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Haloacetic Acids in Drinking Water - EPA Method 552.2

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1. Scope and Application

1.1. Method 552.2 is used to determine the concentrations of various haloacetic acids in drinking water. The pH of water samples is adjusted to < 0.5 and the water samples are extracted with MTBE. The acids are converted to the methyl esters by the addition of acetic methanol and heating. The acidic extract is neutralized by a back-extraction with a saturated solution of Sodium bicarbonate. The extract is injected in a temperature programmable gas chromatograph with an electron capture detector. Identifications are obtained by analyzing a standard curve under identical conditions used for samples and comparing resultant retention times. Analytes are quantitated using procedural standard calibration.

1.2. This method is restricted to analysts who have completed the requirements of the initial demonstration SOP. See SOP reference 13.2.

2. Definitions

2.1. Refer to Section 3 and Section 4 of the Georgia EPD Laboratory Quality Assurance Manual for Quality Control definitions.

2.2. Primary Source (PS) – A standard that is used to make up the calibration points of a curve.

2.3. Second Source (SS) – A standard made from a manufacturer other than that of the primary source.

2.4. Initial Calibration Verification (ICV) – An ICV is a second source standard that is used to verify the correctness of the primary source calibration curve. The ICV is run at a level equal to that of a Laboratory Control Sample (LCS) or the midpoint on the calibration curve.

3. Interferences

3.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baselines in chromatograms.

3.1.1. Glassware must be scrupulously cleaned with hot water and detergent followed by de-ionized water then rinsed with methanol followed by 3 rinses with acetone.

3.1.2. The use of high purity reagents and solvents helps minimize interference problems.

3.2. Plastics should never be used at any point in this analysis.

3.3. Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes.

3.3.1. When contamination from one chromatography run to the next is suspected samples are reanalyzed employing the use of any necessary dilutions and solvent blanks to eliminate the problem.

3.4. Matrix interferences may be caused by contaminants that are co-extracted from the sample.

3.4.1. All samples are run on two chromatography columns which greatly minimize interference problems.

4. Safety

4.1. Refer to Laboratory Chemical Hygiene Plan.

5. Apparatus and Equipment

5.1. Sample Container: New Pre-certified 60 ml amber glass vials with a screw cap lined with Teflon.

5.2. Graduated conical centrifuge tubes with Teflon lined screw caps – 15 ml with graduated 1 ml markings.

5.3. Disposable Pasteur Pipets: Glass, used for extract transfer.

5.4. Block Heaters: Capable of holding screw cap conical centrifuge tubes.

5.5. Volumetric Flasks: 5 ml, 10 ml, and 100 ml.

5.6. pH paper: Capable of measuring low pH.

5.7. Micro Syringes: 10 µl, 25 µl, 50 µl, 100 µl, 250 µl, 500 µl, 1000 µl.

5.8. Autosampler vials: 2 ml with Teflon lined septum.

5.9. Graduated cylinders: 50 ml.

5.10. Detergent: Steris Labklenz or equivalent.

5.11. Balance: capable of accurately weighing to 0.01g.

5.12. Balance: capable of accurately weighing to 0.0001g.

5.13. Autopipette Dispenser: Capable of dispensing 4.0 ml ± 0.04 ml of an organic solvent.

5.14. Autopipette Dispenser: Capable of dispensing 2.0 ml ± 0.1 ml of concentrated Sulfuric Acid.

5.15. Chlorine Test Strip: capable of testing residual chlorine up to 10 µg/ml.

5.16. Gas Chromatograph capable of temperature and flow programming, with a linearized electron capture detector (ECD), and a capillary column split/splitless injector.

5.16.1. TotalChrom software or equivalent; capable of temperature and flow programming of a split/splitless injection gas chromatograph.

5.16.2. ZB 1701 capillary column (0.53 mm ID or 0.32 mm ID) or equivalent phase.

5.16.3. Rtx CLP II capillary column (0.53 mm ID or 0.32 mm ID), or equivalent phase.

5.17. Electron capture detector.

6. Reagents and Standards

6.1. Methyl-Tert-Butyl Ether (MTBE): Pesticide grade or equivalent.

6.1.1. Each time a bottle of MTBE is opened for dispensing by autopipette, a peroxide check must be performed. Record the MTBE lot number, the peroxide strip lot number, date of the test, and the ppm result of the test in a log book. The date tested and the result must also be noted on the bottle.

6.2. Methanol: Pesticide grade or equivalent.

6.3. Concentrated Sulfuric Acid: Reagent grade.

6.4. Reagent Water: Purified water which does not contain any measureable quantities of target analytes or interfering compounds for each compound of interest (deionized, HPLC, Milli-Q water or equivalent). Milli-Q water has a resistivity of 18 MΩ·cm or greater @ 25° C and a TOC of 50µg/L or less.

6.5. Sodium Bicarbonate: Reagent grade.

6.6. Saturated Sodium Bicarbonate Solution:

6.6.1. 5 g $NaHCO_3$ w/v dissolved in 50 ml reagent water (see section 6.4.).

6.7. Sodium Sulfate: granular, anhydrous, reagent grade suitable for pesticide analysis or equivalent.

6.7.1. Sodium Sulfate is baked for 4 hours at 450° C then stored in a glass container.

6.8. Ammonium Chloride: reagent grade.

6.9. Ammonium Chloride Preservative Solution:

6.9.1. Dissolve 20 g of reagent grade Ammonium chloride crystals in 500 ml of reagent water. Concentration = 40 mg/ml.

6.10. Copper II Sulfate Pentahydrate: Reagent grade.

6.11. 10% H_2SO_4 in Methanol (v/v):

6.11.1. 10 ml of concentrated Sulfuric acid mixed into 90 ml of Methanol

6.12. Calibration Standard Primary Stock Solutions

6.12.1. *Primary Stock Solution*: Prepared from vendor stock solutions (usually at 1000 µg/ml) in MTBE. Concentrations vary from 50 µg/ml to 200 µg/ml as indicated in Table 6.12.1. (Note: Primary Stock, Spiking stock, ICV stock, Surrogate, Internal Standard stock, and all subsequent dilutions of the above mentioned standards are to have an expiration of 1 month from the ampule being opened and must be stored at -10 °C.)

Table 6.12.1. 1 –Primary Stock Solution in MTBE

Compound	Initial Concentration (µg/ml)	Aliquot (ml)	Final Concentration (µg/ml)
Monochloroacetic Acid	1000	2.0	200
Monobromoacetic Acid	1000	1.0	100
Dichloroacetic Acid	1000	1.0	100
Trichloroacetic Acid	1000	1.0	100
Dibromoacetic Acid	1000	0.5	50

Total Volume of Standard Aliquots	5.5 ml
Addition of MTBE to Standard Aliquots	4.5 ml
Final Volume of Primary Stock Solution in MTBE	10 ml

6.12.2. *Primary Working Solution #1:* Prepared from Primary Stock Solution (see 6.12.1.) in MTBE. Concentrations vary from 0.5 µg/ml to 2.0 µg/ml as indicated in Table 6.12.2. 1:

Table 6.12.2. 1 – Primary Working Solution #1 in MTBE

Compound	Initial Concentration (µg/ml)	Aliquot of Primary 552.2 Stock Solution (µl)	Final Concentration (µg/ml)
Monochloroacetic Acid	200	100 µl	2.0
Monobromoacetic Acid	100		1.0
Dichloroacetic Acid	100		1.0
Trichloroacetic Acid	100		1.0
Dibromoacetic Acid	50		0.5

Total Volume of Standard Aliquots	0.1 ml
Addition of MTBE to Standard Aliquots	9.9 ml
Final Volume of Primary Working Solution #1 in MTBE	10 ml

6.12.3. *Primary Working Solution #2:* Prepared from Primary Stock Solution (see 6.12.2. 1) in MTBE. Concentrations vary from 2.0 µg/ml to 8.0 µg/ml as indicated in Table 6.12.3. 1:

Table 6.12.3. 1 – Primary Working Solution #2 in MTBE

Compound	Initial Concentration (µg/ml)	Aliquot of Primary 552.2 Stock Solution (µl)	Final Concentration (µg/ml)
Monochloroacetic Acid	200	1000 µl	8.0
Monobromoacetic Acid	100		4.0
Dichloroacetic Acid	100		4.0
Trichloroacetic Acid	100		4.0
Dibromoacetic Acid	50		2.0

Total Volume of Standards Aliquots	1.0 ml
Addition of MTBE to Standard Aliquots	24 ml
Final Volume of Primary Working Solution #2 in MTBE	25 ml

6.13. Spiking Solutions

6.13.1. *Analyte Spiking Solution*: Primary Working Solution #2. 100 µl per 40 ml spiked QC sample (LCS, LCSD, MS or MSD). This results in analyte

concentrations equivalent to the Level 4 calibration standard (µg/L). See Table 6.16.3. 1.

6.13.2. *Surrogate Stock Solution*: 100 µg/ml Surrogate Stock Solution in MTBE made from a 1000 µg/ml 2-Bromopropionic acid (2-BPA) vendor stock.

Table 6.13.2. .1 – Surrogate Stock Solution in MTBE

Compound	Initial Concentration (µg/ml)	Aliquot (µl)	Final Concentration (µg/ml)
2-Bromopropionic acid (2-BPA)	1000	1000	100

Total Volume of Standard Aliquots	1.0 ml
Addition of MTBE to Standard Aliquots	9.0 ml
Final Volume of Surrogate Stock Solution in MTBE	10 ml

6.13.3. *Surrogate Spiking Solution*: 10 µg/ml Surrogate Spiking Solution in MTBE made from the 100 µg/ml Surrogate Stock Solution (See 6.13.2. .1). 20 µl per 40 ml QC sample (LCS, LCSD, MS, MSD, and Blank) and field sample. This results in a surrogate concentration of 5.0 µg/L in each sample. See Table 6.13.3. 1.

Table 6.13.3. 1 – Surrogate Spiking Solution in MTBE

Compound	Initial Concentration (µg/ml)	Aliquot (µl)	Final Concentration (µg/ml)
2-Bromopropionic acid (2-BPA)	100	2500	10

Total Volume of Standard Aliquots	2.5 ml
Addition of MTBE to Standard Aliquots	22.5 ml
Final Volume of Surrogate Spiking Solution in MTBE	25 ml

6.13.4. *Internal Standard Spiking Solution*: 5 µg/ml internal standard spiking solution in MTBE made from a 100 µg/ml Dibromochloropropane (DBCP) vendor stock. 500 µl per 1 ml of sample (QC or field) or calibration standard extract. This results in an internal standard concentration of 5.0 µg/L equivalent concentration in each. See Table 6.13.4. 1.

Table 6.13.4. 1 – Internal Standard Spiking Solution in MTBE

Compound	Initial Concentration (µg/ml)	Aliquot (µl)	Final Concentration (µg/ml)
Dibromochloropropane (DBCP)	100	500	5.0

Total Volume of Standard Aliquots	500 µl
Addition of MTBE to Standard Aliquots	9.5 ml
Final Volume of Internal Standard Spiking Solution in MTBE	10 ml

6.13.5 LPC Standard Solution: Prepared by dilution of an LPC vendor standard of varying analyte concentrations from 4.0 µg/ml to 10.0 µg/ml diluted to 100 ml with MTBE to achieve final concentrations of 0.004 µg/ml to 0.010 µg/ml.

Table 6.13.5.1 – LPC Standard in MTBE

Compound	Initial Conc. LPC Vendor Mix (µg/ml)	Aliquot (µl)	Final Concentration (µg/ml)
Bromochloroacetic acid (BCAA)	4.0	100	0.004
Monochloroacetic Acid (MCAA)	6.0		0.006
Chlorodibromoacetic acid (CDBAA)	10.0		0.010
2,3-DBPA	10.0		0.010

Total Volume of Standard Aliquots	100 µl
Addition of MTBE to Standard Aliquots	99.9 ml
Final Volume of LPC Standard Solution in MTBE	100 ml

6.14. Initial Calibration Verification (ICV) Standard Stock Solutions

6.14.1. *ICV Stock Solution*: Prepared from second source vendor stock solutions (usually at 1000 µg/ml) in MTBE. Concentrations vary from 50 µg/ml to 200 µg/ml as indicated in Table 6.14.1. 1:

Table 6.14.1. 1– ICV Stock Solution in MTBE

Compound	Initial Concentration (µg/ml)	Aliquot Second Source Standard (ml)	Final Concentration (µg/ml)
Monochloroacetic Acid	1000	2.0	200
Monobromoacetic Acid	1000	1.0	100
Dichloroacetic Acid	1000	1.0	100
Trichloroacetic Acid	1000	1.0	100
Dibromoacetic Acid	1000	0.5	50
Total Volume of Standards Aliquots			5.5 ml
Addition of MTBE to Standard Aliquots			4.5 ml
Final Volume of ICV Stock Solution in MTBE			10 ml

6.14.2. *ICV Working Solution*: Prepared from ICV Stock Solution (see 6.14.1.) in MTBE. Concentrations vary from 2.0 µg/ml to 8.0 µg/ml as indicated in Table 6.14.2. 1:

Table 6.14.2. 1 – ICV Working Solution in MTBE

Compound	Initial Concentration (µg/ml)	Aliquot of ICV Stock Solution (µl)	Final Concentration (µg/ml)
Monochloroacetic Acid	200	400 µl	8.0
Monobromoacetic Acid	100		4.0
Dichloroacetic Acid	100		4.0
Trichloroacetic Acid	100		4.0
Dibromoacetic Acid	50		2.0

Total Volume of Standards Aliquots	0.4 ml
Addition of MTBE to Standard Aliquots	9.6 ml
Final Volume of ICV Working Solution in MTBE	10 ml

6.15. Should alternate concentrations of vendor standards be required due to availability, adjust aliquots or final concentrations as needed to meet the final concentrations in Tables 6.12.1. 1 through 6.14.2. 1.

6.16. Calibration Curve Standards

6.16.1. Method 552.2 utilizes a procedural curve. All initial calibration, calibration verification, and continuing calibration standards are extracted in the same manner as samples, including the addition of preservation chemicals.

6.16.2. Prepare seven different concentrations equivalent to the concentration levels in Table 6.16.3. 1.

6.16.3. The calibration curve consists of the calibration standards at the following concentrations in µg/L:

Table 6.16.3. 1 552.2 Calibration Levels Concentrations

Compound	Level 1 (µg/L)	Level 2 (µg/L)	Level 3 (µg/L)	Level 4 (µg/L)	Level 5 (µg/L)	Level 6 (µg/L)	Level 7 (µg/L)
Monochloroacetic acid	1.25	2.5	10.0	20.0	30.0	40.0	60.0
Monobromoacetic acid	0.625	1.25	5.0	10.0	15.0	20.0	30.0
Dichloroacetic acid	0.625	1.25	5.0	10.0	15.0	20.0	30.0
Trichloroacetic acid	0.625	1.25	5.0	10.0	15.0	20.0	30.0
Dibromoacetic acid	0.313	0.625	2.5	5.0	7.5	10.0	15.0
SS: 2-BPA	0.313	0.625	2.5	5.0	7.5	10.0	15.0
IS: DBCP	50	50	50	50	50	50	50

6.16.4. The calibration levels are made by dilution of appropriate aliquots of the Primary Working Solutions (Tables 6.12.2. 1 and 6.12.3. 1) into 40 ml of preserved reagent water followed by extraction. Surrogate and internal standards are added as directed in section 10.

Table 6.16.4. 1 552.2 Calibration Level Spike Volumes into 40 ml Water (Procedural Curve)

Level / Amount	Level 1 (µl)	Level 2 (µl)	Level 3 (µl)	Level 4 (µl)	Level 5 (µl)	Level 6 (µl)	Level 7 (µl)
Primary Working Solution #1 (Table 6.12.2. 1)	25.0	50.0					
Primary Working Solution #2 (Table 6.12.3. 1)			50.0	100	150	200	300

6.16.5. The ICV is made at the same concentration as Level 4 of the calibration curve (100 µl aliquot of the ICV Working Solution (Table 6.14.2. 1) into 40 ml of preserved reagent water), and extracted as directed in section 10. Including the addition of internal standard and surrogate.

7. Sample Collection

7.1. Drinking water samples for EPA Method 552.2 are collected in new pre-certified 60 ml amber glass vials with Teflon lined screw caps and preserved with 150 µl of 40 mg/ml Ammonium Chloride Solution (see 6.9.) prior to shipping. Two vials are required for every entry point plus two additional vials are sent for an MS and MSD for every 10th entry point or more frequently if needed.

7.1.1. A residual chlorine check is done in the field by the collector. The collector writes down the numerical value for residual chlorine in mg/L (ppm) on the sampling form.

7.1.2. The shipping and receiving staff log in the samples and enter the information for residual chlorine in the DNR_LAB Labworks field. The analyst prints or checks the backlog to determine samples to be analyzed.

7.1.3. The backlog report contains the residual chlorine concentration determined by the collector. If the residual chlorine measured by the collector is less than 8 mg/L, the 150 µl of Ammonium Chloride Solution in the vial was sufficient to convert free chlorine to monochloramine.

7.1.4. If the collector reports 8 mg/L or more residual chlorine, the sample must be recollected.

7.1.5. If the residual chlorine is not listed on the sampling form then the analyst must test it by using chlorine test strips.

7.2. Samples are cooled to 0-6° C (not frozen) and extracted within 14 days after collection. Extracts must be analyzed within 14 days of extraction and stored at –10° C or less.

8. Calibrations

8.1. <u>Initial Calibration</u>

8.1.1. A seven-point calibration is performed for all single peak components (see Table 6.16.3. 1 for standard concentrations). The calibration system uses traceable certified standards. The calibration is an internal standard, procedural calibration.

8.1.1.1. The calibration may be an internal standard calibration based on mean relative response factors (see calculations 11.1. - 11.2.) with a relative standard deviation (%RSD) of < 20% (see calculation 11.3. or a linear fit or quadratic fit internal standard curve with a correlation coefficient (r^2) of ≥ 0.970 (or a coefficient of variation (r) ≥ 0.985).

8.1.1.2. First Order Linear Calibration using Least Squares Regression:

8.1.1.2.1. If linear regression is used, linearity through the origin cannot be assumed in a linear least squares fit. The instrument responses versus the concentrations of the standards for 7 points is determined using the instrument data analysis software and the regression will produce the slope and intercept terms for a linear equation. The regression calculation will generate a correlation coefficient (r) that is a measure of "goodness of fit" of the regression line to the data. A value of 1.0 is a perfect fit, 552.2 requires a correlation coefficient, $r \geq 0.985$ or $r^2 \geq 0.970$. See calculation 11.4.

8.1.2. Alternatively, second order quadratic fit may be used with an acceptable correlation of coefficient of $r \geq 0.985$ (or $r^2 \geq 0.970$). Note: quadratic fit will be calculated by chromatographic software. See calculation 11.5.

8.2. Retention Time Windows

8.2.1. Once per year or after major maintenance, retention time windows must be established. The width of the retention time windows for each analyte, surrogate, and internal standard is defined as ± 3 times the standard deviation of the mean absolute retention time established over the course of a day (24-hours) for all CCCs analyzed during that period. See calculation 11.7.

8.3. Calibration Verification

8.3.1. A second source calibration verification standard (ICV) must be analyzed after each initial calibration and at least once per quarter, even if the system has not been recalibrated. All analytes must be within ± 30% Drift of the expected values (see calculation 11.9.)

8.4. Record Keeping:

8.4.1. Documentation of an instrument calibration is reviewed for adherence to quality criteria and archived with the project records.

8.5. Daily Calibration Verification and Continuing Calibration:

8.5.1. A continuing calibration check standard (CCC) ensures the instrument target compound retention times and quantitation parameters meet method performance criteria. Preceding each analysis set, after every tenth sample analysis and after the final sample analysis, a calibration standard, alternating at two different concentration levels (Levels 3 and 4), should be analyzed as a continuing calibration check to verify that instrument calibration accuracy does not exceed +/- 30% Drift from the expected value. See calculation 11.9.

8.5.1.1. If the CCC fails and can be immediately reanalyzed and meets the method criteria at this time then the samples that were analyzed immediately before this CCC are considered to be valid.

8.5.1.2. If the CCC fails and is not immediately reanalyzed, then the samples bracketed by the failed CCC must be reanalyzed with CCCs that pass method criteria.

8.5.1.3. If a valid CCC cannot be achieved then the instrument is considered to be out of calibration for the compounds in this method and the instrument must be recalibrated.

8.5.1.4. When the acceptance criteria for the continuing calibration verification are exceeded high, i.e., high bias, and there are associated samples that are non-

detects, then those non-detects may be reported. Otherwise, the samples affected by the unacceptable calibration verification shall be reanalyzed after a new calibration curve has been established, evaluated, and accepted.

8.5.2. An LPC (Laboratory Performance Check) standard is run at the beginning of each sample sequence prior to the analysis of samples to determine signal to baseline noise ratio and chromatographic performance.

Table 8.5.2. 1, LPC Requirements and Acceptance Criteria

Parameter	Analyte	Conc., µg/ml in MTBE	Acceptance Criteria
Instrument Sensitivity	MCAA	0.006	Detection of Analyte: Signal to Noise > 3[1,2]
Chromatographic Performance	BCAA	0.004	0.80 <PGF > 1.15[3,4]
Column Performance	CDBAA 2,3-DBPA	0.0100 0.0100	Resolution > 0.50[5,6]

[1] See 8.5.2.1. [2] See calculation 11.12.1. [3] See 8.5.2.2. [4] See calculation 11.12.2.
[5] See 8.5.2.3. [6] See calculation 11.12.3.

8.5.2.1. MCAA signal to noise ratio must be greater than 3:1 (see calculation 11.12.1.).

8.5.2.2. Chromatographic Performance: the Peak Gaussian Factor (PGF) for BCAA must be between 0.80 and 1.15 (see calculation 11.12.2.).

8.5.2.3. Column Performance: Resolution between CDBAA and 2,3-DBPA must be greater than 0.5 (see calculation 11.12.3.).

8.5.3. Retention Times (RT) are updated once per 24 hour period when GC analyses are performed. The first CCC is processed using Totalchrom or equivalent software. The new RTs are saved in a copy of the processing method used for analyzing this batch of samples. To the existing processing method an extension is added by using – Month-Day-Year. Then hard copies of the calibration parameters are added to the data package for that batch of samples. (**NOTE**: If an analytical sequence is stopped for any reason longer than a typical work shift a new retention time update is necessary for the next sequence.)

8.6. Sample Concentration

8.6.1. Sample results are expressed in µg/L.

8.6.2. If an analyte response is calibrated by Mean Relative Response Factor, ($\overline{RRF}$) (see calculation 11.2.), the chromatographic software calculates the sample concentrations per calculation 11.10.

8.6.3. If an analyte response is calibrated by linear regression or quadratic fit, the chromatographic software calculates the sample concentrations per calculation 11.11.

8.6.4. If the initial sample volume is less than 40 ml then volume from the duplicate sample container may be combined to achieve 40 ml. If a duplicate is not available then the sample is recollected.

9. Quality Control

9.1. Refer to Table 14.1. 1 for Reporting Limits (RLs), Appendix A, Table A.1 for Quality Assurance criteria and Table 14.1. 2 for Quality Control procedures associated with this method.

9.2. A Method Detection Limit Study for all analytes must be performed once per year. See SOP reference 13.6.

9.3. See SOP reference 13.2. for training and certification procedures.

9.3.1. For Initial Demonstrations of Capability (IDC), Method 552.2 specifies 80% - 120% recovery and 20% RSD for IDC replicates.

9.3.2. The EPD Laboratory set Continuing Demonstration of Capability (CDC) criteria as 70% - 130% recovery and 20% RSD for CDC replicates.

9.4. See SOP reference 13.3. for control charting procedures.

9.5. Control Limits:

9.5.1. The default control limits from EPA Method 552.2 are 70 - 130% recovery for LCS recoveries. These are the same as the %Drift for CCCs as LCSs and CCCs are essentially the same per EPA Method 552.2. However, the EPD Laboratory extracts LCS and LCSD QC samples which are separate from the CCCs. The EPD Laboratory applies LCS recovery limits to LCSDs. Note, unless specified by method, the EPD Laboratory does not validate batch quality based on LCSD recoveries.

9.5.2. By default, the EPD Laboratory sets static LCS/LCSD precision control limits to be 0 - 30% RPD.

9.5.3. Ten percent of all routine samples must be spiked. Analysis of MS/MSD pairs as directed in Section 9.6.2. below results in 10% spiked field samples, meeting the method criteria. EPA Method 552.2 requires recovery control limits of 70 - 130% for matrix spike analytes. The EPD Laboratory applies MS recovery limits to MSDs.

9.5.4. The EPD Laboratory sets static MS/MSD precision to be 0 - 30% RPD.

9.5.5. The default control limits for surrogates from EPA Method 552.2 are 70 - 130% recovery. These limits are static, i.e. not adjusted through the use of control charts.

Note: Analysts must use the control limits presented in Appendix A, Table A.1. Those limits cannot exceed the default limits in Table 9.5.5. 1.

Table 9.5.5. 1 - Default QC Limits

	Analyte	Default LCL % Recovery	Default UCL % Recovery	Default Precision %RPD
LCS/LCSD	Monochloroacetic acid	70	130	30
	Monobromoacetic acid	70	130	30
	Dichloroacetic acid	70	130	30
	Trichloroacetic acid	70	130	30
	Dibromoacetic acid	70	130	30
Surrogate	2-BPA	70 (3.5 µg/L)	130 (6.5 µg/L)	NA
MS/MSD	Monochloroacetic acid	70	130	30
	Monobromoacetic acid	70	130	30
	Dichloroacetic acid	70	130	30
	Trichloroacetic acid	70	130	30
	Dibromoacetic acid	70	130	30

9.5.6. See the EPD Laboratory Procedures for Control Charting and Control and Control Limits SOP (SOP reference 13.3.) for further details.

9.6. Batching:

9.6.1. Batch samples in groups of 1 to 20 samples.

9.6.2. For batches of 1 to 10 routine samples, one MS/MSD pair must be spiked. For batches of 11 to 20 routine samples, a second MS/MSD pair must be spiked using different samples for each pair.

9.7. Assessing the Internal Standard Response:

9.7.1. The response of the internal standard must be monitored for all samples and standards analyzed by this method. The internal standard response should not deviate from the mean internal standard response of the calibration curve standards by more than 30% on the quantitative column/detector. If > 30% deviation occurs with an individual extract, a second aliquot of that extract spiked with the appropriate amount of internal standard is analyzed. If this aliquot produces an acceptable internal standard response, report results for this aliquot. If the deviation is greater than 30% for this aliquot the sample is either re-extracted if within method hold times, or recollected. A reanalyzed sample aliquot should be followed by a CCC to validate the calibration of the instrument. This method allows for a second injection of a previously run and validated CCC. If this CCC fails after two attempts (see 8.5.1.) the IS acceptance criterion for quantitative column/detector, the instrument is considered to be out of calibration. A new calibration must be performed and validated before samples may be analyzed using this instrument.

9.8. Performance Test (PT) Sample:

9.8.1. EPA requires that the Laboratory perform a PT sample every 12 months to

maintain certification in EPA method 552.2. Those PT result must fall within acceptable control limits for the PT testing facility. If those results are not within acceptable control limits the Laboratory will have a second chance to pass the PT study within the same 12 months of the study. If the results did not fall within acceptable control limits for the study over the 12-month testing period, the laboratory will be downgraded for those compounds listed in this SOP. With the failure of this nature the laboratory must notify all drinking water facilities within 30 days of the failure after the 12-month period has passed. It is not until the laboratory passes a PT study will the laboratory be able to test for those compounds of interest again.

9.9. Method Detection Limit Study (MDL):

9.9.1. MDL is the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.

9.9.2. The actual MDL varies depending on instrument and matrix.

9.9.3. The MDL must be determined annually for each instrument prior to results being reported for that instrument. The MDL determined for each compound must be less than the reporting limit for that compound.

9.9.4. An MDL study may be done two different ways. The two different ways are considered and initial MDL study and a continuous MDL study. Both ways will be explained below.

9.10. Initial MDL study:

9.10.1. An initial MDL study may occur when a new instrument is brought online, changes to the method (which affect the compound of interest's peak area), and lastly major instrument repairs have been made.

9.10.2. An initial MDL study will consist of the following operating parameters, 7 MDL samples and 7 MDL blanks. The 7 MDL samples study is performed by preparing 7 spiked vials, MDLSpike, spiked at the lowest calibration point of the curve, and preparing 7 clean blank vials filled with DI water, MDLBlank. These 7 sets of spiked and blank vial "pairs" are analyzed over 3 separate days, there may or may not be a non-analysis day between each of the 3 days. A total of 14 vials are prepared, 7 spiked and 7 blanks.

9.11. Continuous MDL study:

9.11.1. A Continuous MDL study is preferred over the initial except in a few cases. For a continuous MDL study to be used on an instrument it must have a minimum of 7 MDL samples and 7 MDL blanks extracted over the course of multiple batches over a year. It is required that at a minimum 2 MDL samples and 2 MDL blanks must be ran per quarter per instrument. If this requirement is not met, then the initial MDL study must be performed for that instrument. (See section 9.10.2 for requirements.)

9.11.2. A continuous format MDL study is performed where one vial is spiked as an MDLSpike, at the lowest point of the calibration curve and analyzed with every batch of samples along with the method blank vial as an MDLBlank.

9.11.3. The results of the MDLBlank will be entered into Labworks using the Method Blank test code, $B_552. The MDLSpike result will be entered using the $ML552. The MDL Spiked Amount will be entered into the test code $MA552. The instrument used for the MDL and Blank analysis will be selected using the test code INSTR-552.

9.11.4. MDL studies must be pulled on a yearly basis or an initial MDL study must be performed before the current MDLs for the instrument expire.

10. Procedure

10.1. Remove sample bottles, standards and reagents, surrogate solution, QC spike solution and internal standard solution from cold storage and allow them to equilibrate to room temperature prior to sample preparation and/or analysis.

10.2. With each batch of samples extracted, prepare a volume comparison (reference) vial. Measure 40 ml of reagent water in a graduated cylinder, pour into a new, pre-preserved 60 ml clear glass vial, cap, and mark the volume on the vial with a permanent marker. *Note: This vial is to also be used as the batch method Blank in section 10.3.*

10.2.1. The analyst that creates the reference vial will adjust sample volumes to 40 ml by pouring out a portion of each sample and comparing it to the mark on the reference vial. During adjustment, a small portion of the sample is poured into the sample's vial cap. If necessary, this portion can be used to adjust the final sample volume.

10.3. Sample Extraction:

10.3.1. A batch consists of a Blank, LCS, LCSD, one or two MS and MSD pairs, and up to 20 samples.

10.3.1.1. Field samples, and the MS and MSD are poured into 60 ml clear glass vials. The volumes are adjusted section 10.2.1. prior to proceeding to the next step.

10.3.2. LCS, LCSD and Blanks are made up with 40 ml of reagent water in pre-preserved 60 ml clear glass vials.

10.3.2.1. The volume comparison (reference) vial prepared in section 10.2. is used as the batch method Blank.

10.3.3. Spike the LCS and LSCD with 100 µl of the Primary Working Solution #2 (see 6.12.3.) each.

10.3.4. Spike the two extra vials of the selected QC sample for the MS and MSD each with 100 µl of the Primary Working Solution #2 (see 6.12.3.).

10.3.4.1. If a second MS and MSD pair are required, select an appropriate sample and spike the second MS and MSD with 100 µl of the Primary Working Solution #2.

10.3.5. At least every 2 weeks, spike two aliquots of reagent water with the Primary

Working Solution #2 (see 6.12.3.) with the amount required to make Level 3 CCCs (see Table 6.16.3. 1).

10.3.6. Add 0.02 ml (or 20 µl) of Surrogate Spiking Solution (see 6.13.3.) to all samples, blanks, and QC samples. Equivalent to 5 µg/L 2-BPA in a 40 ml sample.

10.3.7. To each field sample, QC sample and standard, add 2.0 ml of concentrated Sulfuric acid (see 6.3.), cap and shake. Check the pH by dipping a clean stirring rod, or the tip of a disposable pipette into each vial and touching to a narrow range pH paper (see 5.6.). The pH should be < 0.5. Add additional Sulfuric acid if necessary.

10.3.8. Add ~ 2 g of Copper sulfate ($CuSO_4$) (see 6.10.) and shake while solution is still warm from acid addition. Copper sulfate is used as a visual aid for distinguishing the water and MTBE layers.

10.3.9. Quickly add 16 g of Sodium sulfate (see 6.7.) and shake by hand for 3 – 5 minutes.

10.3.10. Add exactly 4.0 ml of MTBE and shake by hand for 2 minutes.

10.3.10.1. MTBE is dispensed from a bottle mounted autopipette. The autopipette must be calibrated a minimum of once each day of use.

10.3.10.2. If a bottle mounted autopipette is not available, an appropriate class A volumetric glassware may be used (pipette, cylinder, flask, etc.).

10.4. Methylation:

10.4.1. Transfer approximately 3 ml of MTBE layer to 15 ml graduated, conical cylinder.

10.4.2. Add 1 ml of 10% H_2SO_4 in Methanol (v/v) (see 6.11), cap loosely.

10.4.3. Place samples on heating block at 50° C ± 2° C for 2 hours.

10.4.4. Allow samples to cool before removing caps.

10.4.5. Slowly add 4 – 1 ml portions of saturated $NaHCO_3$ solution (see 6.6.) and shake by hand for 2 minutes venting occasionally.

10.4.6. Transfer exactly 1.0 ml of upper MTBE layer to autosampler vial. Add 10µl of the internal standard solution (see 6.13.4.) to each 1.0 ml of extract. Note: Amount of internal standard in the 1 ml extract is equal to 50 µg/L. Either split this 1.0 ml plus internal standard or save a second 1.0 ml aliquot before internal standard addition. The second aliquot can be used if needed for rerun. Remember to add internal standard to the second aliquot, if used.

10.4.7. Store the remaining extracts in a freezer, protected from light, at -10° C or cooler for the remaining hold time then dispose in the proper waste stream.

10.5. Sample Analysis:

10.5.1. Analyze all sample extracts and QC using a Gas Chromatograph equipped with an Electron Capture Detector.

10.5.2. A detect is considered to be positive if the quantitation amount is greater than the reporting limit for that compound. When a positive detect is found then the sample is run on a second dissimilar confirmation column. The blanks, LCS, and MS values are based on the primary column. If the results from this column

are out of acceptable range due to matrix interferences or other problems, the results may be reported from the confirmatory column provided calibration criteria are met.

10.5.3. A single peak analyte is identified as positive if detected within its appropriate retention time window on both columns.

10.6. Dilutions:

10.6.1. Upon analysis of the extract, if a target compound response is greater than that of the highest standard of the calibration curve, the sample must be diluted with the final extraction solvent (MTBE) so that, upon analyzing the dilution (in a valid analysis sequence), the target response is between the lowest concentration standard (or the reporting limit, whichever is higher) and the highest concentration standard.

10.7. PT Study:

10.7.1. Once every 12-month period a PT study must be performed. An accredited testing facility will send the Laboratory an ampule for the compounds of interest listed in this SOP. The testing facility will send direction on how perform the dilutions necessary for the Analyst to spike into a sample. (Note: Please include a copy of instructions from the facility in the batch folder.)

11. Calculations

11.1. Relative Response Factor (*RRF*):

11.1.1. Calculate the relative response factors (*RRF*) for each target compound relative to the appropriate internal standard (i.e., standard with the nearest retention time) using the following equation:

$$RRF = \frac{A_x C_{is}}{A_{is} C_x}$$

11.1.2. Where:

RRF = Relative response factor
A_x = Area of the peak for the compound to be measured
A_{is} = Area of the peak for the internal standard
C_{is} = Concentration of internal standard spiking mixture
C_x = Concentration of the compound in the calibration standard

11.1.3. NOTE: The equation above is valid under the condition that the volume of internal standard spiking mixture added in all field and QC analyses is the same from run to run, and that the volume of sample extract and QC sample extract introduced into the GC is the same for each analysis. C_{is} and C_x must be in the same units.

11.2. Mean Relative Response Factor ($\overline{RRF}$):

11.2.1. Calculate the mean RRF ($\overline{RRF}$) for each compound by averaging the values obtained at the five concentrations using the following equation:

$$\overline{RRF} = \sum_{i=1}^{n} \frac{x_i}{n}$$

11.2.2. Where:

$\overline{RRF}$ = Mean relative response factor
x_i = RRF of the compound
n = Number of values

11.3. Percent Relative Standard Deviation (*%RSD*):

11.3.1. Using the RRFs from the initial calibration, calculate the *%RSD* for all target compounds using the following equations:

$$\%RSD = \frac{\delta_{n-1}}{\overline{RRF}} \; x\; 100$$

and

$$\delta_{n-1} = \sqrt{\sum_{i=1}^{n} \frac{(RRF_i - \overline{RRF})^2}{n-1}}$$

11.3.2. Where:

δ_{n-1} = Sample standard deviation of initial response factors (per compound)
RRF_i = Relative response factor at a concentration level
$\overline{RRF}$ = Mean of initial relative response factors (per compound)
n = Number of values

11.4. First Order Linear Regression Response Equation

$$Y = ax + b$$

This rearranges to:

$$x = Y - b/a$$

11.4.1. Where:

Y = Instrument response
a = Slope of the line
b = Intercept
x = Concentration in the extract or standard

11.4.2. For an internal standard calibration:

$$\frac{A_x}{A_{is}} = a\left(\frac{C_x}{C_{is}}\right) + b$$

11.4.3. Where:

A_x = Area of the peak for the compound to be measured
A_{is} = Area of the peak for the internal standard
C_{is} = Concentration of internal standard spiking mixture
C_x = Concentration of the compound in the calibration standard
a = Slope of the line
b = Intercept

11.4.4. This rearranges to:

$$C_x = C_{is}\left(\left(\frac{A_x}{A_{is}}\right) - \left(\frac{b}{a}\right)\right)$$

11.5. Second Order Quadratic Fit Equation

11.5.1. $Y = ax^2 + bx + c$

11.5.2. Where:

Y = Instrument response
a = Slope of the line
b = Intercept
c = constant
x = Concentration in the extract or standard

11.5.3. Subtract Y from c to get modified equation $0 = ax^2 + bx + c$

11.5.4. Solve for x using the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

11.5.5. A positive and negative value will be generated. Use positive value.

11.5.6. For an internal standard calibration:

$$\frac{A_x}{A_{is}} = a\left(\frac{C_x}{C_{is}}\right) + b$$

11.5.7. Where:

A_x = Area of the peak for the compound to be measured
A_{is} = Area of the peak for the internal standard
C_{is} = Concentration of internal standard spiking mixture
C_x = Concentration of the compound in the calibration standard
a = Slope of the line
b = Intercept

11.5.8. This rearranges to:

$$C_x = C_{is}\left(\left(\frac{A_x}{A_{is}}\right) - \left(\frac{b}{a}\right)\right)$$

11.6. Relative Retention Times (*RRT*):

11.6.1. Calculate the *RRT*s for each target compound over the initial calibration range using the following equation:

$$RRT = \frac{RT_c}{RT_{IS}}$$

11.6.2. Where:

RT_c = Retention time of the target compound
RT_{IS} = Retention time of the internal standard

11.7. Mean Relative Retention Time:

$$\overline{RRT} = \sum \frac{RRT}{n}$$

11.7.1. Where:

$\overline{RRT}$ = Mean retention time for target compound
RRT = Retention time for the target compound
n = number of values

11.8. Dilution Factor

11.8.1. When dilutions are required, sample extracts are diluted and a dilution factor (DF) calculated. If the sample volume is not exactly 50 ml, that must also be factored into the DF as follows:

$$DF = \frac{V_f}{V_{aliquot}} * \frac{V_s}{V_{ideal}}$$

11.8.2. Where:

DF = Dilution factor
V_f = Final volume after dilution
$V_{aliquot}$ = Amount of extract diluted
V_s = Actual sample volume
V_{ideal} = Ideal sample volume of 40 ml

11.8.3. If there is no dilution performed and a sample of exactly 40 ml is used, DF = 1.

11.9. Percent Drift, %Drift

$$\%\text{Drift} = \frac{(\text{Concentration}_{\text{Calculated}} - \text{Concentration}_{\text{Expected}})}{\text{Concentration}_{\text{Expected}}} * 100$$

11.9.1. Where:

Concentration $_{\text{Calculated}}$ = Concentration calculated from result
Concentration $_{\text{Expected}}$ = Theoretical concentration of the standard

11.10. Sample Concentration Calculation for Mean Relative Response Factor Calibrations ($\overline{RRF}$):

$$C_x = \frac{A_x C_{is} DF}{A_{is} \overline{RRF}}$$

11.10.1. Where:

C_x = Compound concentration
A_x = Area of the compound to be measured
A_{is} = Area of the internal standard
C_{is} = Concentration of the internal standard spiking mixture,
$\overline{RRF}$ = Mean relative response factor from the initial calibration

DF = Dilution factor. If 40 ml sample and no dilution is performed, DF = 1

11.10.2. NOTE: The equation above is valid assuming a consistent volume and concentration of the internal standard spiking solution throughout calibration and sample analysis.

11.11. Alternate Sample Concentration Calculation using linear regression:

11.11.1. Utilizing linear regression calculation 11.4 or 11.5 sample concentrations for linear regression or quadratic fit internal standard calibrations are calculated as :

$$C_x = C_{is}\left(\frac{\left(\frac{A_x}{A_{is}}\right) - b}{a}\right) * DF$$

11.11.2. Where:

A_x = Area of the peak for the compound to be measured
A_{is} = Area of the peak for the internal standard
C_{is} = Concentration of internal standard spiking mixture
C_x = Concentration of the compound in the calibration standard
a = Slope of the line
b = Intercept
DF = Dilution factor. If 40 ml sample and no dilution is performed, DF = 1

11.11.3. This rearranges to:

$$C_x = C_{is}\left(\left(\frac{A_x}{A_{is}}\right) - \left(\frac{b}{a}\right)\right)*\text{DF}$$

11.12. LPC Calculations:

11.12.1. Sensitivity:

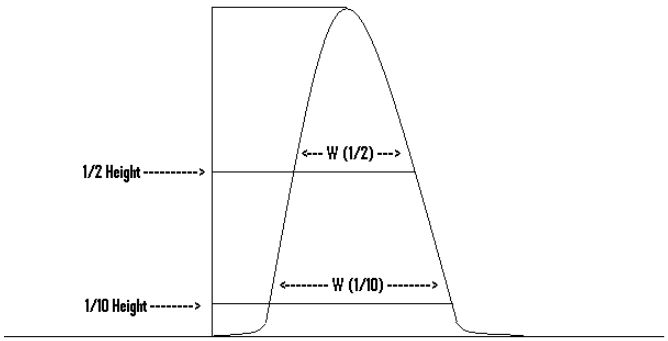
11.12.1.1. Instrument sensitivity is determined by comparing the LPC peak height of the weakest responding analyte, Monochloroacetic acid, in the LPC to signal noise. The height of this peak must be 3 times greater than the largest noise peak.

$$\frac{S}{N} = \frac{\mu V_{Analyte}}{\mu V_{Noise}}$$

11.12.2. Chromatographic Performance (Peak Gausian Factor – PGF):

11.12.2.1. The PGF is calculated on Bromochloroacetic acid in the LPC chromatogram. The PGF is equal to 1.83 times the ratio of that peak's half-

height width and the tenth height peak width:



Peak Gaussian Factor - Measuring width at half peak height - W (1/2) and one tenth height - W (1/10)

11.12.2.2. $PGF = 1.83\left(\frac{W_{1/2}}{W_{10}}\right)$

11.12.2.3. Where:

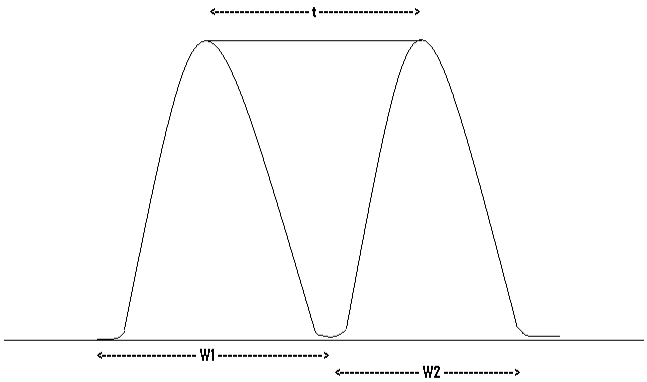
PGF = Peak Gaussian Factor

$W_{½}$ = the peak width at ½ height from base in seconds

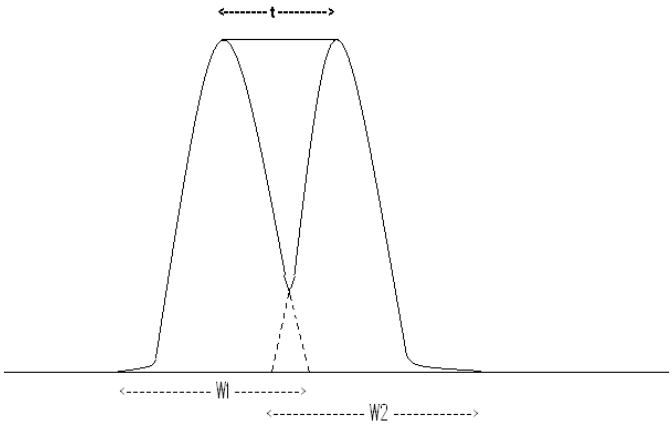
$W_{1/10}$ = the peak width at $^{1}/_{10}$ height from base in seconds

11.12.3. Column Performance (Resolution):

11.12.3.1. Column performance is determined by calculating the resolution factor between Chlorobromoacetic acid and 2,3-DBPA, in the LPC.



Column Performance - Peak Resolution for Resolved Peaks



Column Performance - Peak Resolution for Overlapping Peaks

11.12.3.2. Resolution between two peaks is determined by dividing the difference in the peak apex retention times by the average of the widths of the two peaks at the baseline. If the peaks overlap as in the second example above, estimate the peak widths as shown:

$$R = \frac{t}{\left(\frac{W1 + W2}{2}\right)}$$

11.12.3.3. Where:

R = Resolution between two peaks
t = the difference in elution times between the two peaks
W1, W2 = the peak widths at the baseline of the two peaks

11.11.4 LPCs must be measured with a ruler or other straight edge to mark time values on the chromatograms and calculated manually using equations from section 11.12.

Alternatively, Total Chrom or equivalent chromatography software or the values on the Total Chrom LPC System Suitability Report may be used to calculate LPC results.

12. Waste Management

12.1. See GA EPD Laboratory SOP-EPD Laboratory Waste Management Standard Operating procedures, SOP6-015, online revision.

13. References

13.1. EPA Method 552.2, Revision 1.0, 1995

13.2. GA EPD Laboratory SOP's- Initial Demonstration of Capability SOP 6-001, online revision and/or Continuing Demonstration of Capability SOP 6-002, online revision.

13.3. GA EPD Laboratory SOP- EPD Laboratory Procedures for Control Charting and Control and Control Limits SOP, SOP 6-025, online revsion.

13.4. GA EPD Laboratory SOP- EPD Laboratory Waste Management SOP, SOP 6-015, online revision.

13.5. Manual for the Certification of Laboratories Analyzing Drinking Water, EPA/815-R-05-004, January 2005

13.6. GA EPD Laboratory SOP- Determination of Method Detection Limit, Method Detection Limit SOP 6-007, online revision.

13.7. GA EPD Laboratory Quality Assurance Plan, online revision.

13.8. GA EPD Laboratory Safety/Chemical Hygiene Plan & Fire Safety Plan, online revision.

14. Practical Reporting Limits (RLs), Precision and Accuracy Criteria, and Quality Control Approach

14.1. Refer to Appendix A, Table A.1 for precision and accuracy criteria.

Table 14.1. 1 - RLs for EPA Method 552.2

Parameter/Method	Analyte	Matrix (WATER)	
		RL	Unit
552.2	Monochloroacetic acid	2.0	µg/l
	Monobromoacetic acid	1.0	µg/l
	Dichloroacetic acid	1.0	µg/l
	Trichloroacetic acid	1.0	µg/l
	Dibromoacetic acid	1.0	µg/l

Table 14.1. 2 - Summary of Calibration and QC Procedures for EPA Method 552.2

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
EPA Method 552.2	Haloacetic acids	Seven - point initial calibration for all analytes	Initial calibration prior to sample analysis	RSD for all analytes ≤ 20% or a linear, least squares regression r ≥0.985 ($r^2 \geq 0.970$)	Correct problem then repeat initial calibration	
		Second-source Calibration verification (ICV)	Once per initial calibration	All analytes within ±30% of expected value	Correct problem then repeat initial calibration	
		Retention time window calculated for each analyte	Once per year or after major maintenance that would affect RTs.	±3 times standard deviation for each analyte retention time from study conducted over the course of a day		

Table 14.1. 2 - Summary of Calibration and QC Procedures for EPA Method 552.2

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
EPA Method 552.2	Haloacetic acids	Retention time window update	Must be done every analytical sequence	First CCC of each sequence and the first CCC of each 24 hour period.	Correct problem then reanalyze all samples since the last retention time check	
		Calibration verification (CCC)	Beginning each analysis sequence, prior to the analysis of samples, after every 10 samples, and at the end of the analysis sequence	All analytes within ± 30% of expected value.	Rerun CCC once. If passes use sample results. If does not pass correct problem repeat initial calibration verification, if necessary and reanalyze all samples since last successful calibration verification	
		Laboratory Performance Check (LPC)	Prior to the analysis of each sample sequence	See 8.5.2. for LPC criteria	Correct problem and reanalyze	
		IDC-Demonstrate ability to generate acceptable accuracy and precision using four replicate analyzes of a QC check sample + a blind & a blank. Analyst must also produce a passing MDL study with 7 MDL spikes and 7 MDL blanks.	Once per analyst	All analytes with ± 20% of expected values. RPD < 20%. **See section 9.9 for MDL requirements**	Locate and fix problem then rerun or reextract demonstration for those analytes that did not meet criteria	
		CDC – Continuing Demonstration of Capability	Required every Six Months after IDC for each analyst	See Appendix A, Table A.1	Locate and fix problem then rerun or reextract demonstration for those analytes that did not meet criteria	
		Method Blank Solvent Blank	One per analytical batch	No analytes detected > RL.	Analyze second extract aliquot. If this does not pass correct problem then re-analyze or re-extract the blank, LCS/LCSD and all samples in the affected batch.	

Table 14.1. 2 - Summary of Calibration and QC Procedures for EPA Method 552.2

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
EPA Method 552.2	Haloacetic acids	LCS/LCSD for all analytes	One LCS/LCSD per analytical batch	QC acceptance criteria, see Appendix A	If an LCS/LCSD fail, it may be reran at least 24 hours from the original run or up to 12 hours from the end of the sequence. Then if the rerun of the LCS/LCSD result with a failure then all samples associated with the batch must be re-extracted.	
		Surrogate spike	Every sample, spiked sample, standard and method blank	QC acceptance criteria, see Appendix A	Analyze second extract aliquot. If this does not pass, correct problem then re-extract and re-analyze sample	
		Internal Standard	Every sample, spiked sample, standard, and method blank	± 30% deviation from expected value	Reanalyze extract. If it fails the second analysis, re-extract sample and reanalyze	
		Matrix Spike (MS/MSD)	Minimum frequency of 10% samples. One MS/MSD per batch of 1-10 samples. Two MS/MSD per batch of 11-20 samples.	QC acceptance criteria, see Appendix A	Flag QC sample report.	
		Second-column confirmation	100% for all positive results	If used for quantitation same as for initial or primary column analysis	Same as for initial or primary column analysis	
		MDL study	Once per year or after major maintenance of the instrument	All Spiked MDLs must have a value greater than 0. Minimum Detection Limits established shall be < the RLs in Table 14.1	Re-do MDL Study	

Table 14.1. 2 - Summary of Calibration and QC Procedures for EPA Method 552.2

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
EPA Method 552.2	Haloacetic acids	MDL analysis	Once per batch or as needed to acquire data points per SOP 6-007, online revision	All Spiked MDLs must have a value greater than 0. All other QC in the MDL blank and MDL sample (i.e. Surrogate Spike or Internal Standard, etc. if included) must meet established criteria	Correct problem and re-run the MDL sample or MDL blank once and initiate a corrective action. If the re-run fails a second time, do not use MDL data. Update corrective action, and use associated sample data	
		Results reported between MDL & RL	none	none	None	
		Quarterly ICV	Once per Quarter	All analytes within ± 30% of expected value	Correct problem then repeat calibration	
		Residual Chlorine Check	Whenever needed. If collector does not check residual chlorine.	Must be checked for every sample.	Check residual chlorine levels and add information to extraction sheet.	

15. Associated Labworks Test Codes

15.1. Parent Test Code

15.1.1. $552 – Analysis results

15.2. Extraction Test Code

15.2.1. 552E – 60 mL amber glass vial – Liquid/ Liquid extraction

15.3. QC Test Codes

15.3.1. $B_552 – Extraction Blank Results

15.3.2. $LA552 – LCS/LCSD Spike Amount

15.3.3. $LS552 – LCS Results

15.3.4. $LS552 – LCSD Results

15.3.5. $LR552 – LCS Percent Recovery

15.3.6. $L2552 – LCSD Percent Recovery

15.3.7. $LP552 – LCS/LCSD Precision

15.3.8. $A_552 – MS/MSD Spike Amount

15.3.9. $S_552 – MS Results

15.3.10. $D_552 – MSD Results

15.3.11. $R_552 – MS Percent Recovery

15.3.12. $RD552 – MS Percent Recovery

15.3.13. $P_552 – MS/MSD Precision

15.3.14. $MA552 – MDL Spike Amount

15.3.15. $ML552 – MDL Results

15.3.16. INSTR-552 – Instrument associated with batch

Appendix A – Quality Assurance Criteria for Method EPA 552.2

QC Type	Analyte	Accuracy (%R) LCL - UCL	Precision (%RPD)
LCS/LCSD*	Monochloroacetic acid	71 - 127	30
	Monobromoacetic acid	72 - 124	30
	Dichloroacetic acid	72 - 129	30
	Trichloroacetic acid	70 - 130	30
	Dibromoacetic acid	70 - 130	30
Surrogate**	2-BPA	70 – 130	NA
	2-BPA (as µg/L)	3.5 – 6.5	NA
MS/MSD***	All Analytes	70 – 130	30

*LCS/LCSD recovery based on control charts of data collected from 12/31/2018 to 01/01/2021. The EPD sets a static LCS/LCSD precision of 0-30% RPD.

**EPA Method 552.2 sets a static recovery range of 70-130% for the surrogate.

***EPA Method 552.2 sets a static limit of 70-130% recovery for Matrix Spike analytes. The EPD Laboratory sets a static precision of 0-30% RPD for MS/MSD pairs.

Updates:

Appendix A added. Updated for online revision.