THERMOFISHER METHOD 557.1: DETERMINATION OF HALOACETIC ACIDS IN DRINKING WATER USING TWO-DIMENSIONAL ION CHROMATOGRAPHY WITH SUPPRESSED CONDUCTIVITY DETECTION

Version 1.0
January 2017

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THERMOFISHER METHOD 557.1

DETERMINATION OF HALOACETIC ACIDS IN DRINKING WATER USING TWO-DIMENSIONAL ION CHROMATOGRAPHY WITH SUPPRESSED CONDUCTIVITY DETECTION

1. SCOPE AND APPLICATION

1.1 This method is a direct-inject, multiple-cut, two-dimensional ion chromatography method with suppressed conductivity detection for the determination of haloacetic acids (HAA's) in finished drinking water. Real time chromatographic determination of trace components and elimination of matrix interference in drinking water (matrix elimination) is a key feature of this method. Large-volume injection in the first dimension and analysis in the capillary format in the second dimension is required to obtain the required sensitivity, precision and accuracy for this method. Acceptable method performance has been demonstrated for matrix ion concentrations of 250 mg/L chloride, 250 mg/L sulfate, 150 mg/L bicarbonate and 20 mg/L nitrate. Precision and accuracy data have been generated for the detection of all 9 haloacetic acids in reagent water, synthetic sample matrix, and finished drinking water from both ground water and surface water sources. The single laboratory Lowest Concentration Minimum Reporting Level (LCMRL) has also been determined in reagent water. This method is applicable for the measurement of the following analytes:

Analyte	Chemical Abstracts Services Registry
Bromochloroacetic acid (BCAA)	5589-96-8
Bromodichloroacetic acid (BDCAA)	71133-14-7
Chlorodibromoacetic acid (CDBAA)	5278-95-5
Dibromoacetic acid (DBAA)	631-64-1
Dichloroacetic acid (DCAA)	79-43-6
Monobromoacetic acid (MBAA)	79-08-3
Monochloroacetic acid (MCAA)	79-11-8
Tribromoacetic acid (TBAA)	75-96-7
Trichloroacetic acid (TCAA)	76-03-9

NOTE: Although the method was developed to analyze all nine HAA's to be compatible with EPA Method 557.0 [1], the cut windows could be altered and the analysis run time could be shortened in order to provide faster sample throughput when using the method for compliance monitoring of the five regulated HAA's. See Table 1 and 1A for instrument conditions.

1.2 The chromatographic conditions described in this method were developed using a commercially available Thermo Scientific Dionex ICS-5000 Dual System (see Table 1 and 1A). Capillary format IC (columns, pumps, suppressor and detector must be used in the second dimension in order to obtain the required sensitivity for this method.

1.3 The single laboratory Lowest Concentration Minimum Reporting Level (LCMRL) is the lowest true concentration for which the future recovery is predicted to fall between 50 and 150 percent recovery with 99% confidence. The single laboratory LCMRL' s for the analytes in this method ranged from 0.055 to 0.41 microgram per liter (μg/L), and are listed in Table 2. The single laboratory LCMRL's for the HAA 9 were used for the HAA 5's. The procedure used to determine the LCMRL is described elsewhere.[2]

1.4 Laboratories using this method will not be required to determine the LCMRL, but will need to demonstrate that their laboratory MRL for this method meets the requirements described in Section 9.2.4.

1.5 This method is intended for use by analysts skilled in the operation of two-dimensional ion chromatographic instrumentation, and the interpretation of the associated data.

1.6 METHOD FLEXIBILITY – Changes may not be made to sample collection and preservation (Sect. 8) or to the quality control requirements (Sect. 9). Since this method underwent 5 years of development and is the first multi-cut two-dimensional IC method to be introduced, in order to minimize any changes to the method, all instruments will be installed in the same manner and attempts to improve method flexibility are STRONGLY DISCOURAGED. The optimal conditions have been incorporated into this method.

2. SUMMARY OF METHOD

2.1 Residual chlorine present in drinking water samples is reacted with ammonium chloride to form chloramines, effectively preventing chlorine-mediated formation of method analytes during storage. In addition, the combined chlorine residual prevents microbial degradation in the sample. An aliquot of the sample is injected, without cleanup or concentration, onto an ion exchange column specifically designed to separate method analytes from the following common anions (matrix components) in drinking water: chloride, carbonate, sulfate, and nitrate. The matrix components in the column eluate are diverted to waste; and the analytes of interest are analyzed using suppressed conductivity detection.

NOTE: This is a complex analysis and requires a skilled IC analyst to operate the two-dimensional IC system. The following procedure is to be followed, in order to obtain acceptable data. Several precautions are listed below and MUST be followed to ensure the quality of all data.

PRECAUTION 1: This method involves a capillary system (0.4 mm) in the second dimension. Due to the high mass sensitivity, the method is sensitive to the presence of contaminants and therefore proficient analytical techniques MUST be employed throughout the procedure and care must be exercised to minimize any potential contamination risks. The auto-sampler vials MUST be rinsed well with de-ionized water and dried and/or rinsed with the sample prior to use. All storage bottles or other vials MUST be rinsed well with de-ionized water and dried and/or rinsed with the sample prior to use. Auto-sampler vials and caps are single use only.

PRECAUTION 2: Since this method includes a base and an acid wash cycle in each analysis and the auto-sampler is used for these wash solutions, a first base vial and second acid vial MUST be included for each sample analyzed. See sample tray configuration below.

Sample Tray Layout

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
A	B	A	C	B	A	C	B	A
B	C	B	A	C	B	A	C	B
C	A	C	B	A	C	B	A	C
D	B	A	C	B	A	C	B	A
E	C	B	A	C	B	A	C	

B = Base Wash
A = Acid Wash
C = Sample (either standard or sample)

3. DEFINITIONS

3.1 ANALYSIS BATCH – A sequence of field samples, which are analyzed within a 48-hour period and include no more than 20 field samples. An Analysis Batch must also include all required QC samples, which do not contribute to the maximum field sample total of 20 (See Table 8). For this method, the required QC samples include:

Laboratory Reagent Blank (LRB)
Continuing Calibration Check (CCC) Standards (low, mid and high levels)
Laboratory Fortified Blank (LFB)
Laboratory Fortified Sample Matrix (LFSM)
Laboratory Fortified Synthetic Sample Matrix CCC Standard (LFSSM CCC)
Either a Field Duplicate (FD), a Laboratory Duplicate (LD) or a duplicate of the LFM

3.2 ANALYTE FORTIFICATION SOLUTIONS (AFS) – The Analyte Fortification Solutions are prepared by dilution of the Analyte Secondary Dilution Solutions (SDS) and are used to fortify the LFSMs and the LFSMDs with the HAA's. It is recommended that multiple concentrations be prepared so that the fortification levels can be rotated or adjusted to the concentration of target analyte in the native samples.

3.3 CALIBRATION STANDARD (CAL) – A solution of the target analytes prepared from the Primary Dilution Solution or Stock Standard Solution. The CAL solutions are used to calibrate the instrument response with respect to the analytes' concentration.

3.4 CONTINUING CALIBRATION CHECK STANDARD (CCC) – A calibration check standard containing the method analytes which is analyzed periodically throughout an Analysis Batch, to verify the accuracy of the existing calibration for those analytes.

3.5 LABORATORY DUPLICATES (LD) – Two sample aliquots (LD_1 and LD_2), from a single field sample bottle, and analyzed separately with identical procedures. Analyses of LD_1 and LD_2 indicate precision associated specifically with laboratory procedures by removing variation contributed from sample collection and storage procedures.

3.6 LABORATORY FORTIFIED BLANK (LFB) – An aliquot of reagent water or other blank matrix to which a known quantity of the method analytes is added. The LFB is analyzed exactly like a sample. Its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.7 LABORATORY FORTIFIED SAMPLE MATRIX (LFSM) – An aliquot of a field sample to which a known quantity of the method analytes is added. The LFSM is processed and analyzed exactly like a field sample, and its purpose is to determine whether the field sample matrix contributes bias to the analytical results. The background concentration of the analytes in the field sample matrix must be determined in a separate aliquot and the measured value in the LFSM corrected for the native concentration.

3.8 LABORATORY FORTIFIED SAMPLE MATRIX DUPLICATE (LFSMD) – A second aliquot of the field sample used to prepare the LFSM, which is fortified and analyzed identically to the LFSM. The LFSMD is used instead of the Laboratory Duplicate to assess method precision and accuracy when the occurrence of the target analytes is infrequent.

3.9 LABORATORY FORTIFIED SYNTHETIC SAMPLE MATRIX (LFSSM) – An aliquot of the LSSM (Sect. 7.3) which is fortified with the HAA's. The LFSSM is used to set the start time for the divert and cut windows in the first dimension during the initial demonstration of capability (IDC) (Sect. 9.2). The LFSSM is also used to determine the precision and accuracy of the method during the IDC (Sects. 9.2.2 and 9.2.3). The LFSSM samples are treated like the CCCs.

3.10 LABORATORY FORTIFIED SYNTHETIC SAMPLE MATRIX CONTINUING CALIBRATION CHECK STANDARD (LFSSM CCC) – An aliquot of the LSSM (Sect. 7.3) which is fortified with the HAA's at a concentration equal to one of the CCCs. In this method, LFSSM CCCs should be analyzed periodically throughout each Analysis Batch (Sect. 11.3.5) to confirm that the first dimension heart cutting procedure has acceptable recovery in high inorganic matrices.

3.11 LABORATORY REAGENT BLANK (LRB) – An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to storage containers. The LRB is used to determine if the method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.12 LABORATORY SYNTHETIC SAMPLE MATRIX (LSSM) – An aliquot of reagent water that is fortified with 250 mg/L of the sodium salts of chloride and sulfate, 150 mg/L bicarbonate and 20 mg/ and nitrate.

3.13 LOWEST CONCENTRATION MINIMUM REPORTING LEVEL (LCMRL) – The single-laboratory LCMRL is the lowest true concentration for which the future recovery is predicted to fall between 50 and 150 percent recovery with 99% confidence. [3]

3.14 MATERIAL SAFETY DATA SHEET (MSDS) – Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

3.15 MINIMUM REPORTING LEVEL (MRL) – The minimum concentration that can be reported by a laboratory as a quantified value for the target analytes in a sample following analysis. This defined concentration must meet the criteria defined in Section 9.2.4 and must be no lower than the concentration of the lowest calibration standard for the target analytes.

3.16 PRIMARY DILUTION STANDARD SOLUTION (PDS) – A solution containing the method analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other analyte-containing solutions.

3.17 QUALITY CONTROL SAMPLE (QCS) – A solution containing the method analytes at a known concentration that is obtained from a source external to the laboratory and different from the source of calibration standards. The QCS is used to verify the accuracy of the calibration standards and the integrity of the calibration curve.

3.18 REAGENT WATER (RW) – Purified water which does not contain any measurable quantity of the target analytes or interfering compounds at or above 1/3 the MRL.

3.19 SECONDARY DILUTION STANDARD SOLUTION (SDS) – A solution containing the method analytes prepared in the laboratory from the PDS and diluted as needed to prepare calibration solutions and other analyte solutions.

3.20 STOCK STANDARD SOLUTION (SSS) – A concentrated solution containing the method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source, so that the concentration and purity of analytes are traceable to certificates of analysis.

3.21 CUT WINDOW – The period of time during which the column eluate is diverted to waste for the purpose of diverting matrix components when the analytes of interest are not present.

3.22 COLLECTION WINDOW – The period of time during which the column eluate is directed to the concentrator column for the purpose of focusing or concentrating the method analytes onto the concentrator column.

4. INTERFERENCES

4.1 **This method involves a capillary system (0.4 mm) in the second dimension. Due to the high mass sensitivity, the method is sensitive to contamination and therefore proficient analytical techniques MUST be employed throughout the procedure and care must be exercised to minimize any potential contamination risks.** The extended time required for method development of this multiple-cut, capillary format second dimension method provided insight into the potential interferences for this method and resolution of method interferences.

4.2 REAGENTS AND EQUIPMENT – Method interferences may be caused by contaminants in solvents and reagents (including reagent water). Equipment and containers used for sample collection and storage also have the potential to introduce interferences. The potential for interferences from these sources must be investigated during the IDC (Sect. 9.2) by preparing and analyzing LRBs as described in Section 9.3.1. All laboratory reagents must be routinely

demonstrated to be free from interferences (less than 1/3 the MRL for the method analytes) under the conditions of the analysis. This procedure should be repeated each time a new brand and/or lot of materials are used to ensure that contamination does not hinder analyte identification and quantitation.

NOTE: The auto-sampler vials MUST be rinsed well with de-ionized water and dried and/or rinsed with the sample prior to use. All storage bottles or other vials MUST be rinsed well with de-ionized water and dried and/or rinsed with the sample prior to use.

4.3 MATRIX INTERFERENCES – Matrix interferences are caused by contaminants that are present in the sample. The extent of matrix interferences will vary considerably from source to source depending upon the nature of the water. Interferences can be divided into three different categories: (i) direct chromatographic co-elution, where an interferent response is observed at very nearly the same retention time (RT) as the target analyte making its quantitation difficult; (ii) concentration dependant co-elution, which is observed when the response of higher than typical concentrations of the neighboring peak overlaps into the retention window of the target analyte making its quantitation difficult; and (iii) ionic character displacement, where retention times may significantly shift due to the influence of high ionic strength matrices (high mineral content or total dissolved solids) overloading the exchange sites on the column and significantly shortening the target analyte's retention time affecting its identification and quantitation.

4.3.1 A direct chromatographic co-elution may be solved by changing column selectivity in one or both dimensions of the two dimensional IC method, adjusting eluent strength in one or both dimensions, modifying the eluent composition (if compatible with IC columns), changing the detection system, or selective removal of the interference with sample pretreatment. Sample dilution will have little to no effect on direct chromatographic co-elution. The analyst must verify that any change made to the chromatographic parameters does not induce any negative effects on method performance by repeating and passing all the QC criteria as described in Section 9.2.

4.3.2 Sample dilution may resolve some of the difficulties if the interference is the result of either concentration dependent co-elution or ionic character displacement, but it must be clarified that sample dilution will alter the MRL by a proportional factor equivalent to that of the dilution. Therefore, careful consideration of Data Quality Objectives (DQOs) should be given prior to performing such a dilution. The analysis of a Laboratory Fortified Sample Matrix (Sect. 9.3.5) provides evidence for the presence (or absence) of matrix effects.

4.4 EFFECT OF TEMPERATURE ON ANALYTE STABILITY – MCAA and MBAA at the two lowest concentrations in reagent water standards (0.5 and 5.0 µg/L) are subject to analyte loss when samples are stored at room temperature for extended periods. Consequently, all samples and QC standards prepared in RW, LSSM, and all CCC's MUST be stored at or below 6 °C and immediately returned to cold storage after use. In addition, MBAA, CDBAA, and TBAA degrade readily in aqueous eluent at high pH. Such conditions may exist in the mobile phase of ion exchange columns. The reaction is temperature dependent. For this reason, the separation is performed at sub-ambient temperature, specifically 15 °C, and the auto-sampler

is also maintained at or below 6 °C. At 15 °C, analyte degradation is minimized.

4.5 MANAGING CUT WINDOWS – Analyte retention times may slowly shift toward lower values as the column ages or becomes fouled. Because this method employs multiple cut windows, the analyst must monitor peak locations on a daily basis to ensure that each analyte peak elutes entirely within the preset collection windows. Guidance for verifying cut windows is provided in Section 10.2.2. To avoid loss of column capacity, follow the manufacturer's instructions for proper operating temperature and for storage conditions when the column is not in use.

4.6 PEAK BROADENING AND RETENTION TIME (RT) SHIFTS IN HIGH IONIC STRENGTH MATRICES – When first-dimension heart-cut windows are properly set, this method demonstrates adequate performance in water matrices that contain up to 250 mg/L chloride, 250 mg/L sulfate, 150 mg/L bicarbonate and 20 mg/L nitrate. Near these limits, the analyte peaks will widen, peak height will decrease, and retention times will decrease slightly. These effects are compound dependent, but affect all analytes to some degree. Such effects were minimal in the drinking water matrices evaluated, but were more pronounced in Laboratory Synthetic Sample Matrix (see Figure 2). Method performance has not been evaluated for matrix ion concentrations exceeding these limits. The analyst should monitor all first dimension chromatograms (Sect. 11.3.4) to confirm that sample matrix does not overload the primary column capacity and require dilution.

> NOTE: The concentrations of common anions in the LSSM are at the limits listed above. This method requires the analyst to verify method performance in LSSM during the IDC, and to verify cut windows on a daily basis in LFSSM CCCs (Sect. 10. 3.3) to ensure that these windows are properly set to compensate for the potential effects of high ionic strength matrices.

5. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. Each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining an awareness of OSHA regulations regarding safe handling of chemicals used in this method. A reference file of MSDSs should be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available. [4-6]

6. EQUIPMENT AND SUPPLIES

References to specific brands or catalog numbers are included for illustration only and do not imply endorsement of the product. This does not preclude the use of other vendors' supplies if all the required instrument parameters are met.

6.1 SAMPLE CONTAINERS – Amber glass bottles fitted with polytetrafluoroethylene (PTFE) lined screw caps with sufficient volume to allow preparation of all required sample and QC aliquots.

6.2 VIALS FOR SAMPLE PREPARATION – Amber glass vials with PTFE/silicone septa for use preparing field samples and QC samples. Sixty-milliliter (mL) volatile organic analysis (VOA) vials (Dionex P/N 048781 or equivalent) were used during method development.

6.3 VOLUMETRIC FLASKS – Class A, suggested sizes include 10, 50, 100, 250, 500 and 1000 mL for preparation of standards and eluents.

6.4 GRADUATED CYLINDERS – Suggested sizes include 25 and 1000 mL.

6.5 AUTOSAMPLER VIALS – Glass vials with PTFE/silicone septa (Dionex P/N 079812) (See Section 2.1).

6.6 VOLUMETRIC PIPETTES – Adjustable Class A, for preparing calibration standards, and for measuring aliquots of field samples and QC samples.

6.7 ANALYTICAL BALANCE – Capable of weighing to the nearest 0.0001 g.

6.8 TOP-LOADING BALANCE – Capable of weighing to the nearest 0.01 g. A top-loading balance and disposable pipettes may be used to measure aqueous sample volumes and to prepare aqueous calibration standards

6.9 DISPOSABLE PASTEUR PIPETTES – Plastic transfer pipet (Samco Scientific, P/N 262), used to transfer samples to autosampler vials and for sample preparation.

6.10 DUAL ION CHROMATOGRAPHY SYSTEM WITH SUPPRESSED CONDUCTIVITY DETECTION (IC) – This section describes the instrument configuration that was used to collect the data in Section 17. A Dionex Model ICS-5000+ Dual system, consisting of a Dual Pump (DP) module, Eluent Generator (EG) module, Detector/Chromatography (DC) module, and Autosampler (AS-AP), was used to collect the data presented in this method. The IC system should also have a temperature controlled column compartment and be capable of operating below room temperature (15ºC) and include dual IC pumps and all required accessories, including guard, analytical, and concentrator columns, detector/chromatography module, dual eluent generators, continuously-regenerated anion trap columns, compressed gases, auto-sampler, suppressors, carbonate removal devices (CRD), dual conductivity detectors, and a computer-based data acquisition and control system. Additionally, the system must be capable of performing automated, two-dimensional IC, including performing inline column concentration and matrix elimination steps. A schematic diagram of the instrumentation for this two dimensional IC method is shown in Figure 1. Table 1 provides full details of the instrumental conditions HAA 9 and Table 1A the instrumental conditions for HAA 5.

6.10.1 DUAL PUMP MODULE – A Hybrid Dual Pump Module with dual channel degas devices (Dionex DP-5, P/N 075935), was used to generate the data for this method. Equivalent modules may be used. The dual pump system used for method development was capable of supplying a flow rate of approximately 1.0 mL/min to the first dimension column and approximately 0.012 mL/min to the second dimension column.

6.10.2 ELUENT GENERATOR MODULE – A dual channel EG Module (Dionex EG, P/N 075776) with dual potassium hydroxide cartridges (EluGen® Cartridge, EGC III KOH, P/N 074532 and EGC-KOH Capillary Cartridge, P/N 072076) was used to prepare the potassium hydroxide eluent for both the first and second dimensions of this method. An equivalent eluent generator may be used and/or manually prepared eluents may also be used provided that adequate resolution, peak shape, capacity, accuracy, and precision (Sect. 9.2) are obtained. Care must be exercised with manually prepared hydroxide eluents to prevent formation of carbonate in the eluent from exposure to the atmosphere, which can dramatically alter the chromatography and affect sensitivity.

6.10.2.1 CONTINUOUSLY REGENERATED ANION TRAP COLUMNS – IC eluent purification columns (Dionex CR-ATC, P/N 060477 and Dionex CR-ATC Capillary, P/N 072078 or equivalent). Any in-line, resin-based electrolytic trapping column that provides adequate eluent purification on a continuous basis for ultra trace analysis and performance (Sect. 9.2) may be used. A CR-ATC device, or equivalent, was used for eluent purification for the first dimension eluent and a CR-ATC Capillary device was used for the second dimension eluent.

NOTE: For the configuration in Figure 1, the pump and eluent generator modules in combination must be capable of delivering different isocratic and changing eluent concentrations (gradient) to the columns in the first and second dimension. The same requirement applies for manually prepared eluents with a dual pumping system; the pump system must be capable of delivering two different, independent isocratic and changing concentrations (gradient) of eluents to the first and second dimension columns. In addition, the system should also be capable of providing a step isocratic eluent concentration change or a controlled gradient change to both dimensions independently. This allows the first and second dimension columns to be cycled to a higher eluent concentration in order to clean residual matrix components from the columns prior to introduction of the next sample. This is important to ensure maximum column life and to minimize potential carryover and/or interferences from one sample to the next.

6.10.3 DETECTOR/CHROMATOGRAPHY MODULE – A DC Module (Dionex DC, P/N 075943 or equivalent) equipped with dual injection valves and capable of maintaining both the analytical and capillary columns at 15 °C, and conductivity cell at 25 °C is recommended.

NOTE: For optimal performance of this system, the conductivity cell should be set at a higher temperature than the analytical columns. For example, if the columns are set at 15 °C, the cell should be set at 25 °C. To ensure the capillary column temperature can be maintained at 15 °C, the compartment temperature needs to set at least 2 degrees below the column temperature.

6.10.4 FIRST DIMENSION GUARD COLUMN – An IC column, 4 x 50-mm (Dionex IonPac®AG24A, P/N 076011 or equivalent). Any guard column that provides adequate protection for the analytical column and does not have an adverse effect on the peak shape may be used.

6.10.5 FIRST DIMENSION ANALYTICAL COLUMN – An IC column, 4 x 250 mm (Dionex IonPac®AS24A, P/N 076010 or equivalent). Any analytical column that provides adequate resolution, peak shape, capacity, accuracy, and precision (Sect. 9.2) may be used. The separation mechanism for the first dimension analytical column must differ from the second dimension column in selectivity. This ensures that false identification of target analytes can be minimized.

6.10.6 FIRST DIMENSIOIN ANION SUPPRESSOR DEVICE – An IC eluent suppression device, 4 mm (Dionex Anion Electrolytically Regenerated Suppressor, AERS 500, P/N 82540 or equivalent). An equivalent in-line suppression device that effectively suppresses the conductance of the eluent to water and converts the analyte to the hydronium form prior to conductivity detection, as well as provides adequate efficiency, resolution, peak shape, capacity, accuracy, precision, and a comparable MRL (Section 9.2) may be used. Adequate baseline stability should be attained as measured by a baseline noise of no more than 5 nS per minute over the background conductivity. The first dimension suppressor must be compatible with the first dimension guard and analytical column.

NOTE: The conductivity suppressor was set to perform electrolytic suppression at a current setting of 161 mA. It was important to operate the suppressor in the external water mode to reduce baseline noise and achieve optimal method performance.

6.10.7 FIRST DIMENSION CARBONATE REMOVAL DEVICE – An IC carbonate removal device, 4 mm (Dionex CRD 300, P/N 064637 or equivalent). Any in-line carbonate removal device that effectively removes the carbonate peak from the suppressed eluent stream prior to conductivity detection and provides adequate efficiency, resolution, peak shape, capacity, accuracy, and precision for the HAA's (Section 9.2) may be used. The first dimension CRD must be compatible with (e.g., 4 mm in this example) the first dimension guard and analytical column.

6.10.8 FIRST DIMENSION CONDUCTIVITY DETECTOR – A Conductivity detector and integrated cell (Dionex CD P/N 061716, or equivalent) capable of providing data as required in Section 9.2. A Standard Bore Temperature Stabilizer (0.010-inch ID, Dionex P/N 062561), was also used to equilibrate the temperature of the eluent to that of the first dimension guard and analytical column. Equivalent stabilizers may be used.

NOTE: The conductivity detector cell temperature should be controlled at a temperature above that of the analytical column. For method development, the conductivity detector was set at 25 ºC to minimize bubble formation and condensation between analytical column, suppressor and CRD and to stabilize the temperature of the detector cell itself.

6.10.9 CONCENTRATOR COLUMN – An IC trapping column, 0.75 x 80 mm (Dionex MAC-200, P/N 075461 or equivalent). Any concentrator column that provides effective retention/trapping and release of haloacetic acids while providing the resolution, peak shape, capacity, accuracy, and precision (Sect. 9.2) may be used. The concentrator column should not release sulfonated leachates that would affect the quantitation of haloacetic acids.

6.10.9.1 Alternate concentrator columns are allowed, but prior to their use, they must be evaluated to determine the first dimension cut window (Sect. 10.2.2). They must be determined to have sufficient capacity to quantitatively trap haloacetic acids in the LFSSM CCC (Sect. 10.3.3) and should have relatively low backpressure since the concentrator column is placed as a post-suppressor device.

6.10.10 SECOND DIMENSION GUARD COLUMN – An IC column, 0.4 x 50 mm (Dionex IonPac®AG26, P/N 076019 or equivalent). Any guard column that provides adequate protection for the analytical column and does not have an adverse effect on the peak shape may be used.

6.10.11 SECOND DIMENSION ANALYTICAL COLUMN – An IC column, 0.4 x 250 mm (Dionex IonPac® AS26, P/N 076018 or equivalent). Any analytical column that provides adequate resolution, peak shape, capacity, accuracy, and precision (Sect. 9.2) may be used. The separation mechanism for the second dimension analytical column must differ from the first dimension column.

6.10.12 SECOND DIMENSIOIN ANION SUPPRESSOR DEVICE – An IC eluent suppression device, capillary (Dionex Anion Capillary Electrolytic Suppressor, ACES, P/N 072052 or equivalent). An equivalent in-line suppression device that effectively suppresses the conductance of the eluent prior to conductivity detection, and that provides adequate efficiency, resolution, peak shape, capacity, accuracy, precision, and a comparable MRL (Section 9.2) may be used. Adequate baseline stability should be attained as measured by a baseline noise of no more than 5 nS per minute over the background conductivity. The second-dimension suppressor must be compatible with (e.g., 0.4 mm in this example) the second-dimension guard and analytical column.

NOTE: The conductivity suppressor was set to perform electrolytic suppression at a current setting of 25 mA. It was important to operate the suppressor in the external water mode to reduce baseline noise and achieve optimal method performance.

6.10.13 SECOND DIMENSION CARBONATE REMOVAL DEVICE – An IC carbonate removal device (Dionex CRD 200 Capillary, P/N 072054 or equivalent). Any in-line carbonate removal device that effectively removes the carbonate peak from the suppressed eluent stream prior to conductivity detection of the method analyte and provides adequate efficiency, resolution, peak shape, capacity, accuracy, and precision (Section 9.2) may be used. The second dimension CRD must be compatible with the second dimension guard and analytical column.

6.10.14 SECOND DIMENSION CONDUCTIVITY DETECTOR – A Conductivity detector and integrated cell (Dionex CD P/N 072041, or equivalent) capable of providing data as required in Section 9.2.

NOTE: The conductivity detector cell temperature should be controlled at a temperature above the analytical column. For method development, the conductivity was set at 25 ºC to minimize bubble formation and condensation between analytical column, suppressor and CRD and to stabilize the temperature of the detector cell itself.

6.10.15 AUTOSAMPLER MODULE – An AS-AP Auto-sampler Module with sequential injection, a sample prep option, and a large volume sample needle assembly (Dionex AS-AP P/N 074925) was used to generate data for this method. Any auto-sampler capable of automatically injecting up to 1.0 mL of sample may be used.

6.10.16 DATA SYSTEM – An interfaced data system such as Dionex, Chromeleon Version 7.2 (or equivalent) is required to acquire, store, and output conductivity data. The computer software should have the capability of processing stored conductivity data by recognizing and integrating a peak within a given retention time window. The software should be capable of constructing linear regressions or quadratic calibration curves, and calculating analyte concentrations using the calibrations.

7. REAGENTS AND STANDARDS

7.1 REAGENTS – Reagent grade or better chemicals should be used in all tests. Unless otherwise indicated, it is intended that all reagents will conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS), where such specifications are available. Other grades may be used, provided it is first determined that the reagent is of sufficiently high purity to permit its use if all the requirements of the IDC are met when using these reagents.

7.1.1 AMMONIUM CHLORIDE (NH_4Cl, CAS No. 12125-02-9) – Method preservative (see Table in Section 7.2).

7.1.2 REAGENT WATER (RW) – Purified water that does not contain any measurable quantity of the target analyte or interfering compounds at or above 1/3 the HAA's MRL. The purity of the water required for this method cannot be over emphasized. The reagent water used during method development was purified from tap water using a Millipore ELIX-3 followed by a Millipore Gradient A10 system. The water should contain no particles larger than 0.20 microns.

7.1.3 ELUENT SOLUTIONS – Several hydroxide eluent concentrations were used to collect the data in Section 17. A potassium hydroxide isocratic eluent concentration of 7 mM ramped to 14 mM, followed by a step change to 65 mM was used for the first dimension matrix elimination separation on the AS24A column, and isocratic 5.2 mM step changed to 155 mM, followed by a step change to 100 mM was used for the second dimension separation on the AS26 column. These eluents were automatically prepared using electrolytic eluent generation with the ICS-5000 EG Eluent Generator and EluGen potassium hydroxide cartridges (Sect 6.10.2).

7.1.4 SODIUM BICARBONATE – ($NaHCO_3$, CASRN 497-19-8) – Fluka Cat. No. 71627 or equivalent.

7.1.5 SODIUM CHLORIDE – (NaCl, CASRN 7647-14-5) – Fisher Scientific Cat. No. S-271 or equivalent.

7.1.6 SODIUM NITRATE – ($NaNO_3$, CASRN 7631-99-4) – Fisher Scientific Cat. No. S343-500) or equivalent.

7.1.7 SODIUM SULFATE – (Na_2SO_4, CASRN 7757-82-6) – Fluka Cat. No. 71959 or equivalent.

7.2 AMMONIUM CHLORIDE PRESERVATION SOLUTION - Ammonium chloride is added to all water samples at the time of collection to effectively prevent chlorine-mediated formation of method analytes during storage. In addition, the combined chlorine residual prevents microbial degradation in the sample. Consequently, all standards are prepared in the ammonium chloride preservation solution rather than RW. Prepare the ammonium chloride preservative solution by dissolving 100 mg of NH_4Cl in 1L of reagent water as indicated in the Table below. This preservation solution MUST be added to ALL QC samples including blanks, calibration standards, QCS, CCC and LSSM CCC's. **Store all prepared standards in a refrigerator at or below 6 °C.**

AMMONIUM CHLORIDE PRESERVATION SOLUTION

Compound	Empirical Formula	Weight (mg)	Final Volume (mL)	Final Concentration (mg/L)
Ammonium chloride	**NH_4Cl**	**100**	**1000**	**100**

7.3 LABORATORY SYNTHETIC SAMPLE MATRIX (LSSM) – Prepare the LSSM at the concentrations listed in the table below. The required concentrations of nitrate (20 mg/L), bicarbonate (150 mg/L), chloride (250 mg/L), and sulfate (250 mg/L) are based on the mass of the anion, not the sodium salt. The NH_4Cl preservative is included in the matrix. LFSSM QC samples (Sect. 3.10) can be prepared by diluting the Analyte PDS (Sect. 7.4.1) with the synthetic matrix solution.

PREPARATION OF LSSM Stock and LSSM SOLUTIONS [c]

Compound	Empirical Formula	Salt (gfw)[a]	Anion (gfw)	Salt Mass (mg)	H_2O L	Conc. Stock (mg/L)[b]	Conc. LSSM (mg/L)[c]
Nitrate anion	NO_3^-	84.99	62.00	137	0.5	200	20
Bicarbonate anion	HCO_3^-	84.01	61.02	1030	0.5	1500	150
Chloride anion	Cl^-	58.44	35.45	2060	0.5	2500	250
Sulfate anion	$SO4^{2-}$	142.04	96.06	1850	0.5	2500	250

[a] gfw = gram formula weight of the sodium salt.

[b] Stock concentration = (salt mass)(gfw anion)/(gfw salt)(0.5 L).

[c] 1:10 dilution of stock ammonium chloride solution (e.g., 50 mL to 500 mL), or add 200g of the LSSM stock and 0.200g of ammonium chloride and dilute to 2L with RW

NOTE: the final LSSM samples must contain the ammonium chloride preservation solution and can be added to the individual samples using the concentrated stock solution or a large volume of LSSM containing the ammonium chloride can be prepared and used to prepare all LSSM samples.

7.4 ANALYTE STOCK STANDARD SOLUTION (SSS, 1000 µg/mL) – Obtain the haloacetic acid analytes listed in the table below as certified solutions in methyl-tert-butyl ether (MtBE). Although estimated stability times for standard solutions are suggested in the following subsections, laboratories should use standard QC practices to determine when their standards need to be replaced.

NOTE: Because of the volatility of the Analyte Stock solution solvent (HAA's in methyl t-butyl ether) it is best to chill (at or below 6 ºC) the reagent water used for dilution (ensuring no contamination from the chilling process) immediately prior to use. Two sources of the 9 HAA's in methyl t-butyl ether are listed in the table in order to provide one source for the analyte standard and a second source for the QCS requirement (Sect. 7.4.4). The Analyte Primary Dilution Solution (PDS) and Secondary Dilution Solution SDS) MUST be stored in a refrigerator as well. All QC standards to be used for collection of all data, including all blanks and CCCs prepared in RW and the LSSM MUST also be stored at or below 6ºC. **They MUST be returned to cold storage immediately after use.**

7.4.1 ANALYTE PRIMARY DILUTION SOLUTION (Analyte PDS) (1.0 µg/mL) – Prepare the Analyte PDS by diluting the Analyte Stock Standard solution into reagent water. Store the PDS in a glass vial with a PTFE/silicone septum. The Analyte PDS is used to prepare calibration standards, and to fortify QC samples with the method analytes. An example preparation of the Analyte PDS that was used to collect the first laboratory data is provided in the Table below.

NOTE: Storage stability of the Analyte PDS was evaluated during method development at a single concentration of 1.0 µg/mL. The aqueous Analyte PDS is stable for 60 days when stored at 4 °C.

7.4.2 SECONDARY PRIMARY DILUTION SOLUTION (Analyte SDS) (100 µg/L) – Prepare the Analyte SDS by diluting the Analyte PDS into reagent water. Store the SDS in a glass vial with a PTFE/silicone septum. The Analyte SDS is used to prepare the very low-level calibration standards used in the LCMRL determination. An example preparation of the Analyte SDS that was used to collect the first laboratory data is provided in Table below.

PREPARATION OF PDS AND SDS SOLUTIONS

Analyte Stock	Catalogue Number	Stock Concentration (µg/mL)	Stock Volume (mL)	Final Volume (mL reagent water)	Analyte PDS* Concentration (µg/mL)	Analyte SDS** Concentration (µg/L)
Haloacetic acids in methyl-tert-butyl ether	**Supleco Cat No. 49107-U**	**2000**	**0.025**	**50**	**1.0**	
	Restek Cat. No. 31896	**1000**	**0.05**	**50**	**1.0**	
Analyte PDS		**1.0**	**1.0**	**10**		**100**

*
PDS = Primary Dilution Solution; not analyzed.

**
SDS= Secondary Dilution Solution; not analyzed.

7.4.3 CALIBRATION STANDARDS – This method uses a procedural calibration technique. Prepare procedural calibration standards by diluting the Analyte PDS and SDS with the 100 mg/L NH_4Cl solution (preservative, Sect. 7.2). The lowest CAL standard must be at or below the MRL. A calibration range of 0.05 to 20 µg/L is recommended when the LCMRL must be determined. If the method reporting limit (MRL) is set at 1.0 µg/L and since many surface and ground waters contain trace levels of HAA's, then a calibration range from 0.50 to 20 µg/L would suffice. See Table below for preparing calibration standards.

7.4.4 SECOND SOURCE QUALITY CONTROL SAMPLE (QCS) – A solution containing the method analytes at a known concentration, which is obtained from a source different from the source of calibration standards. The purpose of the QCS is to verify the accuracy of the Primary calibration standards. Prepare the second source PDS (see Table Section 7.4.2) and QCS as listed in Table below.

CALIBRATION STANDARDS & QCS

Dilution Aliquot	Starting Concentration (µg/L)	Final Volume (mL, 100 mg/L ammonium chloride)	Final Concentration (µg/L)
1.0 mL Analyte PDS	1000	50	20
500 µL of Analyte PDS	1000	50	10
250µL of Analyte PDS	1000	50	5.0
100µL of Analyte PDS	1000	50	2.0
50µL of Analyte PDS	1000	50	1.0
*40µL of Analyte PDS	1000	50	0.80
25µL of Analyte PDS	1000	50	0.50
125µL of Analyte SDS	100	50	0.25
50µL of Analyte SDS	100	50	0.10
25µL of Analyte SDS	100	50	0.05
2nd source QCS			
250µL of Analyte PDS Supelco	1000	50	5.0

* include so if it is decided to use a MRL of 1.0 µg/L the new calibration curve can be from 0.8 to 20 µg/L.

NOTE: The stability of calibration standards was evaluated during method development at concentrations of 2.0 and 5.0 µg/L. The aqueous calibration standards are stable for 14 days when stored at 4 °C in glass vials with PTFE/silicone septa. It is recommended that the laboratory independently assess the stability of the aqueous calibration standards to determine safe storage time.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 SAMPLE COLLECTION

8.1.1. Grab samples must be collected in accordance with conventional sampling practices [7]. It is recommended to use amber glass containers with PTFE-lined screw caps and capacities of at least 50 mL.

8.1.2. Prior to shipment to the field, add crystalline or granular ammonium chloride (NH_4Cl) to the sample containers to produce a concentration of 100 mg/L in the Field Sample. For a typical 50-mL sample, this requires 5 mg of ammonium chloride.

Note: Enough ammonium chloride must be added to the sample to convert the free chlorine residual in the sample matrix to combined chlorine. Chloramines, formed by the reaction of hypochlorite with the ammonium ion, do not react further to produce additional haloacetic acids at significant concentrations and protect against microbiological degradation. [8] This concentration of ammonium chloride was determined to convert 8 mg/L of free chlorine residual to combined chlorine.

8.1.3. Fill sample bottles but take care not to flush out the ammonium chloride. Because the target analytes of this method are not volatile, it is not necessary to ensure that the sample bottles are completely headspace free.

8.1.4. When sampling from a cold water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually approximately 3 to 5 minutes). Collect a representative sample from the flowing system using a beaker of appropriate size. Use this bulk sample to generate individual samples as needed.

8.1.5. When sampling from an open body of water, fill a beaker with water sampled from a representative area. Use this bulk sample to generate individual samples as needed.

8.1.6. After collecting the sample, seal the bottle and agitate by hand for 15 seconds.

8.2 SAMPLE SHIPMENT AND STORAGE – Field samples must be chilled during shipment and must not exceed 10 °C during the first 48 hours after collection. Field samples should be confirmed to be at or below 10 °C when they are received at the laboratory. Field samples stored in the lab must be held at or below 6 °C until analysis. Samples should not be frozen.

8.3 SAMPLE HOLDING TIMES – Samples must be analyzed within 14 days of collection. Chlorinated field samples that are preserved in accordance with the method guidance should not exhibit biological degradation of analytes during the allotted 14-day storage time. The residency time in the autosampler must be included when calculating the holding time from collection until analysis.

9. QUALITY CONTROL

9.1. Quality Control requirements include the Initial Demonstration of Capability (IDC) and ongoing QC requirements that must be met when preparing and analyzing field samples. This section describes each QC parameter, its required frequency, and the performance criteria that must be met in order to meet EPA data quality objectives. The QC criteria discussed in the following sections are summarized in Section 17, Tables 7 and 8. These QC requirements are considered the minimum acceptable QC criteria. Laboratories are encouraged to institute additional QC practices to meet their specific needs.

9.2 INITIAL DEMONSTRATION OF CAPABILITY (IDC) – The IDC must be successfully performed prior to analyzing any field samples. Prior to conducting the IDC, the analyst must first meet the calibration requirements outlined in Section 10. Requirements for the IDC are described in the following sections and are summarized in Table 7.

9.2.1 DEMONSTRATION OF LOW SYSTEM BACKGROUND – Analyze a Laboratory Reagent Blank (LRB) processed through all sample collection steps outlined in Section 8.1. Confirm that the LRB is reasonably free of contamination (≤ 1/3 the MRL) and that the criteria in Section 9.2.1 are met.

NOTE: It is a good laboratory practice to include a blank in the calibration of any instrument. The method should also be checked for carry-over by analyzing a RW blank immediately following the highest CAL standard. If this RW sample does not meet the criteria outlined in Section 9.2.1 then carry-over is present and should be identified and eliminated.

9.2.2 DEMONSTRATION OF PRECISION – Prepare and analyze 7 replicate LFBs and LFSSMs fortified near the midrange of the initial calibration curve. The NH_4Cl preservative must be added to the LFBs as described in Section 8.1.2. The percent relative standard deviation (%RSD) of the results of the replicate analyses must be ≤ 30 percent for all the method analytes.

$$\%\ \text{RSD} = \frac{\text{Standard Deviation of Measured Concentrations}}{\text{Average Concentration}} \times 100$$

9.2.3 DEMONSTRATION OF ACCURACY – Using the same set of replicate data generated for Section 9.2.2, calculate average recovery. The average recovery of the replicate values must be within ± 30 percent of the true value.

$$\%\ \text{Recovery} = \frac{\text{Average Measured Concentration}}{\text{Fortified Concentration}} \times 100$$

9.2.4 MINIMUM REPORTING LEVEL (MRL) CONFIRMATION – Establish a target concentration for the MRL based on the intended use of the method. Prepare an initial calibration following the procedures in Section 10.2.3. The lowest calibration standard used to establish the initial calibration (as well as the low-level CCC) must be at or below the concentration of the MRL. Establishing the MRL concentration too low may cause repeated failure of ongoing QC requirements. Confirm or validate the MRL following the procedure outlined below.

9.2.4.1 Fortify and analyze seven replicate LFBs at or below the proposed MRL concentration. The LFBs must contain the method preservative as specified in Section 8.1.2. Calculate the mean (*Mean*) and standard deviation (S) for these replicates. Determine the Half Range for the Prediction Interval of Results (HR_{PIR}) using the equation below.

$$HR_{PIR} = 3.963S$$

where *S* is the standard deviation, and 3.963 is a constant value for seven replicates.[1]

9.2.4.2 Confirm that the upper and lower limits for the Prediction Interval of Results ($PIR = Mean \pm HR_{PIR}$) meet the upper and lower recovery limits as shown below.

The Upper PIR Limit must be ≤ 150 percent recovery.

$$\frac{Mean + HR_{PIR}}{FortifiedConcentration} \times 100 \leq 150\%$$

The Lower PIR Limit must be ≥ 50 percent recovery.

$$\frac{Mean - HR_{PIR}}{FortifiedConcentration} \times 100 \geq 50\%$$

9.2.4.3 The MRL is validated if both the Upper and Lower PIR Limits meet the criteria described above (Sect. 9.2.4.2). If these criteria are not met, the MRL has been set too low and must be determined again at a higher concentration.

NOTE: These equations are only valid for seven replicate samples.

9.2.5 QUALITY CONTROL SAMPLE (QCS) – Analyze a mid-level Quality Control Sample (Sect. 9.3.7) to confirm the accuracy of the calibration curve fit.

9.3 ONGOING QC REQUIREMENTS – This section describes the ongoing QC criteria that must be followed when processing and analyzing field samples. Table 8 summarizes these requirements.

9.3.1 LABORATORY REAGENT BLANK (LRB) – A LRB is analyzed during the IDC and is required with each Analysis Batch (Sect. 3.1, Sect. 11.3.5). The LRB must contain the NH_4Cl preservative. Background from target analytes or contaminants that interfere with the measurement of target analytes must be ≤ 1/3 the MRL. If the target analytes are detected in the LRB at concentrations equal to or greater than this level, then all data for the problem analyte(s) must be considered invalid for all samples which yielded a positive result. **Subtracting blank values from sample results is not permitted.**

NOTE: Although quantitative data below the MRL may not be accurate enough for data reporting, such data are useful in determining the magnitude of background interference. Therefore, blank contamination levels may be estimated by extrapolation, when the concentration is below the MRL.

9.3.2 CONTINUING CALIBRATION CHECK STANDARDS (CCC) – CCC standards are analyzed at the beginning of each Analysis Batch, after every ten field samples, and at the end of the Analysis Batch. See Section 10.3 and Table 8 for concentration requirements and acceptance criteria for the CCC's.

9.3.3 LABORATORY FORTIFIED SYNTHETIC SAMPLE MATRIX CCC STANDARD (LFSSM CCC) – A CCC standard prepared in the LSSM (Section 7.3) at the same concentrations as the CCC Standards should be analyzed at the beginning, middle and end of each Analysis Batch. The LFSSM CCC's are used to ensure the integrity of the sample pre-concentration/matrix elimination step and the chromatographic separation of the HAA's from other interfering anionic species in very high ionic matrices. See Section 10.3.3. and Table 8 for concentration requirements and acceptance criteria.

9.3.4 LABORATORY FORTIFIED BLANK (LFB) – A LFB is required with each Analysis Batch. In successive analysis batches, the LFB fortification level must be rotated between low, medium, and high. The low concentration LFB must be at or below the MRL. Results of LFBs fortified at ≤ MRL must be within 50-150% of the true value. Results of LFB analyses from all other concentrations must be 70-130% of the true value. If the LFB results do not meet these criteria, then all data for the HAA's must be considered invalid for all samples in the Analysis Batch.

> **NOTE:** Because this method utilizes procedural calibration standards, which are fortified reagent waters, there is no difference between the LFB and the Continuing Calibration Check standard. Consequently, the analysis of a separate LFB is not required as part of the ongoing QC; however, the term "LFB" is used for clarity in the IDC and CCC's are used for ongoing QC.

9.3.5 LABORATORY FORTIFIED SAMPLE MATRIX (LFSM) – Analysis of a LFSM (Sect. 3.7) is required in each Analysis Batch. The LFSM is processed and analyzed exactly like a traditional sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The native concentration of the analytes in the sample matrix must be determined in a separate aliquot and the measured value in the LFSM corrected for the native concentrations. If a variety of different sample matrices are analyzed regularly, for example drinking water from groundwater and surface water sources, performance data should be collected for each source.

9.3.5.1 Within each Analysis Batch, a minimum of one field sample must be fortified as an LFSM for every 20 field samples analyzed. The LFSM is prepared by spiking a field sample with an appropriate amount of the HAA Analyte PDS/SDS (Sect. 7.4.2). If the native concentrations of method analytes do not allow this criterion to be met without exceeding the calibration range, dilution with reagent water containing NH_4Cl (100 mg/L) is permitted. The fortification should be delivered in the smallest volume possible to minimize dilution of the sample. Select a fortification concentration that

is equal to or greater than the native concentration, if known. Use historical data and rotate through the designated concentrations when selecting a fortifying concentration.

9.3.5.1 Calculate the percent recovery (%REC) using the equation

$$\%REC = \frac{(A - B)}{C} \times 100$$

A = measured concentration in the fortified sample
B = measured concentration in the unfortified sample
C = fortification concentration

9.3.5.2 Recoveries for samples fortified at concentrations near or at the MRL (within a factor of two times the MRL concentration) must be 50-150%. Recoveries for samples fortified at all other concentrations must be 70-130%. If the accuracy for any analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control in the CCCs and the LFSSM CCC, the recovery is judged to be matrix biased. The result for that analyte in the unfortified sample is labeled "suspect/matrix" to inform the data user that the results are suspect due to matrix effects.

9.3.5.2.1 Field samples that have native HAA concentrations below the MRL and are fortified at concentrations at or near the lowest calibration standard should be corrected for the native levels in order to obtain meaningful percent recovery values. This example and the LRB (Sect. 9.3.1) are the only permitted use of analyte results below the MRL.

9.3.6 LABORATORY DUPLICATE OR LABORATORY FORTIFIED SAMPLE MATRIX DUPLICATE (LD or LFSMD) – Within each Analysis Batch, a minimum of one Laboratory Duplicate (LD) or Laboratory Fortified Sample Matrix Duplicate (LFSMD) must be analyzed. Laboratory Duplicates check the precision associated with laboratory procedures. If target analytes are not routinely observed in field samples, a LFSMD should be analyzed rather than a LD.

9.3.6.1 Calculate the relative percent difference (RPD) for duplicate measurements (LD_1 and LD_2) using the equation

$$RPD = \frac{|LD_1 - LD_2|}{(LD_1 + LD_2)/2} \times 100$$

9.3.6.2 RPDs for Laboratory Duplicates should be $\leq$ 30%. Greater variability may be observed when Laboratory Duplicates have analyte concentrations that are within a factor of 2 of the MRL. At these concentrations Laboratory Duplicates should have RPDs that are $\leq$ 50 percent. If the RPD of any analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control in the

CCCs and LFSSM CCC, the recovery is judged to be matrix influenced. The result for that analyte in the unfortified field sample is labeled "suspect/matrix" to inform the data user that the results are suspect due to matrix effects.

9.3.6.3 If a LFSMD is analyzed instead of a Laboratory Duplicate, calculate the relative percent difference (RPD) for duplicate LFSMs (LFSM and LFSMD) using the equation.

$$RPD = \frac{\left|LFSM - LFSMD\right|}{\left(LFSM + LFSMD\right)/2} \times 100$$

9.3.6.4 RPDs for duplicate LFSMs must be ≤ 30%. Greater variability may be observed when LFSMs are fortified at analyte concentrations that are within a factor of 2 of the MRL. LFSMs fortified at these concentrations must have RPDs that are ≤ 50%. If the RPD of any analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control in the CCCs and LFSSM CCC, the precision is judged to be matrix influenced. The result for that analyte in the unfortified field sample is labeled "suspect/matrix" to inform the data user that the results are suspect due to matrix effects.

9.3.7 QUALITY CONTROL SAMPLES (QCS) –A QCS must be evaluated as part of the IDC (Sect. 9.2.5) and each time new PDS solutions are prepared. If standards are prepared infrequently, analyze a QCS at least quarterly. The QCS should be fortified near the midpoint of the calibration range and analyzed as a CCC. The acceptance criteria for the QCS is the same as for the mid- and high-level CCCs (Section 10.3). If the measured analyte concentrations are not of acceptable accuracy, check the entire analytical procedure to locate and correct the problem.

9.4 METHOD MODIFICATION QC REQUIREMENTS – The analyst is permitted to modify the mobile phase concentration only.

9.4.1 Each time the mobile phase concentration is modified, the analyst must first re-determine the cut windows following Section 10.2.2 using HAA solutions fortified into RW and the LSSM (Sect. 7.3) and then reestablish an acceptable initial calibration (Sect. 10.2.3).

9.4.2 Repeat the procedures of the IDC (Sect. 9.2) and verify that all Ongoing QC criteria can be met for the proposed mobile phase concentration modification (Sect. 9.3).

9.4.3 The analyst is also required to evaluate method performance for the proposed mobile phase concentration modification in real matrices that span the range of waters that the laboratory analyzes. This additional step is required because modifications that perform acceptably during the IDC, which is conducted in reagent water and the LSSM, can fail ongoing method QC requirements in real matrices due to common method interferences. If, for example, the laboratory analyzes finished waters from both surface and groundwater municipalities, this requirement can be accomplished by assessing precision and accuracy (Sects. 9.2.2 and 9.2.3) in a surface water with moderate to high total organic carbon (e.g., 2 mg/L or greater) and a hard groundwater (e.g., 250 mg/L or greater).

9.4.4 The results of Sections 9.4.1 – 9.4.3 must be appropriately documented by the analyst and should be independently assessed by the laboratory's QA officer prior to its application to field samples.

9.4.5 When implementing mobile phase concentration modification, it is the responsibility of the laboratory to closely review the results of Ongoing QC, and in particular, the results associated with the LFSM (Sect. 9.3.5), the LFSMD (Sect. 9.3.6) and the LFSSM CCCs (Sect. 9.3.3). If repeated failures are noted, the modification must be abandoned.

10. CALIBRATION AND STANDARDIZATION

10.1 Demonstration and documentation of acceptable initial calibration for the HAA's is required prior to conducting the IDC and before any field samples are analyzed. Prior to calibration, the analyst must verify the proper timing of cut windows as described in Section 10.2.2. If the initial calibration is successful, continuing calibration check standards are required at the beginning and end of each Analysis Batch, as well as after every tenth field sample.

10.2 INITIAL CALIBRATION – The initial calibration must be established prior to conducting the IDC (Section 9.2) and may be reestablished prior to analyzing field samples. However, it is permissible to verify the calibration with daily CCCs. Calibration should be performed using peak areas and the external standard technique. Calibration using peak heights is not permitted. The initial calibration must be repeated each time a major instrument modification or maintenance is performed.

10.2.1 INSTRUMENT CONDITIONS – Establish proper operating conditions. Operating conditions used during method development are described in Section 17 Table 1. The procedure used to establish the first dimension cut windows is provided in Section 10.2.2 below.

NOTE: For two dimensional ion chromatographic techniques, increased method sensitivity is achieved by injecting larger volumes. For the conditions and equipment reported in this method, the maximum recommended injection volume is 1.0 mL.

10.2.2 FIRST DIMENSION CUT WINDOWS DETERMINATION – Since a large volume (1.0 mL) is injected onto the first dimension column, the effect of high ionic strength matrices on the cut windows and on the HAA's retention time requires careful consideration. Determination of the cut windows is the first step in separating the HAA's from other interfering anionic matrix species. Setting of the cut windows in the first dimension must include evaluation of the retention time for the HAA's in both RW and the LSSM.

10.2.2.1 DETERMINING THE START TIME OF THE COLLECTION WINDOWS – Inject an aliquot (1.0 mL) of 1000 µg/L HAA's fortification in the LSSM (without injection valve #2 on system #2 being activated) to determine the start time for the cut window. The start time for the collection window in the first dimension should be set at 0.50 minutes prior to the start of the HAA's elution in the LSSM.

NOTE: The HAA's in the LSSM may not appear as a distinct peak, but rather as a broad, smeared peak on the first dimension column. However, a distinct rise in baseline is evident when HAA's stars to elute from the column (see Figure 2).

10.2.2.2 DETERMINING THE STOP TIME OF THE COLLECTION WINDOWS – The stop time for the cut windows is established using reagent water. Inject an aliquot (1.0 mL) of 1000 µg/L HAA's standard in RW and determine when the HAA's are completely eluted off the first dimension column. The stop time for the collection windows in the first dimension should be set at 0.20 minutes after the HAA's peak in RW returns to baseline.

NOTE: For the analysis of 5 regulated HAA's only, the stop time for the third collection window in the first dimension should be set at 0.20 minutes after the TCAA peak in RW returns to baseline.

10.2.3 CALIBRATION – Prepare a set of at least five CAL standards as described in Section 7.4.3. The lowest concentration CAL standard must be at or below the MRL. The MRL must be confirmed using the procedure outlined in Section 9.2.4, after establishing the initial calibration. Calibrate the conductivity detector using the external standard technique. Calibration curves may be generated using the IC data system through the use of first (linear) or second (quadratic) order calibration curves. A quadratic fit is recommended for this method. Field samples must be quantified using a calibration curve that spans the same concentration range used to collect the IDC data (Sect. 9.2), i.e., analysts are not permitted to use a restricted calibration range to meet the IDC criteria and then use a larger dynamic range during analysis of field samples. Concentration-based weighting may also be used; however, if this approach is chosen the analyst must confirm this fit does not introduce bias in the higher concentration region of the curve.

10.2.3.1 CALIBRATION ACCEPTANCE CRITERIA – The validation of the calibration is determined by calculating the concentration of the analytes from the regression equation. At least one CAL standard must be at or below the MRL. This calibration point should calculate to be 50 to 150 percent of its true value. All other higher concentration calibration points should calculate to be 70 to 130 percent of their true values. If these criteria cannot be met, the analyst will have difficulty meeting ongoing QC criteria. In this case, corrective action should be taken to reanalyze the calibration standards and/or restrict the range of calibration.

10.3 CONTINUING CALIBRATION CHECK (CCC) STANDARDS – The CCCs verify the calibration at the beginning and end of each group of analyses, as well as after every 10^{th} field sample. The LRBs, LFBs, LFSSMs, LFSMs, LFSMDs, and CCCs are not counted as field samples. The beginning CCC for each Analysis Batch must be at or below the MRL in order to verify instrument sensitivity and the accuracy of the calibration curve prior to the analysis of any field samples. Subsequent CCCs should alternate between a medium and high concentration.

10.3.1 Inject an aliquot of the CCC standards and analyze with the same conditions used during the initial calibration.

10.3.2 Calculate the concentration of the analyte in the CCC standards. The calculated amount for the analytes for mid and high level CCCs must be within ± 30 percent of the true value. The calculated analytes amount for the lowest CCC level must be within ± 50 percent of the true value. If these conditions do not exist, then all data for the analyte must be considered invalid, and remedial action (Sect. 10.3.4) must be taken which may require recalibration. Any results from field samples that have been analyzed since the last acceptable calibration verification are invalid.

10.3.2.1 The analyst should carefully review all first-dimension chromatograms for the CCCs to ensure that the entire chromatographic peak elutes within the cut windows. If this is not the case, the analyst should re-determine the cut windows as per Section 10.2.2.

10.3.3 LABORATORY FORTIFIED SYNTHETIC SAMPLE MATRIX CCC STANDARD (LFSSM CCC) – As chromatographic columns age, column performance can deteriorate. This deterioration will typically result in a decreased retention time for the HAA's, which can affect their retention time in high inorganic matrices. A low-level LFSSM CCC must be analyzed daily at the start of each Analysis Batch to ensure that the first dimension cut windows are functioning properly for high inorganic strength waters. The mid-level LFSSM CCC is analyzed after 10 field samples and the high-level LFSSM CCC analyzed at the end of each analysis batch. The QC acceptance criteria for the LFSSM CCC is the same as for the high-level CCCs (within ± 30%). If these conditions do not exist, then all data for the analytes must be considered invalid, and remedial action should be taken which may require the reestablishing the cut window (Sect. 10.2.2) and recalibration.

10.3.3.1 The analyst should carefully review all first-dimension chromatograms for the LFSSM CCC to ensure that the entire chromatographic peaks elutes within the cut window. If this is not the case, the analyst should re-determine the cut windows as per Section 10.2.2.

10.3.4 REMEDIAL ACTION – Failure to meet CCC or LFSSM CCC QC performance criteria requires remedial action. Maintenance such as confirming the integrity of the trapping efficiency of the concentrator column and matrix elimination step and/or regenerating or replacing the IC guard and analytical columns require returning to the initial calibration step (Sect. 10.2).

11. PROCEDURE

11.1 Important aspects of this analytical procedure include proper field sample collection, preservation and storage (Sect. 8), ensuring that the instrument is properly calibrated (Sect. 10.2) and that all required QC are met (Sect. 9) during each Analysis Batch. This section describes the procedures for field sample preparation and analysis.

11.2 SAMPLE PREPARATION

11.2.1 Do not filter the samples. All field and QC samples must contain the preservative listed in Section 8.1.2, including the LRB. In the laboratory, maintain field samples, QC samples, and calibration standards at or below 6 °C at all times, including the time these are resident in the autosampler awaiting injection.

11.3 SAMPLE ANALYSIS

11.3.1 Establish the instrument operating conditions as described in Table 1 of Section 17. Confirm that the analytes' retention times for the calibration standards are stable.

11.3.2 Establish a valid initial calibration following the procedures outlined in Section 10.2 or confirm that the calibration is still valid by running a low-level CCC as described in Section 10.3. If establishing an initial calibration for the first time, complete the IDC as described in Section 9.2.

11.3.3 Analyze field and QC samples at their required frequencies using the same conditions used to collect the initial calibration. Table 9 shows an acceptable analytical sequence that contains all method-required QC samples.

11.3.4 COMPOUND IDENTIFICATION – Establish an appropriate retention time window for all HAA's elution from the second dimension column in order to identify them in QC and field sample chromatograms.

11.3.4.1 Since the ionic strength of drinking water matrices may vary considerably, **the collection windows (Sect. 10.2.2) for the HAA's in the first dimension must be set wide enough to account for the variability in the ionic strength of the drinking water matrices.** Collection windows (using a 1.0 mL injection volume) of 25 minutes were found to be acceptable for the system used during method development. If the cut windows are not set properly, analyte recoveries may be reduced without affecting the second-dimension retention times.

11.3.4.2 Retention times in the second dimension should be very stable as long as the first-dimension heart-cut windows have been set properly (Sect. 10.2.2). This is because a majority of the common anions, which alter the ionic strength of field samples causing sample-to-sample variation in IC retention time, are eliminated during the heart-cut procedure. Retention times measured for the HAA's in RW and for the LFSSM were essentially identical during method development.

11.3.4.3 The QC requirements for each analysis batch include a first-dimension printout of the final CCC and the high level LFSSM CCC chromatograms to ensure the heart-cut windows are functioning properly. The analyst should also review all first-dimension chromatograms to ensure acceptable chromatographic performance within the first-dimension cut windows. For example, if a sample had a much higher conductivity (significantly above the LFSSM) caused by either very high levels of interfering anions or the HAA's, the first-dimension cut

window would be overwhelmed. In such an instance, the sample should be diluted and reanalyzed.

11.3.4.4 High ionic strength matrices have the potential to cause an increase in background conductivity and severe tailing as the other anions elute from the first dimension column and cause the HAA's retention time to decrease.

11.3.5 THE ANALYSIS BATCH – Establish a valid initial calibration following the procedures outlined in Section 10.2 and confirm that the calibration is valid by analyzing a CCC at or below the MRL as described in Section 9.2.4. Alternately, verify that an existing calibration, established for a previous Analysis Batch, is still valid by analyzing a CCC at or below the MRL. Next, analyze an LRB. Continue the Analysis Batch by analyzing aliquots of field and QC samples at appropriate frequencies (Section 9.3), employing the optimized conditions used to acquire the initial calibration. Analyze a mid-level CCC after every ten field samples and a high-level CCC at the end each Analysis Batch.

NOTE: Each Analysis Batch must begin with the analysis of a CCC at or below the MRL for each analyte that the laboratory intends to report, followed by the analysis of an LRB. This is true whether or not an initial calibration is analyzed. After 20 field samples the low-level CCC and the LRB must be repeated to begin a new Analysis Batch. The acquisition start time of the mid-level CCC at the end of the Analysis Batch must be within 48 hours of the acquisition start time of the low-level CCC at the beginning of the Analysis Batch. Do not count QC samples (LRBs, LDs, LFSMs, LFSMDs) when calculating the frequency of CCCs that are required during an Analysis Batch.

11.3.6 EXCEEDING CALIBRATION RANGE – The analyst must not extrapolate beyond the established calibration range. If an analyte result exceeds the range of the initial calibration curve, the sample may be diluted using reagent water containing 100 mg/L NH_4Cl and the diluted field sample re-injected. Incorporate the dilution factor into final concentration calculations. The dilution will also affect the MRL for the HAA's.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Identify the analytes present in the field and QC Samples as described in Section 11.3.

12.2 Calculate the HAA's concentrations using the multi-point calibration established in Section 10.2. Quantify only those values that fall between the MRL and the highest calibration standard. Field samples with target analyte responses that exceed the highest calibration standard require dilution and reanalysis (Sect. 11.3.6).

12.2.1 As noted in Section 9.3.5.2.1, it may be necessary to extrapolate below the MRL to estimate contaminants in LRBs and to correct for native levels of the HAA's below the MRL when field samples are fortified at or near the MRL. These are the only permitted use of analyte results below the MRL.

12.3 Calculations must utilize all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty), typically two, and not more than three significant figures.

12.4 Prior to reporting data, the laboratory is responsible for assuring that QC requirements have been met or that any appropriate qualifier is documented.

13. METHOD PERFORMANCE

13.1 PRECISION, AND ACCURACY – Tables for these data are presented in Section 17. The LCMRLs for the HAA's are presented in Table 2 and were calculated using a procedure described elsewhere.[1] Single laboratory precision and accuracy data are presented in Tables 3-6.

13.2 Figure 3 is a representation of both the first and second dimension chromatograms for 20 µg/L HAA's fortification in the LSSM.

13.3 Figure 4 shows the second dimension chromatograms for a 2.5 µg/L HAA's fortification to a municipal ground water, disinfected with chlorine.

14. POLLUTION PREVENTION

14.1 For information about pollution prevention that may be applicable to laboratory operations, consult "Less is Better: Laboratory Chemical Management for Waste Reduction" available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C., 20036, or on-line at: https://www.acs.org/content/dam/acsorg/about/governance/committees/chemicalsafety/publications/less-is-better.pdf

15. WASTE MANAGEMENT

15.1 The analytical procedures described in this method generate relatively small amounts of waste since only small amounts of reagents are used. The matrices of concern are finished drinking water or source water. However, the Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations, and that laboratories protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Also, compliance is required with any sewage discharge permits and regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, see the publications of the American Chemical Society's Laboratory Environment, Health & Safety Task Force on the Internet at https://www.acs.org/content/dam/acsorg/about/governance/committees/chemicalsafety/publications/less-is-better.pdf. Additional waste management information can be found in "Laboratory Waste Minimization and Pollution Prevention," Copyright © 1996 Battelle Seattle Research Center, which can be found at http://www.p2pays.org/ref/01/text/00779/index2.htm.

16. REFERENCES

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17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1. ION CHROMATOGRAPHIC CONDITIONS USED TO COLLECT METHOD PERFORMANCE DATA for 9 HAAs

Standard Conditions and Equipment for First Dimension Analyses:

Parameter	**Conditions**[a]
Ion Chromatograph:	Thermo Scientific Dionex ICS-5000 Dual System
Sample loop:	500 µL
Load Volume:	1000 µL
Eluent Generator:	Thermo Fisher Dionex ICS-5000 EG Eluent Generator Module (P/N 074459), with potassium hydroxide Eluent Generator Cartridges (P/N 075778), isocratic 7 mM potassium hydroxide from 0 to 12 minutes, ramped to 14 mM potassium hydroxide from 12 to 32 minutes and step changed to 65 mM potassium hydroxide at 32.1 minutes following the elution
Eluent Flow:	1.0 mL/min
Autosampler:	Thermo Scientific Dionex AS-AP Autosampler Module (P/N 074926) with a diverter valve and a large volume (8.5 mL) buffer line (P/N 075520)
Columns:	Thermo Scientific Dionex IonPac AG 24A Guard 4 x 50 mm (P/N 076011) and Thermo Scientific Dionex IonPac AS 24A Analytical 4 x 250 mm (P/N 076010)
Typical System Back-pressure:	~2300 psi
Conductivity Suppressor:	Thermo Scientific Dionex AERS 500, 4-mm (P/N 082540) with Carbonate Removal Device (CRD) 300, 4-mm (P/N 064637)
Chromatography Module:	Thermo Scientific Dionex ICS-5000 DC Module (P/N 072007) column compartment maintained @ 15º C
Detector:	Conductivity Detector with integrated cell (P/N 079829) held @ 25º C
Total analysis time:	60 min

Standard Conditions and Equipment for Second Dimension Analyses:

Ion Chromatograph:	Thermo Scientific Dionex ICS-5000 Dual System
Sample loop:	Thermo Scientific Dionex MAC-200, 0.75 x 80-mm, concentrator column (P/N 075461)
Load Volume:	Cut-window time set per procedures in **below** (approximately 29.5 mL)
Eluent Generator:	Thermo Scientific Dionex ICS-5000 EG Eluent Generator Module (P/N 074459), with Capillary potassium hydroxide EluGen Cartridges (P/N 072076), isocratic 5.2 mM potassium hydroxide from 0 to 53 minutes, step changed to 155 mM potassium hydroxide at 53.1 minutes, isocratic 155 mM potassium hydroxide from 53.1 to 60 minutes and step change to 100 mM potassium hydroxide at 60.1 minutes following the elution
Eluent Flow:	0.012 mL/min
Autosampler:	None

Columns:	Thermo Scientific Dionex IonPac AG 26 Capillary Guard 0.4 x 50 mm (P/N 076019)and Thermo Scientific Dionex IonPac AS 26 Capillary 0.4 x 250 mm (P/N 076018)
Typical System Back-pressure:	~2300 psi
Conductivity Suppressor:	Thermo Scientific Dionex ACES, (P/N 072052) with Carbonate Removal Device (CRD) 200, Capillary (P/N 072054)
Chromatography Module:	Thermo Scientific Dionex ICS-5000 DC Module (P/N 072007) upper compartment maintained @ 13ºC and IC Cube maintained @ 15º C
Detector:	Conductivity Detector with integrated capillary cell (P/N 072041) held @ 25º C
Total analysis time:	80 min

[a] The chromatograms presented in Figures 2, 3, and 4 were obtained under these conditions.

TABLE 1A. ION CHROMATOGRAPHIC CONDITIONS USED TO COLLECT METHOD PERFORMANCE DATA for 5 regulated HAAs

Standard Conditions and Equipment for First Dimension Analyses:

Parameter	**Conditions[a]**
Ion Chromatograph:	Thermo Scientific Dionex ICS-5000 Dual System
Sample loop:	500 µL
Load Volume:	1000 µL
Eluent Generator:	Thermo Fisher Dionex ICS-5000 EG Eluent Generator Module (P/N 074459), with potassium hydroxide Eluent Generator Cartridges (P/N 075778), isocratic 7 mM potassium hydroxide from 0 to 12 minutes, ramped to 14 mM potassium hydroxide from 12 to 32 minutes and step changed to 65 mM potassium hydroxide at 32.1 minutes following the elution
Eluent Flow:	1.0 mL/min
Autosampler:	Thermo Scientific Dionex AS-AP Autosampler Module (P/N 074926) with a diverter valve and a large volume (8.5 mL) buffer line (P/N 075520)
Columns:	Thermo Scientific Dionex IonPac AG 24A Guard 4 x 50 mm (P/N 076011) and Thermo Scientific Dionex IonPac AS 24A Analytical 4 x 250 mm (P/N 076010)
Typical System Back-pressure:	~2300 psi
Conductivity Suppressor:	Thermo Scientific Dionex AERS 500, 4-mm (P/N 082540) with Carbonate Removal Device (CRD) 300, 4-mm (P/N 064637)
Chromatography Module:	Thermo Scientific Dionex ICS-5000 DC Module (P/N 072007) column compartment maintained @ 15º C
Detector:	Conductivity Detector with integrated cell (P/N 079829) held @ 25º C
Total analysis time:	56 min

Standard Conditions and Equipment for Second Dimension Analyses:

Ion Chromatograph:	Thermo Scientific Dionex ICS-5000 Dual System

Sample loop:	Thermo Scientific Dionex MAC-200, 0.75 x 80-mm, concentrator column (P/N 075461)
Load Volume:	Cut-window time set per procedures in **below** (approximately 17.6 mL)
Eluent Generator:	Thermo Scientific Dionex ICS-5000 EG Eluent Generator Module (P/N 074459), with Capillary potassium hydroxide EluGen Cartridges (P/N 072076), isocratic 5.2 mM potassium hydroxide from 0 to 53 minutes, step changed to 155 mM potassium hydroxide at 53.1 minutes following the elution
Eluent Flow:	0.012 mL/min
Autosampler:	None
Columns:	Thermo Scientific Dionex IonPac AG 26 Capillary Guard 0.4 x 50 mm (P/N 076019)and Thermo Scientific Dionex IonPac AS 26 Capillary 0.4 x 250 mm (P/N 076018)
Typical System Back-pressure:	~2300 psi
Conductivity Suppressor:	Thermo Scientific Dionex ACES, (P/N 072052) with Carbonate Removal Device (CRD) 200, Capillary (P/N 072054)
Chromatography Module:	Thermo Scientific Dionex ICS-5000 DC Module (P/N 072007) upper compartment maintained @ 13ºC and IC Cube maintained @ 15º C
Detector:	Conductivity Detector with integrated capillary cell (P/N 072041) held @ 25º C
Total analysis time:	65 min

TABLE 2. TWO DIMENSIONAL IC LOWEST CONCENTRATION MINIMUM REPORTING LEVEL (LCMRL)

Analyte	LCMRL Fortification Levels (µg/L)	Calculated LCMRL (µg/L)
Monochloroacetic acid	0.050, 0.10, 0.25, 0.40, 0.50, 0.80, 1.0, 2.0	0.085
Monobromoacetic acid	0.050, 0.10, 0.25, 0.40, 0.50, 0.80, 1.0, 2.0	0.10
Dichloroacetic acid	0.050, 0.10, 0.25, 0.40, 0.50, 0.80, 1.0, 2.0	0.41
Bromocholoroacetic acid	0.050, 0.10, 0.25, 0.40, 0.50, 0.80, 1.0, 2.0	0.30
Dibromoacetic acid	0.050, 0.10, 0.25, 0.40, 0.50, 0.80, 1.0, 2.0	0.09
Trichloroacetic acid	0.050, 0.10, 0.25, 0.40, 0.50, 0.80, 1.0, 2.0	0.26
Bromodichloroacetic acid	0.050, 0.10, 0.25, 0.40, 0.50, 0.80, 1.0, 2.0	0.29
Chlorodibromoacetic acid	0.050, 0.10, 0.25, 0.40, 0.50, 0.80, 1.0, 2.0	0.055
Tribromoacetic acid	0.050, 0.10, 0.25, 0.40, 0.50, 0.80, 1.0, 2.0	0.26

TABLE 3. PRECISION AND ACCURACY OF HAA 9 FORTIFIED AT 2.5 AND 10 µg/L IN REAGENT WATER (RW)

Analyte	Fortified Conc. = 2.5 µg/L (n=7)		Fortified Conc. = 10 µg/L (n=7)	
	% Recovery	% RSD	% Recovery	% RSD
Monochloroacetic acid	85.8	1.50	94.8	0.61
Monobromoacetic acid	103.3	0.35	106.1	0.26
Dichloroacetic acid	87.0	3.40	99.3	0.63
Bromochloroacetic acid	94.3	4.37	98.3	1.88
Dibromoacetic acid	90.7	3.77	97.2	1.54
Trichloroacetic acid	88.3	0.37	100.8	0.20
Bromodichloroacetic acid	91.1	3.29	102.4	0.33
Chlorodibromoacetic acid	88.9	0.29	99.2	0.29
Tribromoacetic acid	96.5	1.61	98.4	0.27

TABLE 3-1. PRECISION AND ACCURACY OF HAA 5 FORTIFIED AT 2.5 AND 10 µg/L IN REAGENT WATER (RW)

Analyte	Native Conc., µg/L (n=3)	Fortified Conc. = 2.5 µg/L (n=7)		Fortified Conc. = 10 µg/L (n=7)	
		% Recovery	% RSD	% Recovery	% RSD
Monochloroacetic acid	0.133	91.6	1.57	99.7	0.34
Monobromoacetic acid	ND	100.0	0.46	102.7	0.44
Dichloroacetic acid	ND	92.8	0.99	103.6	0.59
Dibromoacetic acid	ND	98.8	0.68	101.6	0.24
Trichloroacetic acid	ND	90.6	0.25	101.3	0.30

TABLE 4. PRECISION AND ACCURACY OF HAA 9 FORTIFIED AT 2.5 AND 10 µg/L IN LABORATORY SYNTHETIC SAMPLE MATRIX (LSSM)

Analyte	Fortified Conc. = 2.5 µg/L (n=7)		Fortified Conc. = 10 µg/L (n=7)	
	% Recovery	% RSD	% Recovery	% RSD
Monochloroacetic acid	84.5	0.35	93.6	0.41
Monobromoacetic acid	110.3	0.53	112.1	0.48
Dichloroacetic acid	88.3	3.04	99.3	0.97
Bromochloroacetic acid	93.0	4.07	98.5	2.20
Dibromoacetic acid	90.0	8.03	96.2	2.98
Trichloroacetic acid	88.3	0.37	100.1	0.51
Bromodichloroacetic acid	90.7	1.03	101.1	0.42
Chlorodibromoacetic acid	89.7	0.63	99.1	0.50
Tribromoacetic acid	106.8	0.89	98.3	0.82

TABLE 4-1. PRECISION AND ACCURACY OF HAA 5 FORTIFIED AT 2.5 AND 10 µg/L IN LABORATORY SYNTHETIC SAMPLE MATRIX (LSSM)

Analyte	Fortified Conc. = 2.5 µg/L (n=7)		Fortified Conc. = 10 µg/L (n=7)	
	% Recovery	% RSD	% Recovery	% RSD
Monochloroacetic acid	96.5	2.64	102.8	0.52
Monobromoacetic acid	108.5	8.60	109.6	2.00
Dichloroacetic acid	93.0	7.07	96.9	2.34
Dibromoacetic acid	126.6	5.89	106.3	1.19
Trichloroacetic acid	96.6	1.62	107.9	5.19

TABLE 5. PRECISION AND ACCURACY OF HAA 9 FORTIFIED AT 2.5 AND 10 µg/L IN GROUND WATER (GW)

Analyte	Native Conc., µg/L (n=3)	Fortified Conc. = 2.5 µg/L (n=7)		Fortified Conc. = 10 µg/L (n=7)	
		% Recovery	% RSD	% Recovery	% RSD
Monochloroacetic acid	0.41	91.9	3.41	92.9	1.53
Monobromoacetic acid	0.41	110.6	0.52	115.9	0.36
Dichloroacetic acid	1.04	77.8	1.88	87.3	0.32
Bromochloroacetic acid	1.80	90.3	1.99	101.7	0.96
Dibromoacetic acid	0.76	100.8	1.54	101.4	0.88
Trichloroacetic acid	0.81	99.1	1.54	103.5	0.28
Bromodichloroacetic acid	1.54	101.7	0.79	103.5	0.18
Chlorodibromoacetic acid	0.98	97.3	0.57	102.7	0.20
Tribromoacetic acid	0.65	87.6	3.33	108.4	0.72

TABLE 5-1. PRECISION AND ACCURACY OF HAA 5 FORTIFIED AT 2.5 AND 10 µg/L IN GROUND WATER (GW)

Analyte	Native Conc., µg/L (n=3)	Fortified Conc. = 2.5 µg/L (n=7)		Fortified Conc. = 10 µg/L (n=7)	
		% Recovery	% RSD	% Recovery	% RSD
Monochloroacetic acid	0.44	96.4	2.63	100.0	0.36
Monobromoacetic acid	0.45	98.0	0.46	102.4	0.42
Dichloroacetic acid	1.23	78.3	1.62	81.2	0.81
Dibromoacetic acid	1.60	95.5	0.65	101.0	0.29
Trichloroacetic acid	1.03	91.7	0.79	101.1	0.21

TABLE 6. PRECISION AND ACCURACY OF HAA 9 FORTIFIED AT 2.5 AND 10 µg/L IN SURFACE WATER (SW)

Analyte	Native Conc., µg/L (n=3)	Fortified Conc. = 2.5 µg/L (n=7)		Fortified Conc. = 10 µg/L (n=7)	
		% Recovery	% RSD	% Recovery	% RSD
Monochloroacetic acid	1.42	81.9	2.52	82.5	1.21
Monobromoacetic acid	ND	111.0	0.35	112.7	0.19
Dichloroacetic acid	17.8*	77.4	0.80	69.2*	0.73
Bromochloroacetic acid	0.96	108.7	0.50	106.3	0.18
Dibromoacetic acid	0.39	104.0	0.50	103.9	0.17
Trichloroacetic acid	20.51*	75.6	0.25	81.6	0.35
Bromodichloroacetic acid	0.59	90.7	1.62	97.9	0.38
Chlorodibromoacetic acid	ND	104.9	0.99	101.7	0.56
Tribromoacetic acid	0.46	101.6	0.90	97.9	1.82

*The native levels of DCAA and TCAA were near or above the highest calibration standard which put the spike levels above the highest calibration standard. The sample required dilution and re-analysis.

TABLE 6-1. PRECISION AND ACCURACY OF HAA 5 FORTIFIED AT 2.5 AND 10 µg/L IN SURFACE WATER (SW)

Analyte	Native Conc., µg/L (n=3)	Fortified Conc. = 2.5 µg/L (n=7)		Fortified Conc. = 10 µg/L (n=7)	
		% Recovery	% RSD	% Recovery	% RSD
Monochloroacetic acid	1.93	101.6	1.12	104.3	1.98
Monobromoacetic acid	ND	98.2	0.18	101.7	0.32
Dichloroacetic acid	15.8*	66.0*	2.03	75.1	0.63
Dibromoacetic acid	0.54	87.6	1.91	103.6	0.79
Trichloroacetic acid	21.16*	85.7	0.39	84.1	0.16

*The native levels of DCAA and TCAA were near or above the highest calibration standard which put the spike levels above the highest calibration standard. The sample required dilution and re-analysis.

TABLE 6A. PRECISION AND ACCURACY OF HAA 9 FORTIFIED AT 2.5 AND 10 µg/L IN SURFACE WATER (SW) DILUTED 1:5 PRIOR TO SPIKING

Analyte	Native Conc., □g/L (n=3)	Fortified Conc. = 2.5 µg/L (n=7)		Fortified Conc. = 10 µg/L (n=7)	
		% Recovery	% RSD	% Recovery	% RSD
Monochloroacetic acid	0.41	78.2	2.56	82.3	5.02
Monobromoacetic acid	ND	105.2	0.38	105.1	4.94
Dichloroacetic acid	2.28	72.1	2.02	77.6	3.5
Bromochloroacetic acid	ND	102.4	4.31	93.8	4.98
Dibromoacetic acid	0.10	87.6	3.66	91.0	5.08
Trichloroacetic acid	3.88	101.8	0.19	98.9	3.36
Bromodichloroacetic acid	0.33	87.2	0.36	94.6	4.89
Chlorodibromoacetic acid	ND	86.7	0.52	92.6	5.06
Tribromoacetic acid	ND	103.2	1.65	96.7	4.70

TABLE 6A-1. PRECISION AND ACCURACY OF HAA 5 FORTIFIED AT 2.5 AND 10 µg/L IN SURFACE WATER (SW) DILUTED 1:5 PRIOR TO SPIKING

Analyte	Native Conc., µg/L (n=3)	Fortified Conc. = 2.5 µg/L (n=7)		Fortified Conc. = 10 µg/L (n=7)	
		% Recovery	% RSD	% Recovery	% RSD
Monochloroacetic acid	0.34	86.8	2.58	90.8	5.12
Monobromoacetic acid	ND	98.2	0.67	97.5	4.94
Dichloroacetic acid	3.02	76.1	1.74	79.8	3.67
Dibromoacetic acid	ND	102.6	0.47	97.5	4.87
Trichloroacetic acid	4.18	105.1	0.25	100.9	3.42

TABLE 7. INITIAL DEMONSTRATION OF CAPABILITY QUALITY CONTROL REQUIREMENTS

Method Reference	Requirement	Specification and Frequency	Acceptance Criteria
Section 9.2.1	Demonstration of Low System Background	Analyze a LRB prior to any other IDC steps.	Demonstrate that all HAA's are below 1/3 of the MRL (Section 9.3.1) and that possible interferences from sampling protocols do not prevent the identification and quantification of the HAA's.
Section 9.2.2	Demonstration of Precision	Analyze 7 replicate LFBs and LFSSMs fortified near the mid-point of the calibration curve	%RSD must be ≤ 30%.
Section 9.2.3	Demonstration of Accuracy	Calculate average recovery for replicates used in Section 9.2.2.	Mean recovery within ± 30% of true value.
Section 9.2.5	Quality Control Sample	During IDC, each time a new analyte PDS is made, every time the instrument is calibrated and at least quarterly.	The result for the HAA's must be within 70-130% of the true value.

TABLE 8. ONGOING QUALITY CONTROL REQUIREMENTS (SUMMARY)

Method Reference	Requirement	Specification and Frequency	Acceptance Criteria
Section 8.3	Sample Holding Time	14 days when collected and stored according to Sections 8.1 and 8.2 with appropriate storage.	Sample results are valid only if samples are analyzed within sample hold time.
Section 9.3.1	Laboratory Reagent Blank (LRB)	Analyze a LRB as part of the IDC (Section 9.2), as part of each calibration, and with each Analysis Batch	Demonstrate that all HAA's are below 1/3 of the MRL and that possible interferences from sampling protocols do not prevent the identification and quantification of the HAA's.
Section 9.3.2 And 10.3	Continuing Calibration Check (CCC) Standards	Verify initial calibration by analyzing a low-level CCC at the beginning of each Analysis Batch. Subsequent CCCs are required after every 10 field samples, and after the last field sample in a batch. Low CCC – at or below the MRL concentration Mid CCC – near midpoint in calibration curve High CCC – near the highest calibration standard.	For each CCC the result must be: For CCCs ≤ MRL: % Rec within ± 50% of the true value For CCCs > MRL: %Rec within ± 30% of the true value Recalibration is recommended if these criteria are not met.
Section 9.3.3	Laboratory Fortified Synthetic Sample Matrix CCCs (LFSSM CCC)	In order monitor the cut windows during an Analysis Batch, a low, mid and high-level CCC standard, prepared in the LFSSM (Sect. 9.3.3) are required at the beginning, middle and end of each Analysis Batch.	For the LFSSM CCC the result must be within ± 30% of the true value
Section 9.3.4	Laboratory Fortified Blank (LFB)	Analyze a LFB with each analysis batch, rotating between low, medium and high concentration from batch to batch. Low LFB – at or below the MRL concentration Mid LFB – near midpoint in calibration curve High LFB – near the highest calibration standard.	For each LFB the result must be: For LFBs ≤ MRL: % Rec within ± 50% of the true value For LFBs > MRL: %Rec within ± 30% of the true value Recalibration is recommended if these criteria are not met.

TABLE 8. ONGOING QUALITY CONTROL REQUIREMENTS (Continued)

Method Reference	Requirement	Specification and Frequency	Acceptance Criteria
Section 9.3.5	Laboratory Fortified Sample Matrix (LFSM)	Analyze one LFSM per Analysis Batch (20 field samples or less). Fortify the LFSM with the HAA's at a concentration close to but greater than the native concentration (if known). Calculate LFSM recoveries.	Recoveries for the LFSM must be calculated (Sect. 9.3.5**.1).** The result must be: For LFSMs ≤ MRL: % Rec within ± 50% of the true value For LFSMs > MRL: %Rec within ± 30% of the true value
Section 9.3.6	Laboratory Duplicate (LD) or Laboratory Fortified Sample Matrix Duplicate (LFSMD)	Analyze at least one LD or LFSMD or with each Analysis Batch (20 samples or less), whichever is more frequent.	RPD must be calculated (Sect. 9.3.6.1 for LD and Sect. 9.3.6.3 for LFSMD). The result must be: For LFSMDs ≤ MRL: RPD within ± 50% of the true value For LFSMDs > MRL: RPD within ± 30% of the true value
Section 9.3.7	Quality Control Sample (QCS)	During IDC, each time a new analyte PDS is made, every time the instrument is calibrated and at least quarterly.	Results must be within ± 30% of the expected value.
Section 10.2	Initial Calibration	Use external standard calibration technique to generate a first or second order calibration curve. Use at least 5 standard concentrations. Check the calibration curve as described in Section 10.2. Analyze a QCS near the mid-point of the calibration curve.	When each calibration standard is calculated as an unknown using the calibration curve, the result should be: For CALs ≤ MRL: % Rec within ± 50% of the true value For CALs > MRL: %Rec within ± 30% of the true value Recalibration is recommended if these criteria are not met.

TABLE 9. SAMPLE ANALYSIS BATCH WITH QC REQUIREMENTS

Injection #	Sample Description	Acceptance Criteria
1	Laboratory Reagent Blank (LRB)	≤ 1/3 MRL
2	CCC at the MRL	Recovery of 50 - 150%
3	LFSSM CCC at low level	Recovery of 50 – 150%
4	Sample 1	normal analysis
5	Sample 2	normal analysis
6	Sample 2 - Laboratory Fortified Sample Matrix (LFSM)	Recovery of 70 - 130%
7	Sample 2 - Laboratory Fortified Sample Matrix Duplicate (LFSMD)	%RPD = ±30%
8	Sample 3	normal analysis
9	Sample 4	normal analysis
10	Sample 5	normal analysis
11	Sample 6	normal analysis
12	Sample 7	normal analysis
13	Sample 8	normal analysis
14	Sample 9	normal analysis
15	Sample 10	normal analysis
16	CCC at mid level	Recovery of 70 - 130%
17	LFSSM CCC at mid level	Recovery of 70 - 130%
18	Sample 11	normal analysis
19	Sample 12	normal analysis
20	Sample 13	normal analysis

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TABLE 9. (Continued)

Injection #	Sample Description	Acceptance Criteria
21	Sample 14	normal analysis
22	Sample 15	normal analysis
23	Sample 16	normal analysis
24	Sample 17	normal analysis
25	Sample 18	normal analysis
26	Sample 19	normal analysis
27	Sample 20	normal analysis
28	CCC at high level*	Recovery of 70 - 130%
29	LFSSM CCC at high level*	Recovery of 70 - 130%

* Also requires first dimension chromatogram printout

Figure 1: Method System Schematic