



Determination of Haloacetic Acids and Dalapon in Drinking Water by SPE and GC/ECD*

UCT Part Numbers:

EUQAX156 (Quaternary Amine with Cl⁻ counter ion, 6 mL cartridge)**

CLTTP050 (CLEAN-THRU[®] Tips)

AD0000AS (cartridge adapter)

RFV0075P (75 mL reservoir)

ECSS25K (sodium sulfate anhydrous, ACS, 60 mesh)

Method 552.1 Revision 1.0

Summary

Method 552.1 is a gas chromatographic method for determination of haloacetic acid compounds, including Dalapon in drinking water, ground water, raw water and other waters at any intermediate stage of treatment. This method is used over the concentration ranges typically found in drinking water ranging from less than 1 to over 50 µg/L. The observed MDL's may vary according to the particular matrix analyzed and the specific instrumentation employed.

In this procedure, a 100 mL sample of water is adjusted to pH 5 and then extracted using an anion exchange cartridge. Method 552.1 suggests the use of polymeric-based anion exchange resins. This application uses silica-based anion exchange, therefore the conditioning steps have been modified to accommodate this silica-based sorbent. Exceptional recoveries are reported as shown in the data below.

Haloacetic Acids

The following RCRA compounds are determined by method 552.1 in water

Analyte	Abbreviation	CASRN
Monochloroacetic acid	MCAA	79-11-8
Dichloroacetic acid	DCAA	79-03-9
Trichloroacetic acid	TCAA	66-03-9
Monobromoacetic acid	MBAA	79-08-3
Bromochloroacetic acid	BCAA	5589-96-8
Dibromoacetic acid	DBAA	631-64-1
Dalapon		75-99-0

Safety

- The toxicity or carcinogenicity of each reagent used in this method has not been defined

Sample Collection, Preservation, and Storage

- Collect samples in all glass amber bottles with PTFE lined screw caps
- Prior to sample collection add ammonium chloride (NH_4Cl) to the bottles to produce a concentration of 100 mg/L
- Alternatively, add 1.0 mL of a 10 mg/mL aqueous solution of NH_4Cl during collection then shake well
- Refrigerate at 4°C or keep on ice and away from light until extraction
- Analyze within 48 hours after collection

Interferences

Care and attention to potential interferences will result in better analysis

- Method interferences may be caused by contamination of solvents, reagents, glassware or other lab apparatus
- Glassware must be scrupulously clean
- Heat all glassware except volumetric flasks in a muffle oven at 400°C. Thermally stable compounds such as PCB's may not be eliminated by this treatment. Thorough rinsing with reagent grade acetone may be substituted for the heating step
- Glassware must be rinsed with 1:9 HCl prior to use
- Reduced analyte recoveries may be observed in high ionic strength matrices particularly waters containing sulfate concentrations above 200 mg/L
- Improved recoveries may be obtained by sample dilution but at the expense of higher MDL's
- Tribromoacetic acid has not been included because of problems associated with stability and chromatography
- Organic acids and phenols, especially chlorinated compounds, are the most direct potential interferences with this method
- For each set of samples analyzed, the reagent blank concentration values exceeding 0.1 $\mu\text{g/L}$ can be subtracted from the sample concentration
- Interfering contamination may occur when a sample with a low concentration of analytes is analyzed following a sample of relatively high concentration. Routine between-sample rinsing of the sample syringe and associated equipment with methyl- *t*-butyl ether (MTBE) can minimize sample cross-contamination

Standard Stock Solution

Prepare a stock solution of each analyte of interest at a concentration of 1-5 mg/mL in MTBE. Method analytes may be obtained as neat materials or ampulized solutions (>99% purity) from commercial suppliers

Prepare Primary Dilution Standard (PPDS)

Prepare PPDS solutions by combining and diluting stock standard solutions with methanol. Prepare stock standard solutions in the 1-2 mg/mL range for all analytes including the surrogate. Aliquots of each stock standard solution (approximately 50-250 µL) are added to 100 mL methanol to yield a primary dilution standard containing the following approximate concentrations of analytes

Analyte	Concentration, µg/mL
Monochloroacetic Acid (MCAA)	3
Monobromoacetic acid (MBAA)	2
Dalapon	2
Dichloroacetic acid (DCAA)	3
2-bromopropionic acid ^b	1
Trichloroacetic acid (TCAA)	1
Bromochloroacetic acid	2
Dibromoacetic acid	1

The primary dilution standards are used to prepare calibration standards of at least three concentration levels (optimally five) of each analyte with the lowest standard being at or near the MDL of each analyte. The concentrations of the other standards should define a range containing the expected sample concentrations or the working range of the detector.

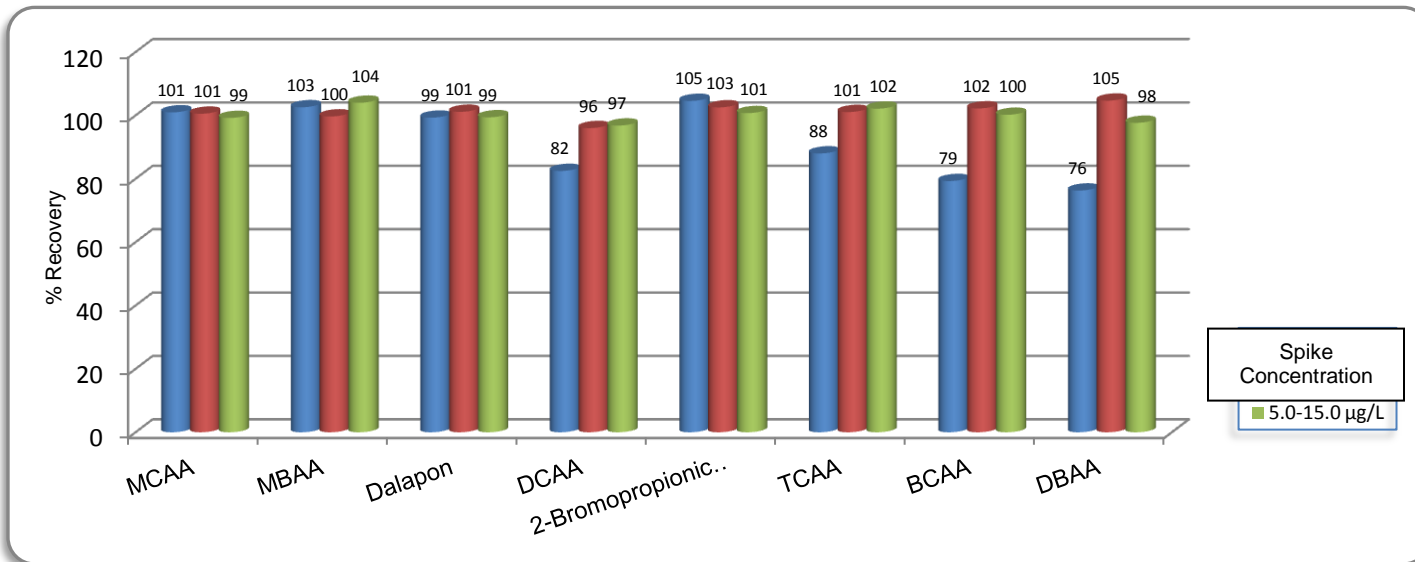
Calibration Standards

- Perform by extracting calibration standards in fortified reagent water using the SPE cartridge
- Prepare a five-point calibration curve 100- mL reagent water samples at pH 5 with 20, 50, 100, 250, and 500 µL of the primary dilution standard
- Analyze each calibration standard in triplicate including a reagent water blank
- Include the surrogate 2-bromopropionic acid with the calibration standards in the table

Internal Standard Fortifying Solution

- Prepare a solution of 1,2,3-trichloropropane at 1 mg/mL by adding 36 µL of the neat material to 50 mL of MTBE. From this stock standard solution, prepare a primary dilution standard at 10 mg/L by the addition of 1-100 mL MTBE

Analyte Recovery at Various Spike Concentrations (N=7)



Procedure

1. Cartridge Conditioning

- Assemble a glass block manifold system
- Place **EUQAX156** cartridge(s) in the bulkhead fittings of the vacuum manifold. If nylon fittings are used, Clean-Thru[®] tips are recommended to prevent damage to the fittings by sulfuric acid
- Attach adapters and reservoirs to the cartridges
- Add a 10 mL aliquot of methanol (MeOH) to the cartridge
- Draw slowly through at 2 mL/min flow
- Add 10 mL of reagent water then slowly draw through

Note: After the conditioning steps do not let the cartridge go dry before addition of sample

2. Sample Extraction

- Check the sample pH (preferably with a pH meter) to assure pH 5 ± 0.5
- Add 250 μL of the surrogate primary dilution standard to water sample
- Add the 100 mL sample to the cartridge while drawing through under vacuum
at 2 mL/minute
- After the sample has passed through the cartridge, draw 10 mL of MeOH through the cartridge to dry the sorbent

3. Cartridge Elution

- a) Disassemble the vacuum manifold and insert a screw cap culture tube
- b) Add 2 mL of 10% H₂SO₄/MeOH to the cartridge
- c) Elute at a rate of 1.5 mL/minute (slow drip)
- d) Repeat with a second aliquot of 2 mL of 10% H₂SO₄/MeOH

4. Derivatization and Solvent Partition

- a) To each of the elutant samples from 3) d) add 2.5 mL of MTBE
- b) Agitate in a vortex mixer for 5 seconds
- c) Place the culture tubes containing the MTBE in a heating block at 50° C for 1 hour
- d) Remove from heating block and add to each tube 10 mL of a 10% solution of sodium sulfate (NaSO₄)
- e) Agitate for 10 seconds on a vortex mixer
- f) Allow the phases to separate for 5 minutes
- g) Transfer the upper MTBE layer to a 15 mL graduated conical centrifuge tube
- h) Add another 1 mL portion of MTBE
- i) Agitate using a vortex mixer, allow to settle then transfer with a Pasteur pipette to the other MTBE collected in step g)
- j) Add 200 µL IS to each extract then additional MTBE to bring the final volume to 5 mL
- k) Transfer a portion of the extract to capped GC vials
- l) Sample is ready for analysis by GC-ECD

5. Sample Analysis—Gas Chromatography

- a) Inject 2 µL using the recommended conditions listed below

GC/ECD Conditions

GC: Agilent 6890N coupled with ECD, equipped with 7683 auto sampler and Chemstation software for data acquisition and analysis. Other instruments may be used
GC capillary column: Restek Rtx®-1701, 30m x 0.25mm x 0.25µm

Injector: 2 µL splitless injection at 200 °C, with a split delay of 0.5 min.

Liner: 4 mm splitless gooseneck, 4mm ID x 6.5mm OD x 78.5mm (UCT **GCLGN4MM**)

Oven temperature program:

- Initial oven temperature of 55 °C
- hold for 5 minutes
- ramp at 7 °C/min to 115 °C
- ramp at 40 °C/min to a final temperature of 280 °C
- hold for 2.3 minutes
- Total run time 20 minutes

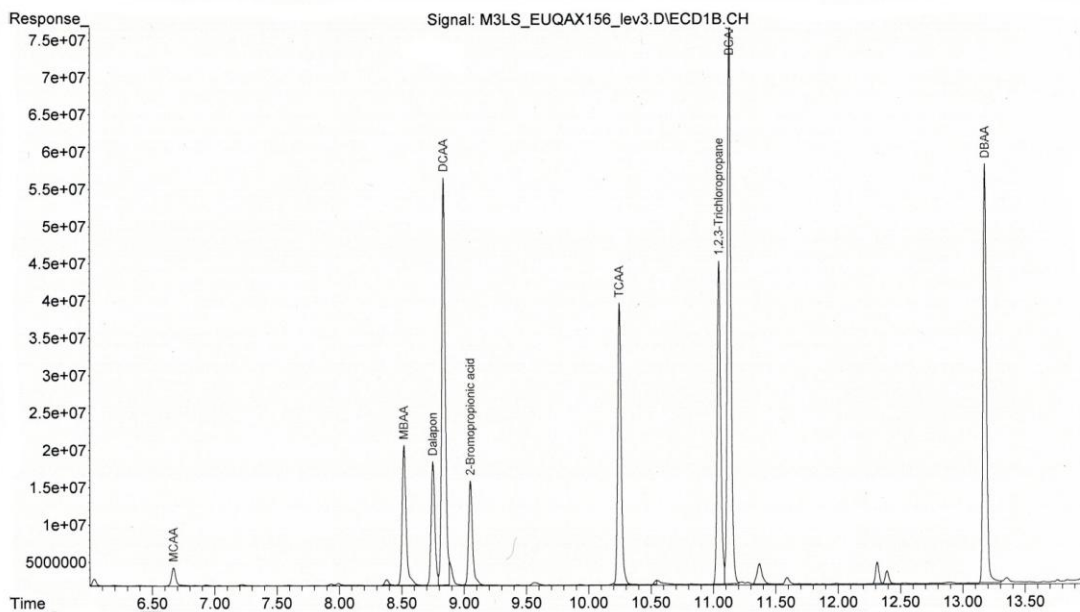
Carrier gas: He flow of 1.5 mL/min

ECD temperature: 280 °C

Make up: N₂ at 30 mL/min

Date rate: 20 Hz, save data from 6 to 14 minutes

Chromatogram Showing Elution of Haloacetic Acids



Analyte Elution Order	RSD% @ 0.5-1.5 µg/L	MDL µg/L @ 0.5-1.5 µg/L	RSD% @ 2.5-7.5 µg/L	RSD% @ 5.0-15.0 µg/L
MCAA	4.6	0.22	1.9	2.2
MBAA	3.2	0.10	1.6	2.0
Dalapon	1.3	0.04	1.0	1.0
DCAA	1.5	0.06	1.1	1.5
2-bromopropionic acid (surrogate)	2.6	0.04	0.6	1.7
TCAA	1.9	0.03	2.2	1.0
1,2,3-trichloropropane (IS)				
BCAA	10	0.25	2.4	3.4
DBAA	10	0.12	2.1	7.6

*For complete details on Method 552.1, August 1992, the analyst is referred to: Hodgeson, Jimmie W, Becker, David, (Technology Applications, Inc., "Determination of Haloacetic acids And Dalapon In Drinking Water by Ion-Exchange Liquid-Solid Extraction and Gas Chromatography with an Electron Capture Detector", Environmental Monitoring Systems Laboratory,, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH 45268

**Other cartridge and sorbent masses are available from UCT