# Research Associated with the Development of EPA Method 552.2

**Anne M. Pawlecki-Vonderheide***
International Consultants, Inc., 26 W. Martin Luther King Drive, Cincinnati, OH 45219

**David J. Munch**
U.S. Environmental Protection Agency†, Office of Water, Technical Support Center, Cincinnati, OH 45268

**Jean W. Munch**
U.S. Environmental Protection Agency†, National Exposure Research Laboratory, Office of Research and Development, Cincinnati, OH 45268

## Abstract

**The work presented in this paper entails the development of a method for haloacetic acid (HAA) analysis, Environmental Protection Agency (EPA) method 552.2, that improves the safety and efficiency of previous methods and incorporates three additional trihalogenated acetic acids: bromodichloroacetic acid, chlorodibromoacetic acid, and tribromoacetic acid, which are not included in the previous two methods, standard method 6251B and EPA method 552.1. The final procedure includes a microextraction coupled with derivatization by acidic methanol. All nine possible brominated and chlorinated HAAs are detectable at concentrations of less than 1 µg/L. The objective of this paper is to describe the various approaches that were explored, the conclusions that were drawn from the associated studies, and the reasoning behind the changes that were incorporated into EPA method 552.2.**

## Introduction

Disinfection of water by chlorination can lead to the formation of haloacetic acids (HAAs), which are part of a much larger group of compounds known as disinfection byproducts (DBPs). DBPs are formed by the reaction of free chlorine with naturally occurring organic matter in many drinking water sources. Many of these compounds are suspected carcinogens, and the Environmental Protection Agency (EPA) has included many DBPs in the Information Collection Rule (ICR) (Federal Register Vol. 61, No. 94, pp. 24354–88) and may regulate them in the future. The nine possible brominated and chlorinated HAAs are of the greatest interest. Two analytical methods are currently approved for analysis of HAAs in the ICR: standard method 6251B (1) and EPA method 552.1 (2). The former method utilizes liquid–liquid extraction and diazomethane as a derivatizing agent. Diazomethane efficiently esterifies the haloacetic acids to their methyl esters; however, public concerns over the toxic properties and explosive characteristics of diazomethane have prompted the EPA to investigate alternative derivatization techniques. The second method, EPA method 552.1, utilizes a solid-phase extraction procedure that is subject to considerable variability in sample matrices containing competing ionic species (2).

In order to analyze for the haloacetic acids, the compounds are first extracted from the aqueous sample. This is followed by a derivatization procedure whereby the analytes, which are carboxylic acids, are converted to their methyl ester forms. This conversion is necessary for chromatographic purposes, and the sample extracts are subsequently analyzed by a gas chromatographic system using electron-capture detection (GC–ECD).

Standard method 6251B requires the extraction of the haloacetic acid compounds from the aqueous sample with methyl *tert*-butyl ether (MTBE). Diazomethane, the derivatizing agent, is added directly to the MTBE extract, and a very quick, clean esterification takes place. The alkylating agent is the extremely reactive methyl diazonium ion, which is generated by proton transfer from the carboxylic acid to diazomethane.

$$RCO_2H + CH_2N_2 \longrightarrow [RCO_2^-CH_3N_2^+] \longrightarrow RCO_2CH_3 + N_2$$

EPA method 552.1 requires extraction of the HAA compounds from the aqueous sample by passing the sample through a column of ion-exchange resin. The compounds are then eluted with a 10% solution of $H_2SO_4$ in methanol. This acidic methanol solution also affects the esterification of the haloacetic acids upon heating. This reaction, classically known as the Fisher esterification, is an acid-catalyzed reaction of carboxylic acids with alcohols to form esters.

$$RCO_2H + R'OH \xrightarrow{H^+} RCO_2R' + H_2O$$

This is an equilibrium process; using an excess of the alcohol drives the reaction to completion. In addition to problems associated with poor analyte recoveries in high ionic strength matrices, another drawback to this method is the GC

* Author to whom correspondence should be addressed.
† Though the information presented in this article has been funded entirely by the Environmental Protection Agency under contract #68-C3-0346, it does not necessarily reflect the views of the Agency, and no official endorsement should be inferred.

column degradation caused by the acidic extracts, which is produced as a result of the acidic methanol esterification.

## Experimental

### Instrumentation

A Hewlett-Packard 5880 GC with an ECD was used. A DB-5.625 (fused silica with chemically bonded 5% phenylmethylpolysiloxane) fused-silica column (30 m × 0.25-mm i.d., 0.25-µm film thickness) and a DB-1701 (fused silica with chemically bonded 14% cyanopropylphenyl–methylpolysiloxane) fused-silica column (30 m × 0.25-mm i.d., 0.25-µm film thickness) were used. Splitless injection mode was employed with a 30-s delay; helium linear velocity was measured at 25 cm/s.

**Table I. Detection Limits for the HAAs**

| HAA | Method detection limit* (µg/L) |
|---|---|
| Monochloroacetic acid (MCAA) | 0.273 |
| Monobromoacetic acid (MBAA) | 0.204 |
| Dichloroacetic acid (DCAA) | 0.242 |
| Dalapon | 0.119 |
| Trichloroacetic acid (TCAA) | 0.079 |
| Bromochloroacetic acid (BCAA) | 0.251 |
| Dibromoacetic acid (DBAA) | 0.066 |
| Bromodichloroacetic acid (BDCAA) | 0.091 |
| Chlorodibromoacetic acid (CDBAA) | 0.468 |
| Tribromoacetic acid (TBAA) | 0.820 |

* Statistically derived and calculated by multiplying the standard deviation of the replicates by the student's *t*-value appropriate for a 99% confidence level and a standard deviation estimate with *a* degree of freedom one less than the number of replicates.

### Reagents

Analytical standards were purchased as ampulized solutions from Supelco (Bellefonte, PA) and Ultra Scientific (North Kingstown, RI). Trimethylsilyldiazomethane (TMSD) was purchased from Fluka (Ronkonkoma, NY). All solvents were of analytical grade.

## Results and Discussion

### Method development

*Extraction*

In a comparison of the two existing extraction procedures of standard method 6251B and EPA method 552.1, the MTBE microextraction of standard method 6251B was considered more favorable. It is much more efficient in extracting the target analytes in high ionic strength waters than the solid-phase extraction of method 552.1. Furthermore, it is a fairly simple procedure and utilizes relatively small amounts of solvent (a 30-mL volume of sample is extracted with 3 mL of MTBE). Subsequently, the extraction of method 552.2 (3) was patterned after the extraction procedure of standard method 6251B.

Before the extraction solvent is added, several reagents are added to the aqueous sample. First, 2 mL of sulfuric acid is added to lower the pH of the sample to less than 0.5, thereby insuring that the target analytes are in their acid forms. Next, 2 g of copper(II) sulfate pentahydrate are added to color the

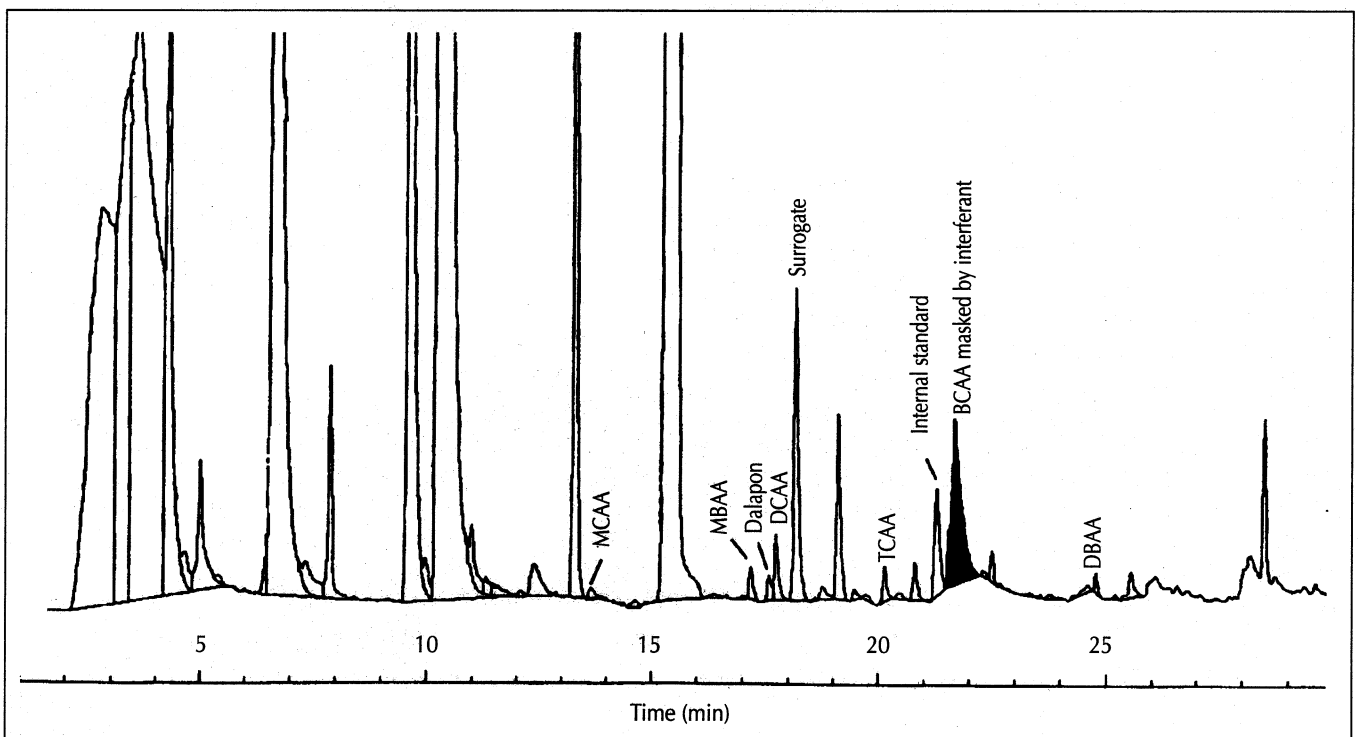


**Figure 1.** TMSD derivatization of HAA on the DB-1701 column.

aqueous phase and make it easier to distinguish between the aqueous and organic phases. Finally, 16 g of sodium sulfate are added to increase the ionic strength of the aqueous phase and drive the HAAs into the organic phase.

*Derivatization*

Both TMSD and acidic methanol were evaluated as derivatization techniques. TMSD was found to be an effective agent for derivatizing the phenoxy herbicides of EPA method 515.2 (4) and was considered as a potential derivatizing agent for the HAAs.

Commercially prepared HAA methyl esters were analyzed alongside HAAs that had been esterified with TMSD. Esterification efficiencies (corrected for molecular weight) were calculated by considering the amounts of the commercially prepared esters as the true value and the amounts obtained from the ester derivatized in the laboratory with TMSD as the observed value (Table II). The resulting recoveries, which ranged from approximately 80 to 100%, proved the procedure to be an efficient means of esterification; however, the elution of the ester of bromochloroacetic acid (BCAA) was masked by an undetermined interferant on the DB-1701 column originally used for primary analysis (Figure 1). Furthermore, as can be seen in Figure 1, the high background noise and many interferants required the analyte peaks to be carefully integrated to ensure correct baseline assignment and to preserve peak integrity.

The purity of the TMSD was checked to locate the source of the interferant. Derivatization of calibration standards from a second vendor yielded chromatograms that contained the same interferant peaks as those from the original vendor. Several modifications of the temperature program were made, but none were successful in chromatographically separating the interferant from the ester of BCAA on the primary column. Choosing a different stationary phase was considered, but this

**Table II. Esterification Efficiencies of HAAs Derivatized with TMSD Compared with those Obtained from Derivatization with Acidic Methanol**

| Analyte | Average esterification efficiency using TMSD as the derivatizing agent (%) | Average esterification efficiency using acidic methanol as the derivatizing agent (%) |
|---|---|---|
| Monochloroacetic acid | 83 | 84 |
| Monobromoacetic acid | 98 | 90 |
| Dalapon | 91 | 79 |
| Dichloroacetic acid | 98 | 98 |
| Trichloroacetic acid | 92 | 70 |
| Bromochloroacetic acid | unable to quantitate | 88 |
| Dibromoacetic acid | 97 | 100 |

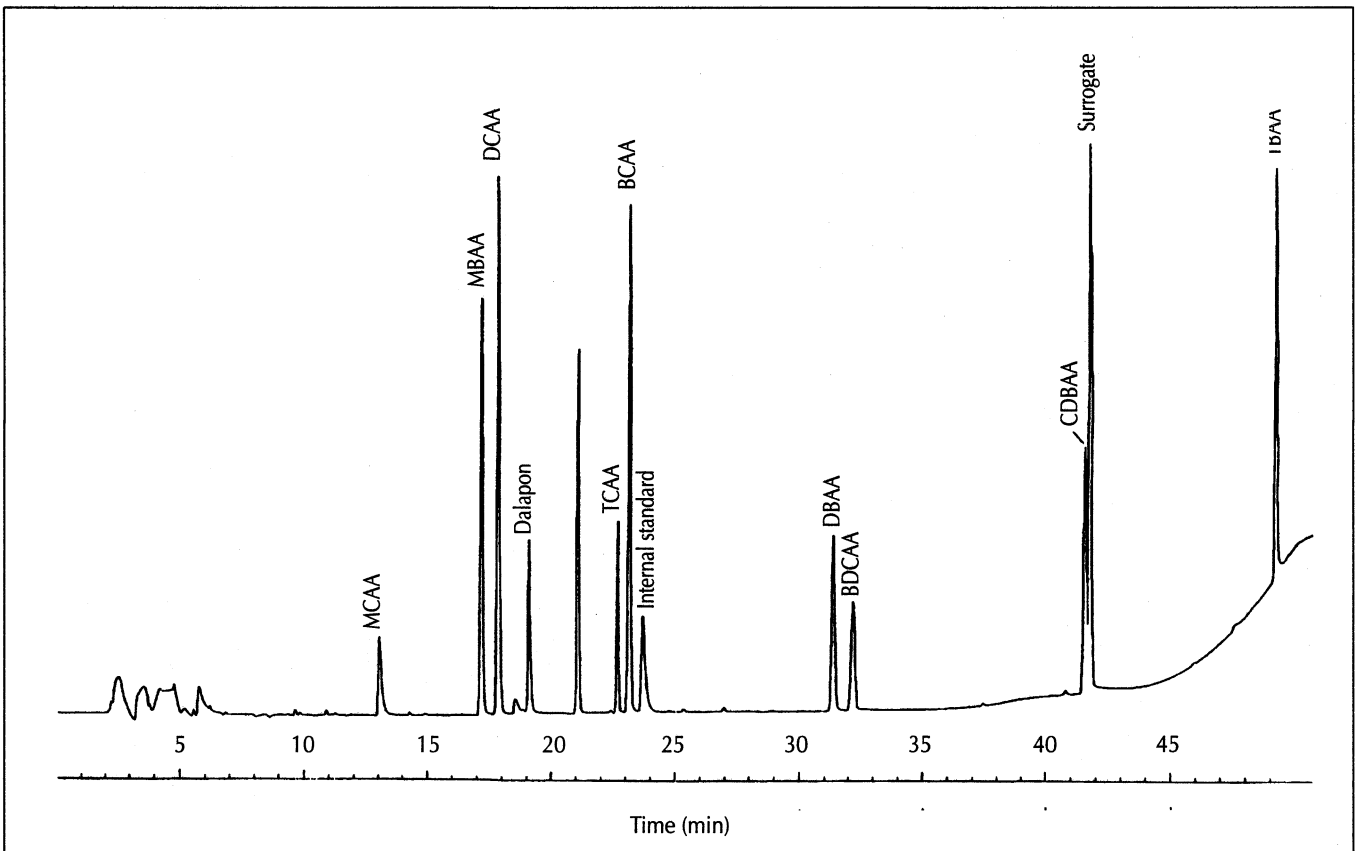


**Figure 2.** Elution of method analytes on the primary column (DB-5.625).

course of action was not pursued because of the high background signal and many interfering peaks generated by the TMSD that may have caused additional coelution problems.

Acidic methanol derivatization was used for the analysis of six HAAs in EPA method 552.1. However, the resulting acidic extract was believed to degrade chromatographic column performance over time, and the derivatization of three additional HAAs, bromodichloroacetic acid, chlorodibromoacetic acid, and tribromoacetic acid (TBAA), had not been demonstrated.

The methylation procedure used in method 552.1 was modified to include a back-extraction with a saturated sodium bicarbonate solution to neutralize the acidic extracts and prevent any damage to the GC column. The esterification efficiency of this new procedure was evaluated and found to be comparable to that obtained using TMSD (Table II). In addition, minimal interferences were observed, compared with those observed with TMSD.

One problem was discovered in the acidic methanol derivatization procedure. The TBAA ester gave a much lower response than the other haloesters when analyzed at comparable concentration levels. Peters et al. (5) discovered that TBAA underwent a partial decarboxylation during esterification with $H_2SO_4$–methanol. To confirm this observation, the acidic methanol esterification procedure was performed on a calibration standard that contained only TBAA. The analysis of this standard produced a chromatogram that contained two peaks of approximately the same size. The peak that eluted first was suspected to be bromoform, the product of decarboxylation of TBAA, and the peak that eluted second was at the retention time of the ester of TBAA. Analysis of a standard containing only bromoform confirmed that TBAA did decarboxylate when esterified using the acidic methanol procedure. The bromoform peak can be observed in Figure 2 as a substantial peak eluting between the esters of Dalapon (2,2'-dichloropropionic acid) and trichloroacetic acid.

Because a significant amount of the TBAA underwent decarboxylation when it was esterified using acidic methanol, the detection limit was considerably higher than those of the remaining analytes (Table I). Further work with TBAA showed that its decarboxylation was reproducible. The relative standard deviations calculated from replicate analyses ranged from 5 to 15% in several fortified matrices. These matrices included Ohio River water, water from a local well with significant hardness, Cincinnati tap water, and water that demonstrated a high total organic carbon (TOC) content. Although the detection limit of TBAA was considerably higher then the detection limits observed for the remaining analytes, an accurate determination of its concentration could be made because the loss due to decarboxylation was reproducible and was compensated for by the use of procedural calibration standards.

*Chromatography*

Chromatographic studies were performed using a Hewlett-Packard model 5880 GC equipped with a linearized ECD. Initial analyses were performed using a 30-m × 0.25-mm-i.d. DB-1701 chromatographic column. Derivatization with acidic methanol

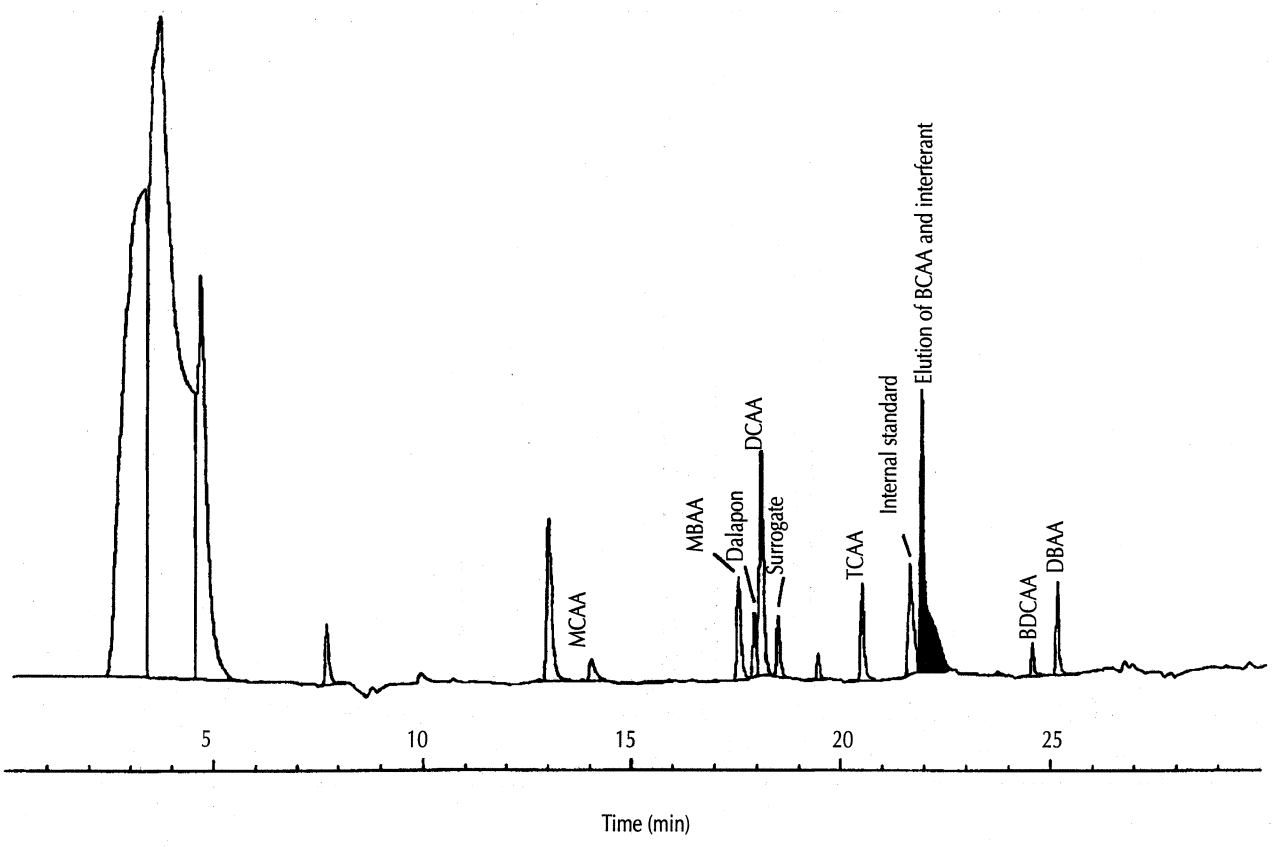


**Figure 3.** Acidic methanol derviatization of HAAs on the DB-1701 column.

yielded a peak that eluted as a back shoulder to the ester of BCAA (Figure 3). An extract exhibiting this interfering peak was analyzed using a Varian Saturn III ion trap mass spectrometer. The spectra obtained was tentatively identified as dimethyl sulfide through a computerized spectral library search. Quantitative analysis could have been performed by manual integration including only the peak area of the target ester; however, this approach was considered unacceptable for a primary column analysis. Modifications to the temperature program of the instrumental analysis in an attempt to separate the ester of BCAA and dimethyl sulfide were unsuccessful.

**Table III. Chromatographic Conditions for HAA Analysis**

| Column stationary phase | Primary analysis: DB-5.625<br>Confirmation analysis: DB-1701 |
|---|---|
| Column length | 30 m |
| Column inner diameter | 0.25 mm |
| Column film thickness | 0.25 µm |
| Injector temperature | 200°C |
| Detector temperature | 260°C |
| Linear velocity | 24 cm/s |
| Injection type | Splitless injection with 30-s delay |
| Temperature program | 35°C for 10 min, increase at 5°C/min,<br>75°C for 15 min, increase at 5°C/min,<br>100°C for 5 min, increase at 5°C/min,<br>135°C for 2 min. |

Because the most likely source of the dimethyl sulfide was the use of sulfuric acid in the derivatization step, the use of hydrochloric acid in the preparation of the acidic methanol rather than sulfuric acid was considered. An article by Shorney and Randtke (6) studied the stability of the haloacetic acids in the presence of HCl–methanol as compared with $H_2SO_4$–methanol. The results of their tests indicated that the HAAs were more susceptible to speciation shifts in the presence of HCl rather than $H_2SO_4$. Changes in analyte concentrations of 14–38% when using HCl were documented as compared with changes of less than 10% when using $H_2SO_4$.

For this reason, all further attention to this problem was concentrated on chromatographic separation of the dimethyl sulfide from analytes of interest rather than eliminating its source. Complete resolution between all the analytes of interest and known potentially interfering compounds was achieved using a 30-m × 0.25-mm-i.d. DB-5.625 column. However, Dalapon was observed to coelute with the original surrogate, 2-bromopropionic acid.

Attempts to separate the ester of Dalapon from the ester of the surrogate by varying the temperature program were unsuccessful. Two different surrogate compounds were considered, 2-chloropropionic acid and 3-chloropropionic acid, but their neat materials were found to contain trace amounts of Dalapon. Using the conditions detailed in Table III, the surrogate used by Shorney and Randtke (6), 2,3-dibromopropionic acid, did not interfere with any of the HAA analytes (Figure 2). Although not suitable for automated quantitative analyses (BCAA must be

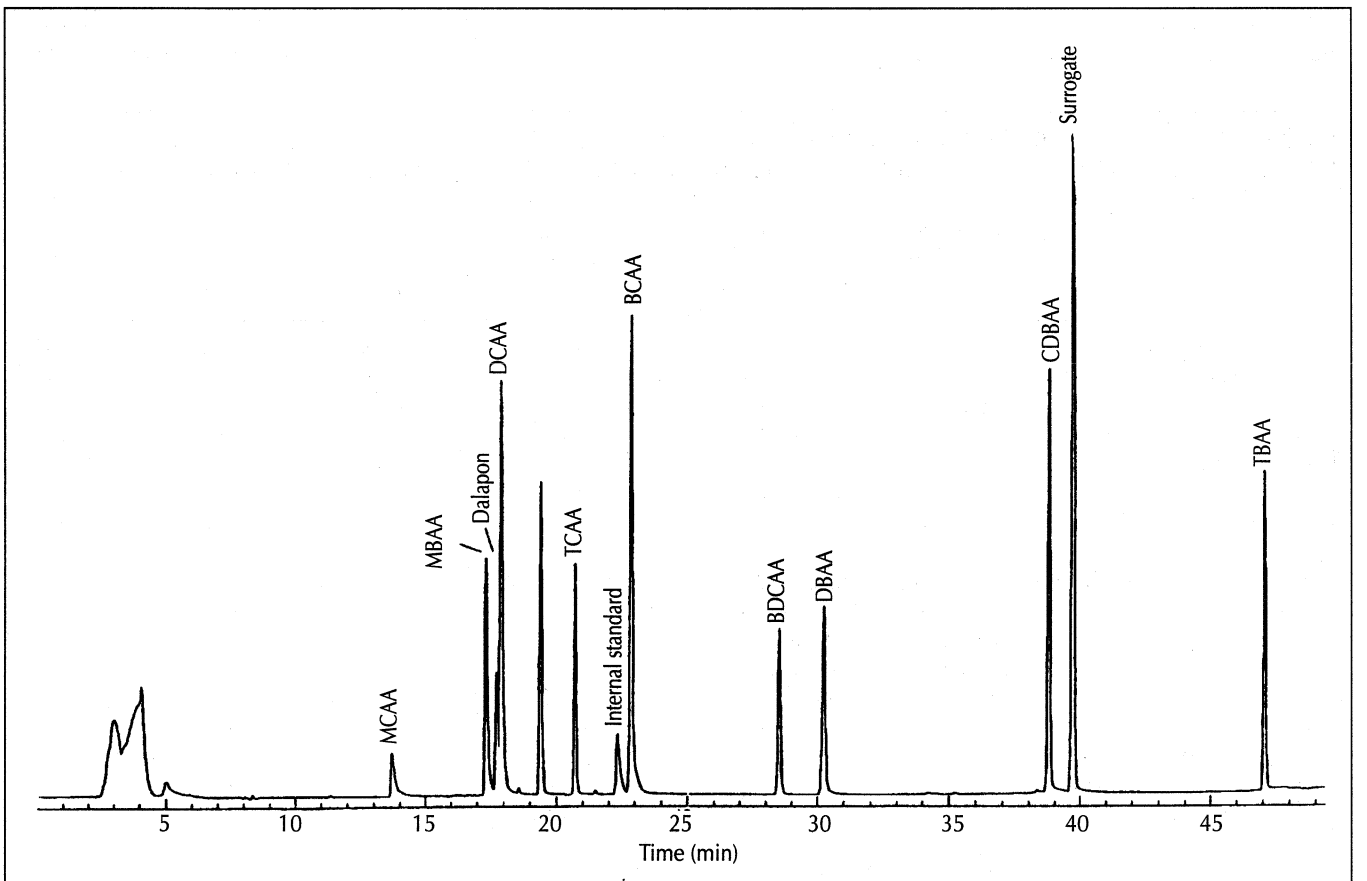


**Figure 4.** Elution of method analytes on the confirmation column (DB-1701).

manually integrated), the DB-1701 column was still recommended for use as the confirmation column for this analysis (Figure 4). Because the temperature programming was the same for the primary and confirmation analyses, the two could be performed simultaneously.

Once the final chromatographic column and program were established, other DBPs that would also be extracted by the MTBE were examined, particularly the trihalomethanes. This was done to ensure that these compounds did not interfere in the chromatographic analysis of the HAAs. The retention time data in Table IV show that the trihalomethanes did not interfere.

**Table IV. Retention Times of Trihalomethanes and HAAs on the DB-5.625 Column**

| HAA analysis | Retention time (min) | Trihalomethane analysis |
|---|---|---|
| | 5.56 | Chloroform |
| | 9.51 | Bromodichloromethane |
| Monochloroacetic acid | 12.20 | |
| | 14.45 | Chlorodibromomethane |
| Monobromoacetic acid | 15.75 | |
| Dichloroacetic acid | 16.37 | |
| Dalapon | 17.60 | |
| | 19.58 | Bromoform |
| Trichloroacetic acid | 21.13 | |
| Bromochloroacetic acid | 21.60 | |
| 1,2,3-Trichloropropane | 22.17 | |
| Dibromoacetic acid | 29.78 | |
| Bromodichloroacetic acid | 30.58 | |
| Chlorodibromoacetic acid | 39.72 | |
| 2,3-Dibromopropionic acid | 39.92 | |
| Tribromoacetic acid | 47.28 | |

## Associated studies

Several studies were conducted involving other factors that influence HAA analysis. Background on each of the experimental subjects as well as the results obtained and their effects are discussed below.

### *Removal of monochloramine*

Ammonium chloride was added to field samples as a dechlorinating agent and preserved the samples by converting the highly reactive free chlorine to the less reactive monochloramine. Subsequently, the free chlorine was unable to alter HAA speciation or to react with existing organic precursor material to form additional DBPs.

This study concerned the removal of the monochloramine prior to extraction of the HAAs. The extraction procedure required the pH of the aqueous sample to be lowered to less than 0.5. This acidic environment presented the potential for the monochloramine to undergo hydrolysis, thus releasing free chlorine. This essentially reversed the work of the dechlorinating agent, ammonium chloride. The experiment involved the use of sodium sulfite to eliminate any interferences arising from the presence of monochloramine

**Table V. Results of Seven Replicates of Chlorinated Surface Water with 100 mg/L of Ammonium Chloride, 2 Drops of 100 g/L Sodium Sulfite Added Just Prior to Extraction and Fortified with a Mid-Level Standard of HAAs and Dalapon**

| Analyte | Background concentration (ug/L) | True value (ug/L) | Average concentration (ug/L) | SD (ug/L) | Recovery (%) | RSD (%) |
|---|---|---|---|---|---|---|
| Monochloroacetic acid | 4.75 | 3.0 | 7.68 | 0.500 | 97.7 | 6.5 |
| Monobromoacetic acid | 0.535 | 2.0 | 2.64 | 0.372 | 105 | 14 |
| Dichloroacetic acid | 61.5 | 3.0 | 65.5 | 4.24 | * | 6.5 |
| Dalapon | 2.97 | 2.0 | 5.62 | 0.702 | 132 | 12 |
| Trichloroacetic acid | 35.1 | 1.0 | 38.9 | 5.07 | * | 13 |
| Bromochloroacetic acid | 11.4 | 2.0 | 16.2 | 1.50 | * | 9.3 |
| Dibromoacetic acid | 1.25 | 1.0 | 2.55 | 0.320 | 130 | 12 |

**Results of Seven Replicates for the Trihalogenated Acetic Acids (Except TCAA)**

| | Background concentration (µg/L) | Spike concentration (µg/L) | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|---|---|
| Bromodichloroacetic acid | 1.00 | 2.0 | 4.33 | 8.34 | 10.8 | 10.6 | 2.94 | 7.72 | † |
| Chlorodibromoacetic acid | † | 5.0 | 3.93 | 9.59 | 11.8 | 12.2 | .997 | 8.19 | † |
| Tribromoacetic acid | † | 10 | 4.56 | 13.3 | 17.1 | 13.3 | † | 10.9 | † |

* Recoveries for DCAA, TCAA, and BCAA were not computed because the extremely high background levels caused the spike level to be insignificant.
† Below the detection limit.

in the samples. Two sets of seven replicates of chlorinated surface water containing the HAA compounds were analyzed. Only ammonium chloride was added to the first set of replicate samples, whereas the second set contained ammonium chloride as well as two drops of a 100-g/L sodium sulfite solution that was added to each replicate just prior to extraction. The recoveries for the three additional trihalogenated HAAs, bromodichloroacetic acid (BDCAA), chlorodibromoacetic acid (CDBAA), and TBAA, were extremely variable; their concentrations ranged from less than the detection limit to several times the expected concentrations in the samples to which sodium sulfite was added just prior to extraction (Table V). Due to the unexplained variability of results obtained when sodium sulfite was added and the fact that no problems were observed associated with the presence of chlorine for the minimal amount of time between acidification of the samples and extraction, subsequent studies were not pursued.

**Table VI. Holding Time Study for Aqueous Samples**

| | Results of Seven Replicates of Fortified Reagent Water | | | | |
|---|---|---|---|---|---|
| Analyte | True value (µg/L) | Average concentration (µg/L) | SD (µg/L) | Recovery (%) | RSD (%) |
| **Day 0** | | | | | |
| Monochloroacetic acid | 3.0 | 2.99 | 0.117 | 99.7 | 3.9 |
| Monobromoacetic acid | 2.0 | 2.09 | 0.063 | 104 | 3.0 |
| Dichloroacetic acid | 3.0 | 3.14 | 0.104 | 105 | 3.3 |
| Dalapon | 2.0 | 1.91 | 0.200 | 95.5 | 10.7 |
| Trichloroacetic acid | 1.0 | 1.01 | 0.031 | 101 | 3.1 |
| Bromochloroacetic acid | 2.0 | 2.10 | 0.057 | 105 | 2.7 |
| Dibromoacetic acid | 1.0 | 1.05 | 0.022 | 105 | 2.1 |
| Bromodichloroacetic acid | 2.0 | 1.99 | 0.118 | 99.5 | 5.9 |
| Chlorodibromoacetic acid | 5.0 | 5.00 | 0.416 | 100 | 8.3 |
| Tribromoacetic acid | 10 | 10.3 | 0.926 | 103 | 9.0 |
| **Day 7** | | | | | |
| Monochloroacetic acid | 3.0 | 3.00 | 0.201 | 100 | 6.7 |
| Monobromoacetic acid | 2.0 | 1.89 | 0.038 | 94.5 | 2.0 |
| Dichloroacetic acid | 3.0 | 2.64 | 0.083 | 88.0 | 3.1 |
| Dalapon | 2.0 | 1.80 | 0.104 | 90.0 | 5.8 |
| Trichloroacetic acid | 1.0 | 0.958 | 0.057 | 95.8 | 5.9 |
| Bromochloroacetic acid | 2.0 | 1.78 | 0.065 | 89.0 | 3.7 |
| Dibromoacetic acid | 1.0 | 0.873 | 0.037 | 87.3 | 4.2 |
| Bromodichloroacetic acid | 2.0 | 2.20 | 0.176 | 110 | 8.0 |
| Chlorodibromoacetic acid | 5.0 | 4.96 | 0.273 | 99.2 | 5.5 |
| Tribromoacetic acid | 10 | 9.23 | 0.890 | 92.3 | 9.6 |
| **Day 14** | | | | | |
| Monochloroacetic acid | 3.0 | 2.76 | 0.153 | 92.0 | 5.5 |
| Monobromoacetic acid | 2.0 | 1.86 | 0.098 | 93.0 | 5.3 |
| Dichloroacetic acid | 3.0 | 2.75 | 0.128 | 91.7 | 4.7 |
| Dalapon | 2.0 | 1.91 | 0.117 | 95.5 | 6.1 |
| Trichloroacetic acid | 1.0 | 0.954 | 0.050 | 95.4 | 5.2 |
| Bromochloroacetic acid | 2.0 | 1.88 | 0.122 | 94.0 | 6.5 |
| Dibromoacetic acid | 1.0 | 0.915 | 0.053 | 91.5 | 5.8 |
| Bromodichloroacetic acid | 2.0 | 2.09 | 0.210 | 104 | 10 |
| Chlorodibromoacetic acid | 5.0 | 5.29 | 0.291 | 106 | 5.5 |
| Tribromoacetic acid | 10 | 8.64 | 0.780 | 86.4 | 9.0 |

*Laboratory performance check standard*

This study involved the establishment of a laboratory performance check standard. This is a quality control measure designed to ensure proper performance of the GC by evaluation of three instrument parameters: detector sensitivity, peak symmetry, and peak resolution. It also serves as a check on the continuity of the instrument's performance. The laboratory performance check standard allows the analyst to ascertain whether sensitivity has changed drastically since the analysis of the method detection limit study (3). Sensitivity is measured by calculating the ratio of the peak signal of the MCAA ester (measured as the height of the peak) to the baseline noise (measured as maximum baseline variation in units of height over a width equal to the width of the base of the peak). This ratio is known as the signal-to-noise ratio and must be greater than 3 to be acceptable. The instrument parameter of peak symmetry is a measure of the chromatographic performance. It is measured by calculating the peak Gaussian factor (PGF) of the BCAA ester using the following equation:

$$\text{PGF} = \frac{1.83 \times W_{1/2}}{W_{1/10}} \qquad \text{Eq 1}$$

where $W_{1/2}$ is the peak width at half the height, and $W_{1/10}$ is the peak width at one-tenth the height. For the chromatographic performance to be considered acceptable, the PGF must fall between 0.80 and 1.15. The final instrument parameter, peak resolution, is a measure of the column performance. It is measured by calculating the resolution ($R$) between the esters of CDBAA and the surrogate, 2,3-dibromopropionic acid, using the following equation:

$$R = \frac{t}{W_{\text{ave}}} \qquad \text{Eq 2}$$

where $t$ is the difference in elution times between the two peaks, and $W_{\text{ave}}$ is the average peak width of the two peaks as measured at the baseline. Resolution gives a measure of the degree of separation of two peaks under specific chromatographic conditions and must be greater than 0.50 to be considered acceptable. Inability to demonstrate acceptable instrument performance as measured by these three parameters indicates the need for re-evaluation of the instrument system. This laboratory performance check standard was instituted to guarantee that instruments are performing

optimally and therefore ensure the highest degree of accuracy in quantitation.

*Holding times*

The final study conducted concerned holding time analyses for both the aqueous samples and for the MTBE extracts. For the holding time study of the aqueous samples, 21 replicates of fortified reagent water were prepared. A set of seven replicates was extracted and analyzed on day 0, and the remaining 14 samples were stored at 4°C until analyses on days 7 and 14. Percent recoveries and relative standard deviations (RSDs) calculated from these analyses are reported in Table VI. All results were between 87 and 110%, and all of the target analytes were considered stable in an aqueous matrix stored at 4°C for up to 14 days.

For the holding time analysis of the MTBE extracts, a set of seven replicates of fortified reagent water was extracted and analyzed on day 0. The MTBE extracts were then stored at 4°C and were again analyzed on days 7 and 14 (Table VII). For the day 7 and day 14 analyses, the analyte recoveries for the mono- and dihalogenated HAAs and Dalapon were greater then 89%, which demonstrated the stability of these compounds for up to 14 days when stored in MTBE at 4°C.

For the day 7 analyses, a 96% recovery of the ester of BDCAA was obtained, whereas the esters of CDBAA and TBAA were recovered at approximately 80%, as compared with the day 0 analysis. Recoveries continued to drop for the day 14 analysis; BDCAA was recovered at approximately 80%, CDBAA was recovered at approximately 60%, and TBAA was recovered at approximately 60%. Because of this declining trend in recoveries, stability of the trihalogenated analytes was not satisfactorily demonstrated when stored at 4°C for more than 7 days.

**Table VII. Holding Time Study for MTBE Extracts**

| | Results of Seven Replicates of MTBE Extracts | | | | |
|---|---|---|---|---|---|
| Analyte | True value (µg/L) | Average concentration (µg/L) | SD (µg/L) | Recovery (%) | RSD (%) |
| **Day 0** | | | | | |
| Monochloroacetic acid | 3.0 | 2.99 | 0.117 | 99.7 | 3.9 |
| Monobromoacetic acid | 2.0 | 2.09 | 0.063 | 104 | 3.0 |
| Dichloroacetic acid | 3.0 | 3.14 | 0.104 | 105 | 3.3 |
| Dalapon | 2.0 | 1.91 | 0.200 | 95.5 | 10.7 |
| Trichloroacetic acid | 1.0 | 1.01 | 0.031 | 101 | 3.1 |
| Bromochloroacetic acid | 2.0 | 2.10 | 0.057 | 105 | 2.7 |
| Dibromoacetic acid | 1.0 | 1.05 | 0.022 | 105 | 2.1 |
| Bromodichloroacetic acid | 2.0 | 1.99 | 0.118 | 99.5 | 5.9 |
| Chlorodibromoacetic acid | 5.0 | 5.00 | 0.416 | 100 | 8.3 |
| Tribromoacetic acid | 10 | 10.3 | 0.926 | 103 | 9.0 |
| **Day 7** | | | | | |
| Monochloroacetic acid | 3.0 | 2.92 | 0.105 | 97.3 | 3.6 |
| Monobromoacetic acid | 2.0 | 2.14 | 0.126 | 107 | 5.9 |
| Dichloroacetic acid | 3.0 | 3.26 | 0.166 | 109 | 5.1 |
| Dalapon | 2.0 | 1.89 | 0.145 | 94.5 | 7.7 |
| Trichloroacetic acid | 1.0 | 1.07 | 0.068 | 107 | 6.4 |
| Bromochloroacetic acid | 2.0 | 2.25 | 0.248 | 112 | 11 |
| Dibromoacetic acid | 1.0 | 1.07 | 0.045 | 107 | 4.2 |
| Bromodichloroacetic acid | 2.0 | 1.93 | 0.125 | 96.5 | 6.5 |
| Chlorodibromoacetic acid | 5.0 | 4.04 | 0.486 | 81 | 12 |
| Tribromoacetic acid | 10 | 8.53 | 1.20 | 85.3 | 14 |
| **Day 14** | | | | | |
| Monochloroacetic acid | 3.0 | 2.85 | 0.219 | 95.0 | 7.7 |
| Monobromoacetic acid | 2.0 | 2.05 | 0.075 | 102 | 3.7 |
| Dichloroacetic acid | 3.0 | 3.11 | 0.118 | 104 | 3.8 |
| Dalapon | 2.0 | 1.78 | 0.132 | 89.0 | 7.4 |
| Trichloroacetic acid | 1.0 | 0.997 | 0.034 | 99.7 | 3.4 |
| Bromochloroacetic acid | 2.0 | 2.09 | 0.107 | 104 | 5.1 |
| Dibromoacetic acid | 1.0 | 1.04 | 0.038 | 104 | 3.7 |
| Bromodichloroacetic acid | 2.0 | 1.63 | 0.201 | 81.5 | 12 |
| Chlorodibromoacetic acid | 5.0 | 3.18 | 0.576 | 63.6 | 18 |
| Tribromoacetic acid | 10 | 5.72 | 0.833 | 57.2 | 15 |

*Standard preparation*

Previous methods have allowed the use of methanol for the preparation of calibration and surrogate standards. Throughout the course of this research, it was discovered that TBAA decarboxylates when stored in this solvent. Furthermore, Xie et al. (7) showed that the HAAs are subject to spontaneous methylation over time when stored in methanol. As a result, MTBE is required for the preparation of all standards, including fortification standards. Because MTBE is not as miscible with water as methanol, it may seem unsuitable to use it as the solvent to prepare standards. However, method 552.2 describes the preparation of fortification standards of high concentrations, thereby reducing the volume of MTBE that is injected into the water to a minimum.

## Conclusion

The effective features of two previously published methodologies for HAA analysis, standard method 6251B and EPA method 552.1, were incorporated into the new method, EPA method 552.2. In addition, several advantageous modifications, including the expansion of the analyte list to include three trihalogenated acetic acids, were accomplished. It is anticipated that the analysts using this method will find it to be an easily understood means for obtaining accurate quantitation for HAA compounds.

## References


1. Standard Methods for the Examination of Water and Wastewater, Method 6251B, 19th edition, American Public Health Association, Washington, DC, 1995.
2. U.S. EPA. Methods for the determination of organic compounds in drinking water—Supplement II. Determination of haloacetic acids and dalapon in drinking water by ion-exchange liquid–solid extraction and gas chromatography with electron capture detection. (Method 552.1) Environmental Monitoring Systems Laboratory, Cincinnati, OH, 1992.
3. U.S. EPA. Methods for the determination of organic compounds in drinking water—Supplement III. Determination of haloacetic acids and dalapon in drinking water by liquid–liquid extraction, derivatization and gas chromatography with electron capture detection (Method 552.2). EPA/600/R-95/131.
4. U.S. EPA. Methods for the determination of organic compounds in drinking water—Supplement III. Determination of chlorinated acids in drinking water by liquid–liquid extraction, derivatization and gas chromatography with electron capture detection (Method 515.2). Environmental Monitoring Systems Laboratory, Cincinnati, OH, 1995.
5. J.B.R. Peters, C. Erkelens, E.W.B. De Leer, and L. De Galan. The analysis of halogenated acetic acids in dutch drinking water. *Wat. Res.* **25:** 473–77 (1991).
6. H.L. Shorney and S.J. Randtke. Improved methods for haloacetic acid analysis. Proceedings, Water Quality Technology Conference, 453–75 (1994).
7. Y. Xie, D.A. Reckhow, and R.V. Rajan. Spontaneous methylation of haloacetic acids in methanolic stock solutions. *Environ. Sci. Technol.* **27:** 1232–34 (1993).


Manuscript accepted January 2, 1997.