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Optimizing the determination of haloacetic acids in drinking waters

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Abstract

Three methods are currently approved by the US Environmental Protection Agency for the compliance monitoring of haloacetic acids in drinking waters. Each derivatizes the acids to their corresponding esters using either acidic methanol or diazomethane. This study was undertaken to characterize the extent of methylation of these analytes by these methods, and to fully optimize methylation chemistries to improve analytical sensitivity, precision and accuracy. The approved methods were shown to have little to no esterification efficiencies for the brominated trihaloacetic acids (HAA3). Methylation with acidic methanol was determined to be more efficient and rugged than methylation with diazomethane. A new higher boiling solvent, tertiary-amyl methyl ether, is reported which has significantly improved methylation efficiencies for HAA3. Additional modifications to the method have been made that improve method ruggedness. The revised method, EPA Method 552.3, outperforms the currently approved methods, especially for HAA3.

Keywords: Water analysis; Derivatization, GC; Methylation; Haloacetic acids; Diazomethane

1. Introduction

Haloacetic acids (HAAs) are formed during the disinfection of drinking water by the interaction of hypochlorous acid (or hypochlorite) with naturally occurring organic matter and bromide, if present. Because some of these compounds like dichloroacetic acid are classified as probable human carcinogens [1], they are regulated by the US Environmental Protection Agency (EPA) under the Stage 1 Disinfectants/Disinfection Byproducts (D/DBP) Rule [2].

There are nine haloacetic acid (HAA) congeners that contain chlorine or bromine. Five of the HAAs (HAA5) are regulated under the Stage 1 D/DBP Rule, including monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA) and dibromoacetic acid (DBAA). The four unregulated congeners include bromochloroacetic acid (BCAA) and the brominated trihaloacetic acids, bromodichloroacetic acid (BDCAA), chlorodibromoacetic acid (CDBAA), and tribromoacetic acid (TBAA).

Three methods are currently approved by the EPA for compliance monitoring of HAA5 in drinking waters under the Stage 1 Rule—EPA Methods 552.1 and 552.2, and Standard Method 6251B [3–5]. All three methods can also be used to determine BCAA concentrations; EPA Method 552.2 includes all nine HAAs as analytes. The two EPA methods include dalapon, a chlorinated herbicide which is structurally similar to the HAAs. Each method converts the acids to their corresponding methyl esters using either acidic methanol [3,4] or diazomethane [5] prior to analyzing them by gas chromatography with electron capture detection.

Because methylation of some of the HAAs is not 100% complete for either methylation reaction, a procedural standard technique is used to establish the calibration curves. This technique involves taking the calibration standards (reagent water fortified with the free acids) through the entire method procedure, thus compensating for less than 100% conversion of the acids to their corresponding methyl esters. The actual methylation efficiencies can have a large effect on method precision and accuracy, especially if they are low.

Drinking water utilities are not required to collect data on BCAA or the brominated trihaloacetic acids (HAA3) during compliance monitoring, but water utilities that are making

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changes in their treatment processes may want to collect data on the formation of all nine HAAs. This is because some treatment changes cause the speciation of HAAs to shift to the more brominated compounds [6]. Information regarding these changes provides the water utilities with a better understanding of their water quality in relation to DBPs.

Of the currently approved methods, only EPA Method 552.2 provides method performance data for HAA3 [4,7]. Because EPA Method 552.2 was developed prior to the availability of premethylated HAA3 standards, the efficiency of the acidic methanol derivatization was not assessed nor fully optimized. Several researchers have investigated the optimization of derivatization chemistries for HAAs using the diazomethane [8,9] and acidic methanol [10,11] techniques. The purpose of this study was to evaluate the methylation efficiencies for all nine HAAs and dalapon using EPA Method 552.2 and SM 6251B, and, if possible, to improve the derivatization yields for the HAA3s without jeopardizing method performance for the five regulated compounds. Studies were also conducted to improve method robustness. EPA Method 552.1, which uses solid-phase extraction instead of liquid–liquid extraction, was not included in this study because it is subject to low analyte recovery from high ionic-strength waters and is therefore not applicable for use on many drinking water samples [3].

2. Experimental

2.1. Reagents and standards

The haloacetic acids were obtained as solutions in methyl tertiary-butyl ether (MTBE) from Supelco (Bellefonte, PA, USA) in both their free acid form and as methyl esters, either as single-component mixtures (bromodichloroacetic acid, chlorodibromoacetic acid, tribromoacetic acid, and dalapon) or a six-component mixture (>97%). The internal standard (1,2,3-trichloropropane, 99%) and the tested surrogates (2-bromopropanoic acid, >99%; and 2,3-dibromopropanoic acid, 98%; 2-bromobutanoic acid, 97%) were obtained as neat materials from Aldrich (Milwaukee, WI, USA). The surrogate methyl esters were obtained as neat materials from Fluka (Buchs, Switzerland) (2-bromo-2-methylpropanoic acid, methyl ester, 99%) or as solutions in MTBE (2-bromopropanoic acid, methyl ester, and 2,3-dibromopropanoic acid, methyl ester) from Supelco.

MTBE was obtained from Burdick & Jackson (High Purity grade) (Muskegon, MI, USA). Tertiary-amyl methyl ether (TAME) was obtained from Fluka (>97%). Methanol was obtained from either Burdick & Jackson (Purge & Trap grade) or Fisher Scientific (Optima grade) (Pittsburgh, PA, USA). Sodium sulfate, copper sulfate pentahydrate, sulfuric acid, sodium bicarbonate, and ammonium chloride, all American Chemical Society (ACS) grade, were obtained from Fisher Scientific. Reagent water was obtained using a Millipore MilliQ Plus TOC system (Bedford, MA, USA). Peroxide test strips were obtained from Merck KGaA (Darmstadt, Germany).

2.2. Sample preparation

EPA Method 552.2 [4], EPA Method 552.3 [12], or Standard Method 6251B [5] were used to process samples for our experiments. Sample preparation procedures are briefly summarized below.

2.2.1. EPA method 552.2 sample preparation

The surrogate is spiked into a 40-ml sample in an extraction vial. The pH is adjusted to <0.5 with sulfuric acid, followed by addition of sodium sulfate and copper sulfate. The extraction solvent (4-ml MTBE) is added, and the capped vial is shaken for several minutes. Three milliliters of the extraction solvent is placed into a 15-ml conical test tube, 1 ml of 10% sulfuric acid in methanol (v/v) is added, and the capped tube is heated at 50 °C for 2 h. The cooled mixture is neutralized with four milliliters of saturated sodium bicarbonate solution. After neutralization, the aqueous layer is discarded. The internal standard is added to 1.00-ml aliquots of the neutralized extract and the aliquots are sealed in amber vials for GC analysis.

2.2.2. EPA Method 552.3 sample preparation

The surrogate is spiked into a 40 ml sample in an extraction vial. The pH is adjusted to <0.5 with sulfuric acid, followed by addition of sodium sulfate. The extraction solvent (4-ml MTBE or TAME) with internal standard is added, and the capped vial is shaken for several minutes. Three milliliters of the extract solvent is placed into a 15-ml conical test tube, 3 ml of 10% sulfuric acid in methanol (v/v) is added, and the capped tube is heated for 2 h at either 50 °C for MTBE or 60 °C for TAME. To the cooled mixture 7 ml of sodium sulfate solution is added, the tube is mixed, and the aqueous layer is discarded. The remaining extract is neutralized with 1 ml of saturated sodium bicarbonate solution. Aliquots of the extract are placed in amber vials for GC analysis.

2.2.3. Standard Method 6251 sample preparation

The surrogate is spiked into a 40-ml sample in an extraction vial. The pH is adjusted to <0.5 with sulfuric acid, followed by addition of sodium sulfate and copper sulfate. The extraction solvent (4-ml MTBE) is added, and the capped vial is shaken for several minutes. A 2.0-ml aliquot of the extract is passed through a column containing one gram of acidified sodium sulfate. Internal standard is added to the dried extract and diazomethane solution is added. The mixture is allowed to react for 30 min. After methylation, the excess diazomethane is removed by the addition of silica gel. Aliquots of the extract are placed in amber vials for analysis.

2.3. Simulated extraction procedure

In order to determine absolute methylation efficiencies, it was necessary to eliminate the extraction efficiency variable from each method procedure, while maintaining the challenge associated with methylating wet extracts, which was thought to be a concern for the diazomethane techniques. This was accomplished by preparing simulated extracts. Acidified reagent water containing the appropriate salt(s) was shaken with the solvent using the same proportions as specified in each method. The decanted solvent was then spiked with the surrogate, the HAAs and dalapon in the free acid form, and the internal standard, if it was not already present in the solvent. The extract was then derivatized and analyzed according to each method procedure. Absolute methylation efficiencies were determined by calculating analytical recoveries using calibration curves prepared from purchased methyl ester standards.

2.4. Analysis

Extracts were analyzed using an Agilent model 6890 gas chromatograph equipped with an electron capture detector (ECD) and a series 7683 injector (Agilent, Wilmington, DE, USA). Separation was achieved on a J&W DB-1701 capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) (Agilent Technologies, Wilmington, DE, USA). Splitless injections were made by injecting 1-μl aliquots into 2-mm i.d. quartz liners (Restek, Bellefonte, PA, USA) with the injection port set at 210 °C with a 45 s split delay. The detector temperature was 290 °C.

MTBE extracts were chromatographed using the following temperature program: initial temperature of 40 °C, held 10 min, increased to 65 °C at 2.5 °C/min, then to 85 °C at 10 °C/min, and then to 205 °C at 20 °C/min. TAME extracts were chromatographed using the same temperature program, except the initial temperature was set to 55 °C and held for 8 min. The carrier gas employed was helium (99.999% purity) with an inlet pressure of 16 psi (110 kPa). Argon (95%)/methane (5%) (99.999% purity) was used as the ECD make-up gas.

3. Results and discussion

3.1. Evaluation of diazomethane techniques

Standard Method 6251B employs diazomethane to methylate the HAAs prior to analysis. Diazomethane is widely used to methylate a number of functional groups, including carboxylic acids, phenols, and alcohols. With carboxylic acids, the methylation reaction is typically fast, the yield is high, and reaction conditions are mild. The chief drawbacks of using diazomethane to esterify HAAs are its toxicity and its low yield for the brominated trihaloacetic acids. Researchers have reported improved esterification efficiencies

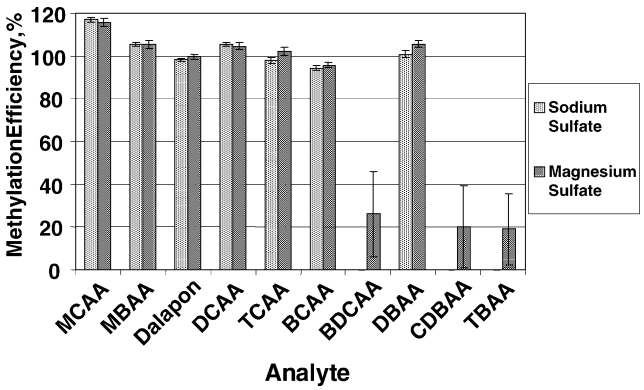

Fig. 1. HAA methylation efficiencies using SM 6251B with sodium sulfate and magnesium sulfate drying agents. Error bars indicate ± one standard deviation based on eight replicates.

for HAA3 using a modification to Standard Method 6251B that uses magnesium sulfate as an alternate drying agent to the prescribed acidified sodium sulfate [8,9]. Studies in the TSC laboratory confirmed esterification of HAA3 following the modified procedure. However, the esterification yields were low for the brominated trihaloacetic acids. In addition, no HAA3 esters were recovered when sodium sulfate was used as a drying agent while employing Standard Method 6251B. Diazomethane esterification efficiencies using the two above-mentioned drying agents are presented in Fig. 1. These data were determined using the simulated extraction procedure described above and therefore the recoveries reported in the figure are absolute esterification recoveries (rather than relative to the procedural calibration curve which would include extraction variability).

In addition to the low esterification efficiencies, a second problem was discovered in the diazomethane simulated extract. After reaction and quenching, the HAA3 were not stable in the extract at room temperature while awaiting analysis (Fig. 2). Sixty percent of the tribromoacetic acid ester degraded during 18 h at room temperature in an autosampler rack. Based on these observations, the research

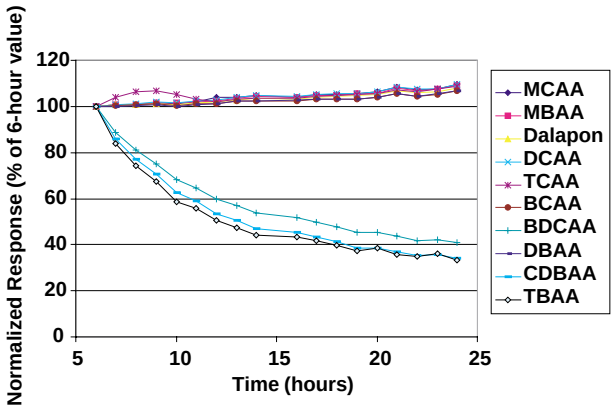

Fig. 2. Short-term stability at room temperature of SM 6251B extract dried with magnesium sulfate.

effort was shifted towards optimizing the acidic methanol derivatization procedure.

3.2. Optimizing Fisher esterification in MTBE

The acidic methanol technique used to methylate the HAAs and dalapon in EPA Method 552.2, termed Fisher esterification, is an acid-catalyzed equilibrium reaction that proceeds through an SN_2 reaction intermediate. The reaction can be driven towards ester formation by the addition of a large molar excess of methanol or by increasing the reaction temperature. A number of experiments were conducted to optimize the temperature and methanol content of the Method 552.2 procedure. Optimizing HAA esterification with MTBE was the topic of a recent study by another author [10]. In that study, methylation efficiencies were reported relative to the unmodified method, which uses a procedural calibration curve thereby masking the absolute esterification efficiencies. The results presented below, which are reported as absolute methylation efficiencies using the simulated extraction procedure described above, are in good agreement with some of the recently reported values.

Fig. 3 shows the effect of variations in temperature on methylation efficiency of the HAAs and dalapon using the conditions outlined in Method 552.2. Method 552.2 employs a 2-h reaction at 50 °C. Increasing the temperature improves the methylation efficiency for most of the compounds and decreasing the temperature significantly reduces methylation efficiency. The data show that the methylation efficiency is less than 50% for the HAA3 even at the highest temperature studied. However, even in its current, unoptimized, form, Method 552.2 exhibits better methylation efficiency than either version of the diazomethane derivatization approach shown in Fig. 1.

Given the low boiling points of the two reaction solvents (methanol, bp 65 °C, MTBE, bp 55 °C), increasing the reaction temperature was not considered a safe option, so the upper temperature limit was kept at 50 °C for further experiments using MTBE. Improving methylation efficiencies by increasing the amount of acidic methanol in the reaction was pursued next.

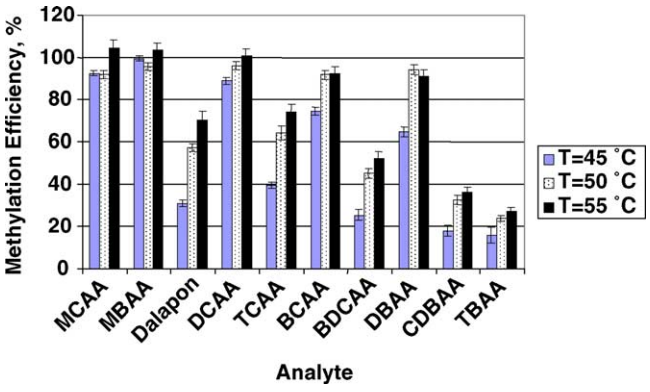

Fig. 3. HAA methylation efficiencies obtained for the Method 552.2 procedure at 45, 50 and 55 °C. Error bars indicate ± one standard deviation based on eight, eight, and four replicates, respectively.

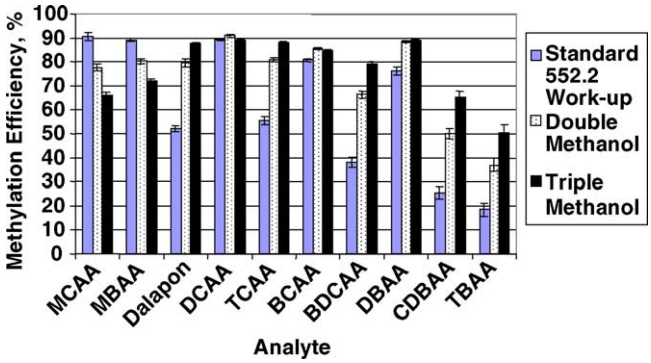

Fig. 4. HAA methylation efficiencies in MTBE with varying amounts of acidic methanol. Error bars indicate ± one standard deviation based on six replicates.

Method 552.2 employs 1 ml of acidic methanol to 3 ml of the MTBE extract in order to methylate the HAAs and dalapon. Two higher levels of acidic methanol were investigated (2 and 3 ml) while keeping the MTBE extract volume constant. As seen in Fig. 4, the methylation efficiency was increased for five analytes with increased amounts of acidic methanol. However, MCAA and MBAA, two of the regulated HAAs, show an apparent decrease in methylation efficiency. Other researchers have attributed this decrease to volatilization of MCAA and MBAA by carbon dioxide which is evolved from the saturated bicarbonate solution during neutralization of the acidic methanol [13]. This loss, which was investigated further during the course of the experiments described in Section 3.3, appeared to place a practical limit to the amount of methanol that could be used for the method.

3.3. Evaluation of TAME as an alternate esterification solvent

Because of the practical limitations posed by MTBE, a search was initiated to identify an alternate solvent for methylation of the HAAs. An ideal replacement for MTBE would have several characteristics. It would have a boiling point that was higher than that of MTBE, but still well below that of the methyl ester of the first analyte eluting from the GC column. The solvent would have a similar polarity to MTBE, would be compatible with electron capture detectors, and would be available in suitable purity at a reasonable cost. These criteria led us to investigate tertiary-amyl methyl ether (TAME). Table 1 contrasts the physical properties of these two solvents.

Fig. 5 presents HAA methylation efficiency in TAME using the same ratio of solvent to acidic methanol that was used in Method 552.2, so that, at 50 °C the only difference between the procedures is the substitution for TAME for MTBE. Methylation efficiencies in TAME at 50 °C are very

Table 1
Comparison of physical properties of MTBE and TAME

Solvent	MTBE	TAME
Boiling point (°C)	55.2	86.3
Water solubility (g)	4.8/100	1.2/100
Purity (%)	>99	>97
ECD response	Acceptable	Acceptable
Cost/analysis (US$)	0.15	0.84

similar to those presented in Fig. 3 for MTBE, and as expected, show improvement at increased temperatures.

Esterification in TAME at elevated temperature has its own set of considerations. With TAME as the extraction solvent, reaction temperature becomes limited by the boiling point of methanol. The method employs a graduated, conical glass tube with a polytetrafluoroethylene-lined screw cap. The reaction tubes cannot be expected to contain significant internal pressure. This factor made itself obvious during the course of our experiments at 60 °C. At one point, reaction tubes were heated in a covered water bath, which had the effect of heating the entire reaction tube, not merely the liquid contents at the tube bottom. Almost half of the tubes lost significant amounts of their contents due to vaporization, which significantly lowered the precision of the assay (%RSD rose as high as 24%—quadruple the normal). This volume loss was not observed when tubes were heated in an open-topped metal heating block or a sand bath. It is postulated that necks of the tubes that extended beyond the sand bath or heating block helped condense the vapor in the tube, whereas in the covered water bath this process was prevented. A water bath may be used for methylation heating, if the surface of the water is covered in such a way as to leave the tops of the tubes unheated. A layer of small plastic spheres on top of the water may be used to accomplish this.

An early attempt to increase analyte methylation efficiencies involved doubling or tripling the methanol content of the reaction mixture without changing the acid concentration of the total reaction mixture, which was 2.5%. This resulted in comparing the methylation of 3 ml of extract with either 1 ml of 10% sulfuric acid in methanol, 2 ml of 6.25%

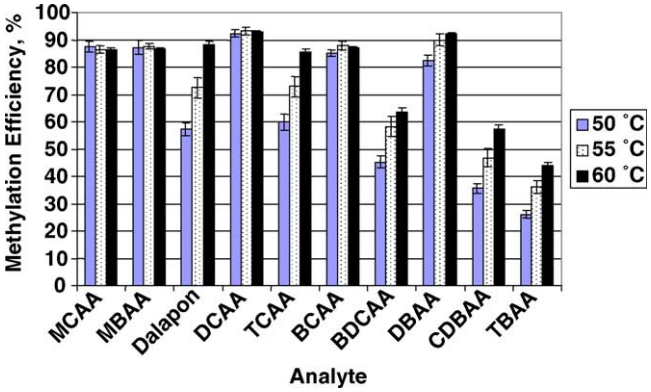

Fig. 5. HAA methylation efficiencies following the Method 552.2 procedure at 50, 55 and 60 °C with TAME as the methylation solvent. Error bars indicate ± one standard deviation based on six replicates.

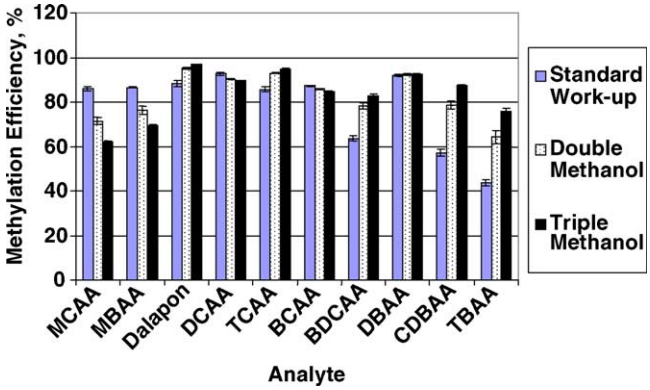

Fig. 6. HAA methylation efficiencies in TAME at 60 °C with varying amounts of acidic methanol. Error bars indicate ± one standard deviation based on six replicates.

solution, or 3 ml of 5% solution. Methylation yields increased with increasing methanol, but not significantly. For further experiments, the acid content of the methanol was kept at 10%, which is the same amount as in Method 552.2.

Increasing methylation by increasing the acidic methanol content of the methylation mixture was investigated next. Fig. 6 presents data from a series of experiments that parallel those presented in Fig. 4. Using a 1:1 volume ratio of acidic methanol/TAME produced the most complete methylation for HAA3; however, similar to the results presented earlier, the recoveries of MCAA and MBAA decreased with increasing amounts of acidic methanol.

This phenomenon was investigated further to determine if the MCAA and MBAA esters were inefficiently extracted from the aqueous phase rather than lost during neutralization. To accomplish this, a derivatization was conducted in TAME using a volume ratio of 2:3 acidic methanol/TAME at 60 °C. The TAME phase was removed after neutralization with a saturated bicarbonate solution, and then a second 3 ml portion of TAME was added to extract the aqueous phase a second time.

These data are presented in Fig. 7. The combined amounts indicate that with the exception of the brominated trihaloacetic acids, esterification proceeds to completion, and that MCAA and MBAA are not extracted completely from the neutralized aqueous phase into the solvent extract. The lower yield for the brominated trihaloacetic acids is attributed to steric hindrance of the SN_2 intermediate. Attempts to reduce the volume of the neutralization phase by using stronger base (e.g. 1 ml of phosphate buffer followed by 1 ml of 3.75 M sodium hydroxide), showed reduced efficiencies and poor precision, which were attributed to base-catalyzed hydrolysis of the esters during neutralization.

3.4. Improving method robustness

3.4.1. Copper sulfate

As methylation efficiencies increased for HAA3, a trend was noted during the evaluation of large sample sets that

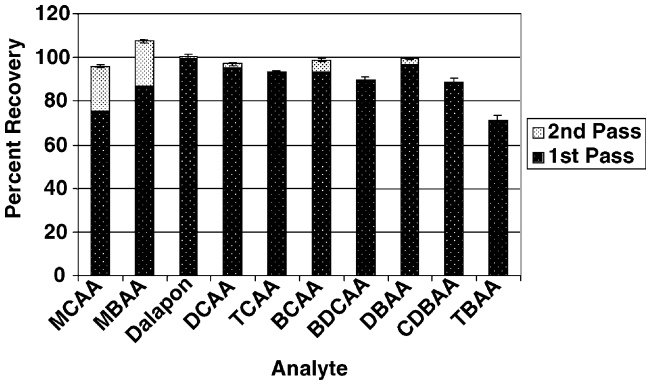

Fig. 7. Investigation of the apparent loss of MCAA and MBAA derivatized using the TAME procedure by extracting the aqueous phase with a second 3 ml portion of TAME. Esterification conducted in TAME at 60 °C with 2 ml of acidic methanol and 3 ml TAME. Error bars indicate the combined uncertainty as ± the sum of one standard deviation for both procedures based on two groups of three replicates each.

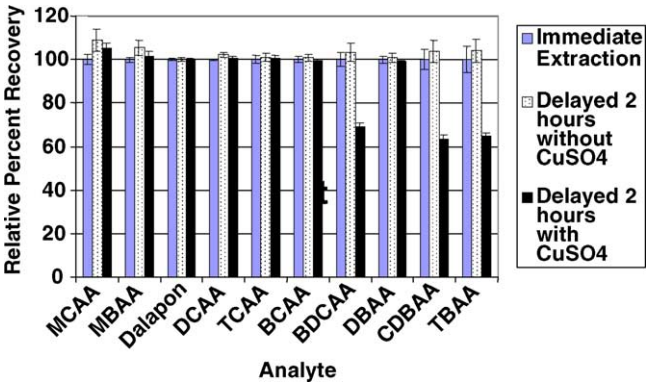

Fig. 8. The loss of HAA3 due to prolonged exposure to copper ion during the initial extraction. Results are normalized to the immediate extraction recoveries. Error bars indicate ± one standard deviation based on three replicates.

manifested itself as very high recoveries for HAA3 (as high as 180% for TBAA in some cases) in natural waters with high mineral content. Quantitation of the fortified samples using both procedural and premethylated standard curves indicated that the high recoveries were associated with low esterification efficiencies during preparation of the calibration curves rather than abnormally high recoveries for the real samples. A series of experiments indicated that copper sulfate, which is used to color the aqueous phase during the initial extraction, was causing degradation of the HAA3, and that this mode of loss was quicker in reagent water than in real matrices. Hard ground waters provided the most protection from this copper-mediated degradation. The mechanism for the ground water protection from copper degradation was determined not to be pH related, since both reagent water and hard water were adjusted to have a pH of <0.5 during the initial extraction.

Since the currently approved methods use copper sulfate during the initial extraction to help differentiate the organic and aqueous layers, this observation warranted careful investigation. Fig. 8 shows three sets of reagent waters fortified with the HAAs and dalapon. Two sets were acidified and salted out in the presence of copper sulfate; one was extracted immediately, while one was held for 2 h at room temperature and then extracted. The third set was prepared similarly and held for 2 h, but copper sulfate was omitted. Each set of values for each analyte is normalized against the set of replicates that were extracted immediately. These data clearly show the loss of BDCAA, CDBAA and TBAA over the 2-h period. During some method development experiments, the loss of TBAA was accompanied by the appearance of bromoform (see Section 3.4.2). However, close examination of the chromatograms in this experiment did not indicate the formation of bromoform as a result of the loss of TBAA. Copper sulfate was removed from the revised method. Copper sulfate is expected to be compatible with the analysis of HAA6 (HAA5 plus BCAA) in the currently approved methods.

3.4.2. Peroxides in solvent

Another potential mode of loss was noted during this work. Occasionally low recoveries of HAA3 methyl esters were noted to coincide with the presence of brominated trihalomethanes, particularly bromoform. Since the method analytes were fortified into reagent water, which had no trihalomethanes, it was theorized that peroxides in the MTBE solvent were causing HAA3 loss either during sample processing or extract storage. A common peroxide test, which was capable of detecting 0.5 ppm of peroxide, gave only faintly positive results when applied to the MTBE that was used for extraction. Reanalysis using a freshly-opened bottle of MTBE returned the HAA3 yields to their expected values. This mode of HAA3 loss was not observed when using TAME for the extraction solvent. It should be noted that the primary source of TAME used for this work was obtained stored over molecular sieves, which may scavenge peroxides and/or necessary precursors to their formation. Analysts should be aware of this potential problem and monitor for bromoform formation in their laboratory fortified blanks and/or calibration standards.

3.4.3. Neutralization of acidic extract

Some laboratories have commented that Method 552.2 requires frequent instrument maintenance due to the degradation of the analytical column. This degradation is due to the routine injection of acidic extracts. The acidity is the result of incomplete neutralization of the acidic methanol. This feedback identified a potential area to improve method robustness.

Because of the limited solubility of sodium bicarbonate in water, a relatively large volume of the saturated solution is required to neutralize the acidic methanol reagent. For example, 9 ml of saturated sodium bicarbonate solution is needed to neutralize 3 ml of 10% sulfuric acid in methanol. The

Table 2
Overall absolute method efficiencies as a function of volume of sodium sulfate solution

Method efficiency-esterification and extraction (%)											
Volume of Na_2SO_4 solution (ml)[a]	MCAA	MBAA	Dalapon	DCAA	TCAA	BCAA	BDCAA	DBAA	CDBAA	TBAA	Volume MTBE recovered (%)
3	64	71	85	86	87	87	79	88	53	36	69
4	67	75	89	89	88	91	84	92	57	37	72
5	68	77	92	91	89	93	88	94	61	41	74
6	71	80	92	93	89	94	87	94	59	40	84
7	71	80	93	93	90	94	92	95	64	45	83
Control[b]	65	75	94	92	92	94	92	95	65	43	73

[a] Three milliliters of MTBE extract was methylated with 3 ml of 10% sulfuric acid in methanol, then separated with various volumes of sodium sulfate solution, followed by a final neutralization with 1 ml of saturated sodium bicarbonate solution.

[b] Two milliliters of MTBE extract was methylated with 2 ml of 10% sulfuric acid in methanol, then neutralized with 6 ml of saturated sodium bicarbonate solution.

saturated bicarbonate solution also creates separate aqueous and organic phases and partitions the HAA esters back into the organic phase. The final neutralization step was modified to first force phase separation using an aqueous solution of sodium sulfate followed by neutralizing the extract. After the phases are separated, the amount of bicarbonate solution required to neutralize the extract varies with the solubility of the aqueous phase in the organic layer, which is higher for MTBE than TAME, and by the ability of the analyst to separate the phases without unnecessarily leaving water with the organic layer. After the extract is separated from the aqueous layer, 1 ml of saturated bicarbonate is sufficient to remove the residual acid and ensure extract neutrality.

3.4.4. Sodium sulfate solution

Because increasing the ratio of acidic methanol/solvent to 1:1 significantly improves the esterification of HAA3, further experiments were conducted in an attempt to improve the recovery of the MCAA and MBAA esters under those methylation conditions. It was postulated that optimization of the back extraction step could also be used to reduce the methanol concentration of the aqueous layer, thereby reducing the solubility of MCAA and MBAA in the aqueous phase for greater recovery of the methyl esters in the solvent extract. A series of experiments was conducted in both MTBE and TAME using 1:1 acidic methanol/solvent esterification conditions and varying the volume of the aqueous sodium sulfate solution over a range of 3–7 ml. The results were compared to those obtained without the sodium sulfate extraction. A summary of the experiments conducted using MTBE is presented in Table 2; comparable results were obtained using TAME. As the volume of sodium sulfate solution is increased, the recovery of all the methyl esters is increased. The back extraction using 7 ml of sodium sulfate solution improved the recovery of MCAA and MBAA almost to the levels achieved in the 2:3 acidic methanol/extract volume ratio, while taking advantage of the increased esterification efficiencies of HAA3 using the 1:1 procedure. For example, the MCAA recoveries in MTBE and TAME were 71 and 68%, respectively, and the recoveries for TBAA were 45 and 82%, respectively. These conditions were incorporated into Method 552.3.

3.4.5. Selection of surrogates

Drinking water samples vary widely in the nature and content of potentially interfering compounds. Some laboratories have observed an interferant with a GC retention time in close proximity to one or more of the surrogates in the EPA-approved methods. While this is not a commonly reported observation, it is desirable to allow analysts to choose an alternate surrogate should they routinely analyze a drinking water matrix that presents this challenge.

The selection of an alternate surrogate can not be based solely on retention time. An appropriate surrogate should have similar extraction and esterification efficiencies to the method analytes and must be stable during sample processing and extract storage. Two alternate surrogates were evaluated, 2-bromo-2-methylpropanoic acid, and 2-bromobutanoic acid. Both surrogates were easily resolved from the HAA analytes on both the primary and secondary column under method conditions, had high esterification efficiencies and were efficiently extracted. However, only 2-bromobutanoic acid had acceptable stability under method conditions.

Surrogate recoveries (calculated against a procedural calibration curve) for 2-bromo-2-methylpropanoic acid were consistently lower that the average recovery for the other method analytes. When data were closely examined, the surrogate recoveries were seen to be inversely correlated with the amount of time that the samples were held after fortification with the surrogate prior to the initial extraction. This was further investigated for both new surrogates by preparing triplicate samples that were fortified with the surrogate and all method analytes and then held for 3 h prior to extracting them. Recoveries for 2-bromo-2-methylpropanoic acid and 2-bromobutanoic acid were 45 and 108%, respectively. The loss of 2-bromo-2-methylpropanoic acid is thought to arise from the lability of its tertiary carbon–bromine bond. As a result of this stability study, EPA Method 552.3 recommends the use of 2-bromobutanoic acid as the surrogate standard.

3.5. Method 552.3 performance

The modifications described above form the technical basis for EPA Method 552.3. Detection limits for the new method are comparable to or better than Method 552.2 detection limits for all HAA analytes. Detection limits for HAA3 are three to eight times lower for HAA3 in the new method.

Single laboratory precision and accuracy were assessed in reagent water, a chlorinated surface water, and a chlorinated ground water and are reported in the method [12]. For samples fortified at 1.0 ug/l, accuracy and precision, expressed as percent recovery and relative standard deviation, ranged from 89.2 to 128% (RSD ranged from 0.90 to 9.5%) in MTBE, and 81.4 to 131% (RSD ranged from 0.36 to 8.8%) for TAME. For samples fortified at 10 ug/l levels, accuracy and precision ranged from 95.9 to 116% (RSD ranged from 0.52 to 6.3%) in MTBE, and 97.1 to 106% (RSD ranged from 0.33 to 3.8%) for TAME. Precision for HAA3 is significantly improved in the new method when using either solvent. Precision for HAA3 in the TAME version of the method was better than the MTBE version.

4. Conclusions

The analytical methods that are currently approved for compliance monitoring of HAAs by EPA have poor esterification for the HAA3 targets, which are not regulated. Attempts to extend the diazomethane chemistries to HAA3 were problematic and indicated poor extract stability. The acidic methanol esterification procedure used in EPA Method 552.2 is the preferred mode of esterification for HAA3; however, in its current form it has esterification efficiencies as low as 25% for TBAA, warranting this study.

As predicted, increasing methanol content and temperature during methylation improved esterification efficiency. With MTBE, the methylation efficiency for the most difficult compound to methylate, TBAA, was nearly doubled to 45%. Using the higher boiling solvent TAME, methylation efficiency for TBAA was increased to 82%. As a direct result, the new method has lower detection limits for HAA3, and markedly improved precision.

Finally, three changes have been made to the new method that should improve its robustness. These include the removal of copper sulfate in the initial extraction, which was shown to degrade HAA3, the incorporation of extract neutralization, which greatly limits the possibility of accidentally injecting acidic extracts, and the option to use TAME, which contained lower levels of peroxides, thus permitting longer extract holding times.

This work formed the basis for EPA Method 552.3, which has been proposed for approval as an additional compliance monitoring method for HAA5 as part of the Stage 2 DBP Rule proposal [14]. Method 552.3 offers superior sensitivity, precision and accuracy for HAA3 compared to the currently approved methods.

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