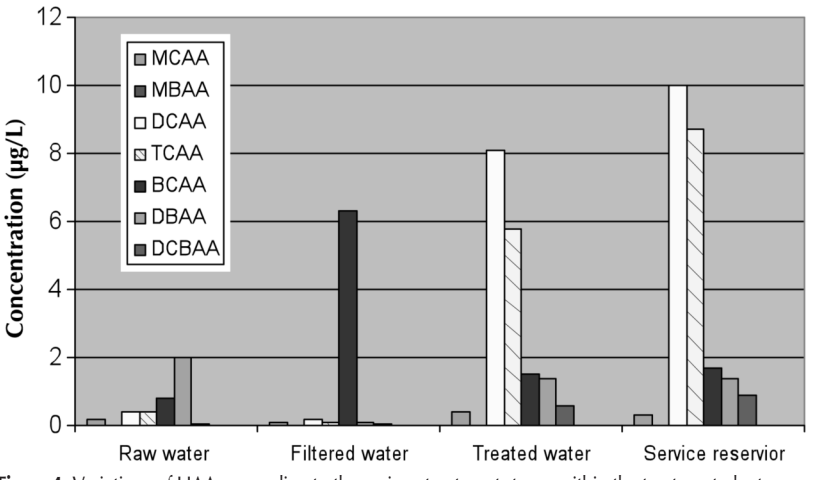

Figure 4. Variations of HAAs according to the various treatment stages within the treatment plant.

acids (TCAA), bromochloroacetic acids (BCAA), and dibromoacetic acids (DBAA) were detected in the real sample using SPE-GC–MS method, LLE-GC–ECD method only manage to detect DCAA, TCAA, and BCAA. This is attributed to the lower method detection limits for HAAs using SPE-GC–MS as compared to the LLE-GC–ECD. The validated SPE-GC–MS method was used to evaluate the concentration of HAAs at different points in the local treatment plant. Results were given in the Figure 4. The presence of HAAs in raw or un-treated water is understandable due to the fact that HAAs are distributed all around the world in lakes, groundwater, surface water, seawater, and soil (32,33), and their production has been attributed to both anthropogenic and natural activities. Chemical and pharmaceutical manufacturing processes like the bleaching of wood pulp by paper mill and cooling water are yet other sources of HAAs in the environ-ment (34).

Despite the similarities in MDL, LOQ, linearity, reproducibility, and specificity of both methods studied, the SPE-GC–MS showed clear advantages over LLE-GC–ECD process, namely the avoidance of using large volume of hazardous organic solvents and the higher selectivity of the mass spectrometric detection. In addition, better detection limits were obtained with the proposed SPE-GC–MS method. This proves that SPE-GC–MS can be used as suitable alterative of LLE for determining the HAAs in water sample. The brief summary of reported GC, IC, LC, ESI, and CE methods for HAAs analysis is given in Table IV.

Conclusions

A sensitive analytical SPE-GC–MS method was developed for determining all nine HAAs in drinking water. The overall method performance criteria is comparable to LLE-GC–ECD and other reported methods. However, if we look at individual HAAs component, some components (notably the bromoderivatives) show better, recovery, MDL, specificity, and linearity. In comparison with GC–ECD method and another reported methods, the GC–MS method offers the following merits: a higher sensitivity for MCAA; fewer interfering peaks and clearer baselines; and better response for brominated trihaloacetic acids. Thus, this new HAA analysis method does not offer a significant time-saving over the approved methods. But up to 10 samples can be processed at the same time with the use of a multi-port SPE vacuum manifold. Consequently, SPE-GC–MS procedure can be proposed as an alternative accurate method for the analysis of HAAs in water

at low µg/L levels, which avoids the need for large amounts of toxic organic solvents.

Acknowledgment

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Table IV. Summary of GC, LC, IC, CE, and ESI Methods for HAA Analysis

Method	Approach	Sample preparation	HAAs Analyzed	MDLs (µg/L)	Comments	Ref.
L.S. Clesceri, 1998	GC–ECD	MTBE extraction and diazomethane methylation	HAAs + BCAA	0.5–1.0	Safety concern regarding diazomethane	3
EPA method 552.1	GC–ECD	Anion exchange column extraction, acidic methanol methylation, and MTBE extraction	HAAs + BCAA	0.07–0.45	Sulfate affect the recoveries of some HAAs; possible GC column damage	19
EPA method 552.2	GC–ECD	MTBE extraction and acidic methanol methylation	HAA9*	0.07–0.82	Losses of TBAA due to decarboxylation	4
Xie	GC–MS	MTBE extraction and acidic methanol methylation	HAA9	0.07–0.83	Matrix interference for CAA and poor methylation efficiency for TBAA	16
Martinez et al. A	GC–MS	MTBE extraction and diazomethane methylation	HAA5 + BCAA	0.5–1	Safety concerns regarding diazomethane	8
Martinez et al. B	GC–MS	SPE preconcentration followed by acidic methanol methylation and MTBE extraction	HAA5 + BCAA	3–20	Low recoveries (18% to 45%) for the SPE process	8
Sarrion et al.	GC/ITMS†	Solid-phase microextraction	HAA9	0.01–0.45	Low extraction efficiencies (6% to 15%) for CAA, BAA, TBAA	20
Kampioti and Stephano	GC	Grob CLSA	DCAA, DBAA	0.05–0.07	Applicability to other HAAs unknown	21
Carrero and Rusling	HPLC	NA‡	HAA5 + TBAA	120–10,000	High detection limits	9
Sarzanini et al.	IC	SPE	HAA5	7–40	High detection limits	10
Lopez-avila et al.	IC	MTBE extraction	HAA9	0.045–1.1	Interference from sulfate	11
Helaleh et al.	IC	NA	CAA, DCAA, TCAA	110–321	High detection limit	12
Liu and Mou	IC	SPE	HAA9	1.1–9.3	High detection limit for TBAA	13
Loos and Barcelo	LC–ESI-MS	NA	HAA9	0.1–1.6	Low recoveries (26%-42%) for CAA,BAA, DBCAA,and TBAA	14
Roehl et al.	IC–ESI-MS	NA	HAA9	0.2–1.0	Expensive detector	22
Magnuson and Kelty	FI§-ESI-MS	MTBE extraction	HAA9	0.1–0.6	Expensive detector	23
Ells et al.	ESI-FAIMS-MS	NA	HAA5 + BCAA	0.5–4	Expensive detector	15
Bruzzoniti et al.	HPIC**	SPE	HAA9	8.0–210	Tedious, high detection limit	31
Kim et al.	CE–UV	MTBE extraction	HAA9 except TCAA	2–5	Not applicable to TCAA	24
Xie et al.	CE–UV	MTBE extraction	HAA9	1.3–7.7	Time consuming LLE	25, 26
Ahrer and Buchberger	CE–UV	MTBE extraction	HAA9	0.3–7.6	Low extraction efficiency (30%) for CAA and BAA	27
Martinez et al. A	CE–UV	MTBE extraction	HAA5 + BCAA	2–5	Unstable baseline using indirect detection	28
Martinez et al. B	CE–UV	SPE	HAA5	2–5	Low recoveries (40%) for CAA and BAA; Unstable baseline using indirect detection	28
Martinez et al.C	CE–UV	SPE	HAA5	Low µg/L	Unstable baseline using indirect detection	29
Lopez-Avila et al.	CE–CD††	NA	HAA9	~ 100	Incomplete resolution of nine HAAs peaks	30

* HAA9 = CAA+BAA+DCAA+BCAA+TCAA+BDCAA+CDBAA+TBAA.
† ITMS = Ion trap mass spectrometry. ‡ NA = not applicable. § FI = Flow injection.
** HPIC = High-performance ion chromatography. †† CD = Conductivity detector.

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