standing committee of analysts

The Determination of Haloacetic Acids in Raw and Potable Waters

Methods for the Examination of Waters and Associated Materials

June 2021

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Methods for the Examination of Waters and Associated Materials

This booklet contains two techniques for the determination of haloacetic acid compounds in waters

Method A using Gas Chromatography-Mass Spectrometry (GCMS)

Method B using Liquid Chromatography-Mass Spectrometry (LCMS)

Each method has been validated in only one laboratory and consequently details are included for information purposes only as an example of the type of procedures that are available to analysts. Information on routine multi-laboratory use of these methods would be welcomed to assess their full capabilities.

Whilst this booklet may report details of the materials actually used, this does not constitute an endorsement of these products but serves only as an illustrative example. Equivalent products are available and it should be understood that the performance characteristics of the method might differ when other materials are used. It is left to users to evaluate methods in their own laboratories.

Contents

About this series

Introduction

This booklet is part of a series intended to provide authoritative guidance on recommended methods of sampling and analysis for determining the quality of drinking water, ground water, river water and sea water, waste water and effluents as well as sewage sludges, sediments, soils (including contaminated land) and biota. In addition, short reviews of the most important analytical techniques of interest to the water and sewage industries are included.

Performance of methods

Ideally, all methods should be fully evaluated with results from performance tests. These methods should be capable of establishing, within specified or pre-determined and acceptable limits of deviation and detection, whether or not any sample contains concentrations of parameters above those of interest.

For a method to be considered fully evaluated, individual results from at least three laboratories should be reported. The specifications of performance generally relate to maximum tolerable values for total error (random and systematic errors) systematic error (bias) total standard deviation and limit of detection. Often, full evaluation is not possible and only limited performance data may be available.

In addition, good laboratory practice and analytical quality control are essential if satisfactory results are to be achieved.

Standing Committee of Analysts

The preparation of booklets within the series “Methods for the Examination of Waters and Associated Materials” and their continuing
revision is the responsibility of the Standing Committee of Analysts (established 1972 by the Department of the Environment). At present, there are eight working groups, each responsible for one section or aspect of water quality analysis. They are

1 General principles of sampling and accuracy of results
2 Microbiological methods
3 Empirical, Inorganic and physical methods
4 Metals and metalloids
5 Solid substances
6 Organic impurities
7 Biological, biodegradability and inhibition methods
8 Radiochemical methods

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, in co-operation with the working group and main committee. The names of those members principally associated with these methods are listed at the back of this booklet.

Publication of new or revised methods will be notified to the technical press. If users wish to receive copies or advanced notice of forthcoming publications or obtain details of the index of methods then contact the Secretary on the SCA’s web-page:-
http://www.standingcommitteeofanalysts.co.uk/Contact.html

Every effort is made to avoid errors appearing in the published text. If, however, any are found, please notify the Secretary. Users should ensure they are aware of the most recent version they seek.

Andy Fegan
Secretary
April 2021

Warning to users

The analytical procedures described in this booklet should only be carried out under the proper supervision of competent, trained analysts in properly equipped laboratories.

All possible safety precautions should be followed and appropriate regulatory requirements complied with. This should include compliance with the Health and Safety at Work etc Act 1974 and all regulations made under the Act, and the Control of Substances Hazardous to Health Regulations 2002 (SI 2002/2677). Where particular or exceptional hazards exist in carrying out the procedures described in this booklet, then specific attention is noted.

Numerous publications are available giving practical details on first aid and laboratory safety. These should be consulted and be readily accessible to all analysts. Amongst such publications are; “Safe Practices in Chemical Laboratories” and “Hazards in the Chemical Laboratory”, 1992, produced by the Royal Society of Chemistry; “Guidelines for Microbiological Safety”, 1986, Portland Press, Colchester, produced by Member Societies of the Microbiological Consultative Committee; and “Safety Precautions, Notes for Guidance” produced by the Public Health Laboratory Service. Another useful publication is “Good Laboratory Practice” produced by the Department of Health**.**

The Determination of Haloacetic Acids in Raw and Potable Waters

1 Introduction

Water disinfectants, such as chlorine, are used to protect public health. They attack, deactivate and kill all sorts of microorganisms that could threaten water consumer health. Disinfection is a major factor in reducing health risks from pathogens, however disinfection is a double-edged sword. Disinfectants themselves can react with naturally occurring organic materials in water to form unintended organic by-products which pose health risks.

When free chlorine is added to source waters containing natural organic material (NOM) chemical reactions will occur, which produce disinfection by-products (DBPs). NOM is a precursor for disinfection by-product formation. NOM in source waters are generally naturally occurring organic substances, such as humic and fulvic acids. These acids belong to a family of compounds having similar structure and chemical properties and are formed during the decomposition of vegetation.

Organic DBPs are formed when the organic matter remaining in the water after treatment reacts with the water disinfectant, e.g. chlorine. The production of organic DBPs is well understood, in fact there are over 500 organic DBPs that have been identified to date.

Disinfection By-Product Precursor in Water		**Disinfectant Added**		**Disinfection By-Products in Water**
Total Organic Carbon (TOC) - Natural Organic Matter (NOM) - Dissolved Organic Carbon (DOC), (TOC passing through a 0.45µm filter) - Algal Organic Matter - Effluent Organic Matter Bromide and Iodide Pollutants, etc.	**+**	Chlorine Chloramines Chlorine Dioxide Ozone	**=**	Trihalomethanes, Haloacetic acids, Chlorite, Chlorate, Bromate, Haloacetonitriles, Chloral hydrate, Cyanogen halides, Nitrosamines, Halonitromethanes, etc.

The most prevalent organic disinfection by-products are trihalomethanes, which have a set parametric value in the drinking water regulations and haloacetic acids.

Water companies are responsible for ensuring the drinking water they supply is clean and wholesome. Regulation 4 of the Water Supply (Water Quality) Regulations 2016 prescribes that to be regarded as wholesome, water must not contain excess concentrations or values of particular properties, elements, organisms and substances.

The monitoring requirements for all disinfection by-products in drinking water are derived from the Water Safety Plans (WSP) of each individual water company. The WSP's are based on extensive risk assessments and risk management plans in a water supply chain from catchment to consumer.

Haloacetic acids (HAAs) are compounds which consist of carboxylic acids containing chlorine and/or bromine in the place of one or more hydrogen atom. They are formed through the disinfection process of drinking water. Drinking water contaminated with haloacetic acids may cause irritation to eyes and skin and increase the risk of cancer.

The five most commonly produced HAAs are collectively referred to as the HAA_5 and are listed below:

Monochloroacetic acid (MCAA)	$ClCH_2COOH$
Dichloroacetic acid (DCAA)	$Cl_2CHCOOH$
Trichloroacetic acid (TCAA)	Cl_3CCOOH
Monobromoacetic acid (MBAA)	$BrCH_2COOH$
Dibromoacetic acid (DBAA)	$Br_2CHCOOH$

In addition to the HAA_5, four additional HAAs can be formed which are known in combination with the HAA_5 as the HAA_9. The four additional HAAs are:

Bromodichloroacetic acid (BDCAA)	$BrCl_2CCOOH$
Dibromochloroacetic acid (DBCAA)	$Br_2ClCCOOH$
Bromochloroacetic acid (BCAA)	$BrClHCCOOH$
Tribromoacetic acid (TBAA)	Br_3CCOOH

2,2-Dichloropropanoic acid, (Dalapon), is a colourless liquid with an acrid odour sold as sodium or magnesium salt. Dalapon is a selective herbicide used to control perennial grasses

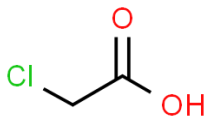
The methods listed have examples of target compound calibrations that are used to provide estimations of amounts of compounds present – the range of these calibrations may be adjusted accordingly to suit requirements.

* Note: this book in no way endorses a particular instrument manufacturer or supplier, this is listed as a guide only to the configuration set up in the specific analytical sections to enhance understanding.

2 Structures and description

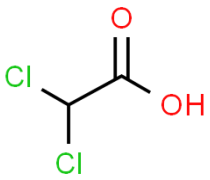
The following is a list of substances contained in this document, their structures, CAS numbers and other relevant information sources to aid in the use of this document

Monochloroacetic acid (MCAA)



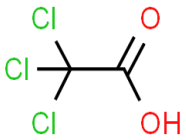
CAS: 79-11-8
Molecular weight: 94.49

Dichloroacetic acid (DCAA)



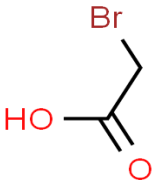
CAS: 79-43-6
Molecular weight: 128.94

Trichloroacetic acid (TCAA)



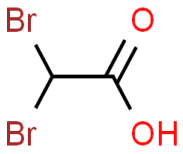
CAS: 76-03-9
Molecular weight:163.38

Monobromoacetic acid (MBAA)



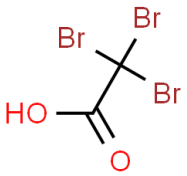
CAS: 79-08-3
Molecular weight:138.95

Dibromoacetic acid (DBAA)



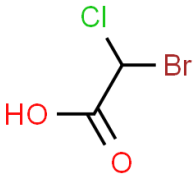
CAS: 631-64-1
Molecular weight:217.84

Tribromoacetic acid (TBAA)



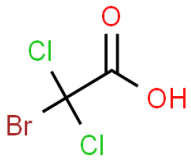
CAS: 75-96-7
Molecular weight:296.74

Bromochloroacetic acid (BCAA)



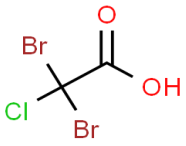
CAS: 5589-96-8
Molecular weight:173.39

Bromodichloroacetic acid (BDCAA)



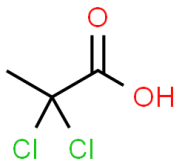
CAS: 71133-14-7
Molecular weight:207.83

Dibromodichloroacetic acid (DBCAA)



CAS: 5278-95-5
Molecular weight:252.29

Dalapon



CAS: 75-99-0
Molecular weight:142.96

3 Sample stability

Compound	Matrix / Stability time (Days)			Sample Container	Preservative	Comments	Number of replicates
	Drinking Water	Surface Water	Ground Water				
Monochloroacetic acid	7	21	No data available	Glass (Amber)	Sodium thiosulfate or ammonium chloride	Up to 10 days if using ammonium chloride preservative	12
Monobromoacetic acid	5	7	No data available	Glass (Amber)	Sodium thiosulfate or ammonium chloride	Up to 14 days if using ammonium chloride preservative	12
Dichloroacetic acid	14	28	No data available	Glass (Amber)	Sodium thiosulfate or ammonium chloride	No additional comments	12
Bromochloroacetic acid	14	28	No data available	Glass (Amber)	Sodium thiosulfate or ammonium chloride	No additional comments	12
Dibromoacetic acid	14	28	No data available	Glass (Amber)	Sodium thiosulfate or ammonium chloride	No additional comments	12
Dalapon	21	28	No data available	Glass (Amber)	Ammonium chloride	Data from one lab only - ALS - Elvington final	12
Trichloroacetic acid	21	28	No data available	Glass (Amber)	Sodium thiosulfate or ammonium chloride	No additional comments	12
Bromodichloroacetic acid	21	28	No data available	Glass (Amber)	Ammonium chloride	Data from one lab only - ALS - Elvington final	12
Dibromochloroacetic acid	21	28	No data available	Glass (Amber)	Ammonium chloride	Data from one lab only - ALS - Elvington final	12
Tribromoacetic acid	21	28	No data available	Glass (Amber)	Ammonium chloride	Data from one lab only - ALS - Elvington final	12

4 References

Water quality — Sampling Part 3: Preservation and handling of water samples (ISO 5667-3:2012).

Standing Committee of Analysts. The Stability and Preservation of Drinking, Ground and Surface Water Samples 2018, November 2018.

United States Environmental Protection Agency Publication No EPA 815-B-03-002. EPA Method 552 Revision 1.0. July 2003. Determination of Haloacetic Acids and Dalapon in Drinking Water by Liquid-Liquid Microextraction, Derivatization, and Gas Chromatography with Electron Capture Detection.

Study into the formation of disinfection by-products of chloramination, potential health implications and techniques for minimisation, First Report, Cranfield University

A The Determination of Haloacetic Acids Raw and Potable Waters by Gas Chromatography-Mass Spectrometry.

A1 Performance characteristics of the method

A1.1	**Substances determined**	Bromoacetic acid, Bromochloroacetic acid, Bromodichloroacetic acid, Chloroacetic acid, Dalapon, Dibromoacetic acid, Dibromochloroacetic acid, Dichloroacetic acid, Tribromoacetic acid, Trichloroacetic acid
A1.2	**Type of sample**	Raw waters (ground and surface), potable waters.
A1.3	**Basis of method**	Liquid-liquid micro-extraction, followed by derivatization and capillary GC using MS detection.
A1.4	**Range of application**	Typically, up to 125µg L^{-1}
A1.5	**Standard deviation**	See Table A1**.**
A1.6	**Limit of quantitation**	Typically, 1µg L^{-1}, based on a low level standard (2µg L^{-1}). See Table A1.
A1.7	**Bias**	See Table A1.

A2 Principle

An aliquot of sample, after dilution if required, and the addition of internal standard, sulfuric acid and sodium sulfate is extracted with methyl tert-butyl ether (MTBE). Haloacetic acids that have partitioned into the organic phase are converted to their methyl esters by the addition of acidic methanol and heat. The sample extract containing methylated acids is separated from acidic methanol by adding aqueous sodium sulfate solution and is then ready for analysis.

Target analytes are identified and quantified by capillary column gas chromatography using a mass spectrometer detector (GC/MS). Analytes are quantified using procedural standard calibration.

A3 Interferences

Any co-extracted material which has a GC retention time similar to any of the above analytes and which gives a detector response at the monitored masses will interfere.

A4 Hazards

Analysts using this method should familiarise themselves with the COSHH and risk assessments for the analysis. See Safety Data Sheet (SDS) provided by the chemical manufacturer/supplier.

A4.1 Methanol, CH_3OH, CAS No. 67-56-1

A4.2 Methyl tert-butyl ether (MTBE), $(CH_3)_3CCH_3$, CAS No. 1634-04-4

A4.3 Certified Reference Materials

A4.4 Sulfuric acid, H_2SO_4, CAS No. 7664-93-9

A4.5 Helium

A4.6 Syringes

Adequate care should be taken when handling syringes in order to avoid injecting one-self. Damaged and broken syringes should be disposed of in a safe manner, preferably to a “sharps” canister.

A5 Reagents

All reagents should be of sufficient purity that they do not give rise to interferences during the analysis and distilled, deionised or similar grade water should be used throughout. A procedural blank should be run with each batch of samples to check for interferences. All solutions should be mixed well prior to use.

A5.1 Methanol - free from interferants

A5.2 Methyl tert-butyl ether (MTBE) - free from interferants

A5.3 Ammonium chloride

A5.4 Sodium thiosulfate pentahydrate

A5.5 Magnesium sulfate heptahydrate

A5.6 Calcium nitrate tetrahydrate

A5.7 Sodium sulfate

Interferences have been observed when lower quality grades have been used. If interferences are observed, it may be necessary to heat the sodium sulfate at 450°C for 4 hours to remove phthalates and other interfering organic substances. Store in a capped glass bottle rather than a plastic container. Substitution with sodium chloride

is not permitted. Sodium chloride solutions can contain trace levels of bromide, which can promote the formation of brominated haloacetic acids.

A5.8 Sulfuric acid, concentrated

Substitution with hydrochloric acid (HCl) is not permitted. HCl solutions can contain trace levels of bromide, which can promote the formation of brominated haloacetic acids.

A5.9 Water, ultra-pure grade

Ultra-pure grade water should contain no measurable amounts of the compounds of interest. Millipore 'MilliQ SP' water has been found to be satisfactory. This water is used to prepare aqueous stock, intermediate and working solutions.

A5.10 Water, calibration standard matrix water, a mineral water or equivalent

Water should contain no measurable amounts of the compounds of interest. This water is used to prepare the calibration matrix water.

A5.11 Ammonium chloride solution, NH_4Cl, 10% $^{w}/_{v}$, sample preservative solution

Prepared by dissolving 5.00±0.01g ammonium chloride in 50mL of ultra-pure water in a graduated flask. This is used as sample preservative for all samples and to produce the calibration and AQC matrix waters. Store at ambient room temperature or under refrigeration at 1-5°C. Shelf life: 6 months.

A5.12 Sodium sulfate solution, Na_2SO_4, 10% $^{w}/_{v}$

Prepared by dissolving 50.0±0.1g sodium sulfate in 500mL of ultra-pure water in a volumetric flask. Store at ambient room temperature or under refrigeration at 1-5°C. Shelf life: 6 months.

A5.13 Sulfuric acid in methanol solution, 10% $^{v}/_{v}$

Prepared by adding 10mL of concentrated sulfuric acid, dropwise (due to heat evolution), to approximately 60mL of methanol contained in a 100mL volumetric flask. Mix, let cool and dilute to the 100mL mark with methanol. Store at ambient room temperature. Shelf life: 1 day. Prepared fresh for each extraction batch and discard any excess after use.

A5.14 AQC matrix water, synthetic tap water, stock solution

Prepared by dissolving 0.90±0.01g sodium thiosulfate, pentahydrate, 2.00±0.01g magnesium sulphate heptahydrate and 2.00±0.01g Calcium nitrate tetrahydrate in 500mL of ultra-pure water in a graduated flask. This stock solution is used for the preparation of the AQC matrix water, working solution. Store under refrigeration at 1-5°C. Shelf life: 1 month.

A5.15 AQC matrix water, synthetic tap water, working solution

Prepared by measuring 990mL of ultra-pure water into a 1L coloured glass bottle. Using an auto-pipette, add 10mL of synthetic tap water stock solution and 1mL of 10% $^{w}/_{v}$ ammonium chloride solution into the 1L coloured glass bottle. This working solution is used for the preparation of the working AQC and AQC blank standards. Store under refrigeration at 1-5°C. Shelf life: 1 month

A5.16 Calibration matrix water

Prepared by measuring 1000mL of an appropriate mineral water into a 1L coloured glass bottle and using a suitable pipette, add 1mL of 10% $^{w}/_{v}$ ammonium chloride solution. This is used for the preparation of the calibration working standards, instrument sensitivity and drift standards and to dilute samples that are over the calibration range. Store under refrigeration at 1-5°C. Shelf life: 1 month.

A5.17 Certified reference materials

These are stored in the laboratory freezer at less than -17°C. The expiry date is recorded on their certificate when supplied.
Calibration and AQC certified reference materials are sourced from separate independent suppliers where possible (only if this is not possible – then as a minimum – different lot numbers from the same supplier are used).

A5.18 Certified reference stock solutions

Certified reference stock solutions are purchased from approved analytical suppliers, e.g. Supelco, part number 49107-U, 2000mg L^{-1} and Restek, part number 31896, 1000mg L^{-1}. Shelf life: as stated by supplier for both the calibration and AQC solutions. Store in a freezer at less than -17°C.

A5.19 Calibration standard stock solution, dalapon, concentration range 3000 ±1000mg L^{-1}, in methyl tert butyl ether

Accurately weigh out 0.06g of Dalapon to four decimal places. Transfer to a 20mL volumetric flask, dissolve and dilute to the 20mL mark with methyl tert-butyl ether, stopper and mix. Transfer the contents of the flask to an amber hypo-vial and store in a freezer at less than -17°C. Shelf life: 12 months.

Note: The concentration of the stock solution (mg L^{-1}) is determined by applying the following calculation: $C_{STOCK} = M_{CERTIFIED}/V_{FLASK}$

Where; C_{STOCK} is the concentration of the stock solution, $M_{CERTIFIED}$ is the mass of certified reference material in mg and V_{FLASK} is the volume of solution in litres.

A5.20 Calibration standard, high concentration, spiking solution, 30mg L^{-1}, in methyl tert-butyl ether, used to prepare the calibration working standards 3 to 7

Using a micro-syringe transfer 750µL of Supelco, 2000mg L^{-1}, certified reference stock solution and 500µL of dalapon calibration standard stock solution to a 50mL volumetric flask and make up to volume with methyl tert-butyl ether, stopper and mix. Transfer contents to an amber hypo-vial and store in a freezer at less than -17°C. Shelf life: 2 months.

A5.21 Calibration standard, low concentration, spiking solution, 6mg L^{-1}, in methyl tert-butyl ether, used to prepare the calibration working standards 1 to 2

Using a micro-syringe transfer 150µL of Supelco, 2000mg L^{-1}, certified reference stock solution and 100µL of dalapon calibration standard stock solution to a 50mL volumetric flask and make up to volume with methyl tert-butyl ether, stopper and mix. Transfer contents to an amber hypo-vial and store in a freezer at less than -17°C. Shelf life: 2 months.

A5.22 Calibration working standards, 0 (Blank), 5, 10, 25, 50, 75, 100 and 125µg L^{-1} in calibration matrix water

Remove spiking solutions from freezer and allow to equilibrate to room temperature. On each occasion a batch of samples is analysed prepare calibration working standards by adding the required volume of calibration low spiking solution or calibration high spiking solution in the table below into 30mL of calibration matrix water in a 40mL glass vial. Then follow the analytical procedure from **A8.1.4**.

Calibration Working Standard	Volume of Calibration, low concentration, spiking solution added (µL)	Volume of Calibration, high concentration, spiking solution added (µL)	Calibration Working Standard Concentration (µg L^{-1})
Cal Blank			0
Cal 1	25		5
Cal 2	50		10
Cal 3		25	25
Cal 4		50	50
Cal 5		75	75
Cal 6		100	100
Cal 7		125	125

A5.23 Internal standard stock solutions, 1,2,3-trichloropropane, bromoacetic acid-d3, 2-bromopropionic acid and 2-bromobutanoic acid, concentration range 3000 ±1000mg L^{-1}, in methyl tert butyl ether

Individually, accurately weigh out 0.06g, each of the internal standard compounds to four decimal places of a gram. Transfer to a 20mL volumetric flask, dissolve and dilute to the 20mL mark with methyl tert-butyl ether, stopper and mix. Transfer the

contents of the flask to an amber hypo-vial and store in a freezer at less than -17°C. Shelf life: 12 months

A5.24 Internal standard spiking solution, 30mg L^{-1}, in methyl tert-butyl ether

Using a micro-syringe transfer 500µL of the internal standard stock solutions to a 50mL volumetric flask and make up to volume with methyl tert-butyl ether, stopper and mix. Transfer contents to an amber hypo-vial and store in a freezer at less than -17°C. Shelf life: 2 months.

A5.25 AQC standard stock solution, dalapon, concentration range 3000±1000mg L^{-1}, in methyl tert butyl ether

Accurately weigh out 0.06g of dalapon to four decimal places of a gram. Transfer to a 20mL volumetric flask, dissolve and dilute to the 20mL mark with methyl tert-butyl ether, stopper and mix. Transfer the contents of the flask to an amber hypo-vial and store in a freezer at less than -17°C. Shelf life: 12 months.

A5.26 AQC standard spiking solution, 30mg L^{-1}, in methyl tert-butyl ether, used to prepare the AQC working standard

Using a micro-syringe transfer 750µL of the Restek, 1000mg L^{-1}, certified reference stock solution and 250µL of the dalapon AQC standard stock solution to a 25mL volumetric flask and make up to volume with methyl tert-butyl ether, stopper and mix. Transfer contents to an amber hypo-vial and store in a freezer at less than -17°C. Shelf life: 2 months.

A5.27 AQC working standards, Blank and 80µg L^{-1} in AQC matrix water

Remove spiking solution from freezer and allow to equilibrate to room temperature. On each occasion a batch of samples is analysed prepare AQC working standards by adding the required volume of AQC spiking solution in the table below into 30mL of AQC matrix water in a 40mL glass vial. Then follow the analytical procedure from **A8.1.4.**

AQC Working Standard	Volume of AQC spiking solution added (µL)	AQC Working Standard Concentration (µg L^{-1})
AQC Blank		0
AQC	80	80

A5.28 Instrument sensitivity check working standard, 10µg L^{-1} in calibration matrix water

To a 40mL glass vial, add 30mL of calibration matrix water. Inject 50µL of the calibration low spiking solution, prepared as the calibration working solution 2. Then follow the analytical procedure from **A8.1.4**.

A5.29 Calibration drift check working standard, 100µg L^{-1} in calibration matrix water

To a 40mL glass vial, add 30mL of calibration matrix water. Inject 100µL of the calibration high spiking solution, prepared as the calibration working solution 6. Then follow the analytical procedure from **A8.1.4**.

A5.30 Helium

A6 Apparatus

In addition to normal laboratory glassware and apparatus the following may be required.

A6.1 Gas Chromatograph/Mass Spectrometer

Agilent, 7890A gas chromatograph and 5975C inert XL mass spectrometer with triple axis detector fitted with a capillary column, Agilent J & W GC columns, HP-5MS, part number 19091S-433, 30m x 0.25mm ID, 0.25µm film thickness

A6.2 Platform Shaker, e.g. Edmund Buhler GmbH, mechanical shaker

A6.3 Refrigerator and freezer, set at 1-5°C and less than -17°C, with valid calibration status.

A6.4 Analytical Balance, four decimal place, for the preparation of stock solutions.

A6.5 Top Pan Balance, two decimal place.

A6.6 Micro-syringes with valid calibration status, 100µL and 250µL capacity

A6.7 Electronic digital auto-pipette with valid calibration status, 1-10mL capacity

A6.8 Water Bath with valid calibration status.

A6.9 Vortexer, used to mix sample extracts.

A6.10 Timer, with valid calibration status.

A6.11 Dispensers, inert, suitable for dispensing methyl tert-butyl ether.

A6.12 Micro-pipettes of various sizes.

A6.13 Volumetric Flasks glass, various sizes.

A6.14 Measuring Cylinder, 1000mL capacity.

A6.15 Hypo-vials, amber glass, 50mL and caps.

A6.16 Amber glass bottles, 250mL capacity, with PTFE lined screw caps containing 250µL 10% $^{w}/_{v}$ ammonium chloride solution, used for sample collection.

A6.17 EPA clear glass vials, 40mL capacity, and cap with PTFE lined septa, used for sample preparation.

A6.18 Pasteur pipettes, glass, disposable.

A6.19 Test tubes, clear glass, disposable, 10mL capacity, screw capped and screw caps with septa.

A6.20 Auto-sampler vials, amber glass, silanized, 2mL capacity, screw capped with 0.5mL graduations and screw caps with septa.

A6.21 Vial Inserts, glass, for 2mL auto-sampler vials.

The following instrument conditions have been used and found to be satisfactory.

A6.22 Typical Operating Conditions for the Gas Chromatograph

INSTRUMENT CONTROL PARAMETERS	
CONTROL INFORMATION	
Sample Inlet	GC
Injection Source	GC ALS
Mass Spectrometer	Enabled
OVEN	
Oven Program	On Initial Temperature 35°C for 3.5 minutes then 25°C minute^{-1} to 110°C for 0 minutes then 40°C minute^{-1} to 150°C for 0 minutes then 50°C minute^{-1}to 300°C for 0 minutes
Run Time	10.5 minutes
FRONT INJECTOR	
Syringe Size	10µL
Injection Volume	2µL
MULTIMODE INLET, He	
Mode	Splitless
Temperature	170°C
Pressure	15.672 psi
Total Flow	55mL minute^{-1}
Septum Purge Flow	3mL minute^{-1}
Temperature Program	On
Gas Saver	20mL minute^{-1} after 2 minutes
Purge Flow to Split Vent	50mL minute^{-1} at 1 minute
Cryo	Off
Liner	Agilent MS Certified, splitless inlet liner, single taper, with glass wool, volume 900µL, id 4mm, part number 5188-6568

THERMAL AUX 2 (MSD Transfer Line)	
Temperature	300°C
COLUMN #1	
Carrier Gas	Helium (He)
Capillary Column	Agilent 19091S-433: 1021.53189, HP-5MS 5% Phenyl Methyl Silox, 325°C: 30 m x 250µm x 0.25µm
Mode	Constant Flow
He Flow Rate	2mL $minute^{-1}$

A6.23 Typical Operating Conditions for the Mass Spectrometer

MS ACQUISITION PARAMETERS			
GENERAL INFORMATION			
Tune File	atune.u		
Acquisition Mode	SIM		
MS INFORMATION			
Solvent Delay	3.45 min		
EMV Mode	Gain Factor		
Gain Factor	1.00		
Resolution	Low		
SIM PARAMETERS			
	Mass, (dwell ms)	Mass, (dwell ms)	Mass, (dwell ms)
GROUP 1			
	49.0, (30)	64.0, (10)	108.0, (60)
GROUP 2			
	59.0, (5)	63.0, (5)	83.0, (20)
	85.0, (20)	93.0, (20)	108.0, (5)
	125.0, (5)	152.0, (20)	156.0, (20)
GROUP 3			
	99.0, (15)	107.0, (30)	121.0, (30)
	137.0, (10)	168.0, (10)	171.0, (5)
	173.0, (5)		
GROUP 4			
	61.0, (5)	75.0, (20)	110.0, (5)
	117.0, (20)	119.0, (5)	127.0, (20)
	131.0, (5)	152.0, (20)	154.0, (5)
GROUP 5			
	161.0, (10)	163.0, (30)	165.0, (10)
	171.0, (10)	173.0, (30)	175.0, (10)
GROUP 6			
	187.0, (30)	205.0, (60)	209.0, (30)
GROUP 7			
	231.0, (20)	251.0, (80)	
MS ZONES			
MS Source	230°C maximum 250°C		
MS Quad	150°C maximum 200°C		

TIMED EVENTS	
Timed MS Detector Table Entries	
Time (minutes)	State (MS On/Off)
9.00	Off

A6.24 Typical Retention Times and SIM ions ($^{m}/_{z}$ ions)

Compounds	**Typical Retention Time (minutes)**	**SIM ions (dwell millisecond)**
Monochloroacetic acid	4.05	108 (60), 64 (10), 49 (30)
Monobromoacetic acid-d3	4.99	156 (20), 125 (5)
Monobromoacetic acid	5.02	152 (20), 108 (5), 121 (5), 93 (5)
Dichloroacetic acid	5.17	85 (20), 83 (20), 63 (5), 59 (5)
2-Bromopropanoic acid	5.42	107 (30), 137 (10), 168 (10)
2,2-Dichlororopanoic acid (Dalapon)	5.47	121 (30), 99 (15)
Tribromomethane **	5.63	173 (5), 171 (5)
1,2,3-Trichloropropane	6.04	75 (20), 110 (5), 61 (5)
Trichloroacetic acid	6.04	117 (20), 119 (5)
Bromochloroacetic acid	6.05	127 (20), 131 (5)
2-Bromobutanoic acid	6.32	152 (20), 154 (5)
Dibromoacetic acid	6.76	173 (30), 171 (10), 175 (10)
Bromodichloroacetic acid *	6.83	163 (30), 161 (10), 165 (10)
Dibromochloroacetic acid *	7.46	205 (60), 209 (30), 187 (30)
Tribromoacetic acid *	7.96	251 (80), 231 (20)

* Brominated trihaloacetic acids are particularly sensitive to the condition of the injection port and GC column. If the response for these or other method analytes diminish, trimming approximately 0.25 m from the head of the column and replacing the GC inlet liner often restores the response for these analytes.

** Tribromomethane is not a target analyte. The brominated trihaloacetic acids can exhibit degradation during storage. Tribromoacetic acid (TBAA), the least stable HAA ester, is degraded to tribromomethane. This is thought to occur as a result of peroxide contamination of the solvent, i.e. MTBE. Tribromomethane can be chromatographed and monitored as an indication of high peroxide levels in the solvent. If large tribromomethane peaks are observed in HAA-fortified reagent water samples (or calibration standards), the ether solvent should be replaced.

A7 Sample collection and preservation

Samples are taken in 250mL amber glass vials with caps (lined with an appropriate inert material) containing ammonium chloride (250 µL of 10% w/v).

A8 Analytical Procedure

A8.1 Sample pre-treatment and extraction

A8.1.1 Remove the samples from storage and allow the samples to equilibrate to room temperature.

A8.1.2 Weigh 30.0±0.1g (approximately equivalent to 30mL) of sample into a 40mL glass vial, with a PTFE lined screw cap, using a top pan balance.

A8.1.3 Remove the internal standard spiking solution from freezer. Allow the hypo-vial, containing the spiking solution, to equilibrate to room temperature and use this to spike the internal standard spiking solution.

A8.1.4 Using a micro-syringe or Gilson micro-pipette, add 50µL of the internal standard spiking solution. Produces a trichloropropane, monobromoacetic acid-d3, 2-bromopropanoic acid and 2-bromobutanoic acid concentration of 50µg L^{-1}.

Note: When fortifying an aqueous sample with components that are contained in methyl tert-butyl ether solutions, be sure that the needle of the syringe is well below the surface of the water. After injection, cap the sample and mix.

A8.1.5 Adjust the sample to pH ≤0.5 by adding 1.5mL of concentrated sulfuric acid. This will produce a sulfuric acid concentration of approximately 5% $^{v}/_{v}$.

A8.1.6 Using a dispenser, add 3mL of methyl tert-butyl ether to the 40mL glass vial.

A8.1.7 Add 12.0±0.1g of muffled sodium sulfate to the 40mL glass vial. Replace the cap, checking that the PTFE insert is still in place and correctly positioned in the cap. Make sure the cap is on tight. Place the vial on its side if not shaking immediately to prevent clumping.

A8.1.8 Place the sample vials horizontally on a platform shaker and shake longitudinally for 5 minutes set at maximum speed, 300 cycles per minute.

A8.1.9 Allow separation and remove the sample vials from the platform shaker. The sample is allowed to stand until separation is judged to be as complete as possible, typically 5 minutes.

A8.2 Sample methylation with acidic methanol

A8.2.1 Using a Pasteur pipette, transfer approximately 2mL of the upper MTBE layer, without transferring any water, to a 10mL screw capped test tube. Using an auto-pipette or Gilson micropipette, add 2mL of freshly prepared 10% sulfuric acid in methanol to each 10mL test tube. Replace the cap; making sure the cap is on tight.

Note: Important stage of the extraction procedure. Keep the Pasteur pipette tip as high as possible above the aqueous layer. Do not transfer water.

A8.2.2 Place the test tubes in a water bath set at 50°C and heat for 120 minutes. Verify the reaction temperature is at 50°C by using a thermometer. Methylation of the analytes is accomplished during this step. Careful control of both reaction time and reaction temperature are critical to method precision and accuracy.

Note: The reaction temperature is set at its highest practical limit, i.e. 50°C, as MTBE boils at 55°C

A8.2.3 After 120 minutes remove the tubes from the heating source and allow to cool to room temperature (at least 5 minutes) before removing their caps.

A8.3 Process each sample individually from this stage to completion

A8.3.1 Using an auto-pipette, calibrated on that day, add 5mL of 10% $^{w}/_{v}$ sodium sulfate aqueous solution to the tube.

A8.3.2 Vortex the tube for 30 seconds to ensure full equilibration between the phases. Allow the two phases to separate.

Note: Do not allow the tube to stand for more than a few minutes. Adding sodium sulfate solution may cause loss of the formed haloacetic acid esters through acid-catalyzed hydrolysis over prolonged periods.

A8.3.3 Remove and discard all the lower phase layer, i.e. acidic aqueous methanol from the tube with a long Pasteur pipette. Leave no more than 0.2mL of aqueous phase to ensure complete neutralization in the following step.

A8.3.4 Using an auto-pipette, calibrated on that day, add 1mL of 10% $^{w}/_{v}$ sodium sulfate aqueous solution into the tube.

A8.3.5 Vortex the tube for several seconds at least four times to complete the neutralization reaction. Allow the two phases to separate.

A8.3.6 Transfer approximately 1mL of the upper MTBE layer to an amber auto-sampler vial or transfer an appropriate volume of the upper MTBE layer into a glass vial insert in an amber auto-sampler vial and cap ready for analysis, (a glass vial insert can be used to ensure that the solvent level in the vial is sufficient for analysis and

to reduce the risk of water being transferred to the auto-sampler vial). A duplicate auto-sampler vial can be filled using the excess sample extract to allow for repeat analysis if necessary.

Note: Important stage of the extraction procedure. Keep the Pasteur pipette tip as high as possible above the aqueous layer.

Calibration working standard 2, 10µg L^{-1}, is vialed twice as it is also used for the instrument sensitivity check standard.

Calibration working standard 6, 100µg L^{-1}, is vialed twice as it is also used for the instrument drift check standard.

A8.3.7 A set of quality control samples must be extracted with each batch of samples.

A8.3.8 Analyze sample extracts as soon as possible. Store sample extracts in a freezer at less than -17°C. Sample extract stability should be checked by the laboratory.

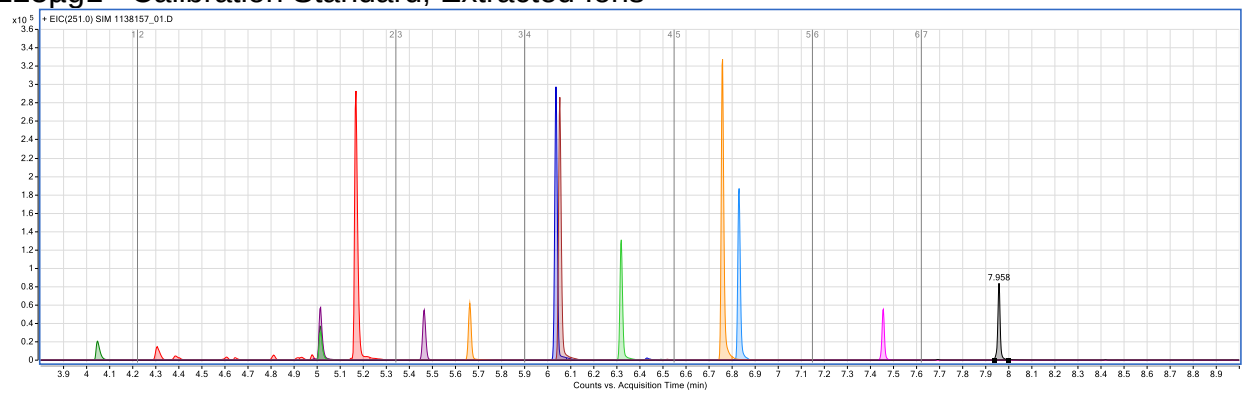
A9 Calculation

Results for target compounds are calculated using the following equation:-

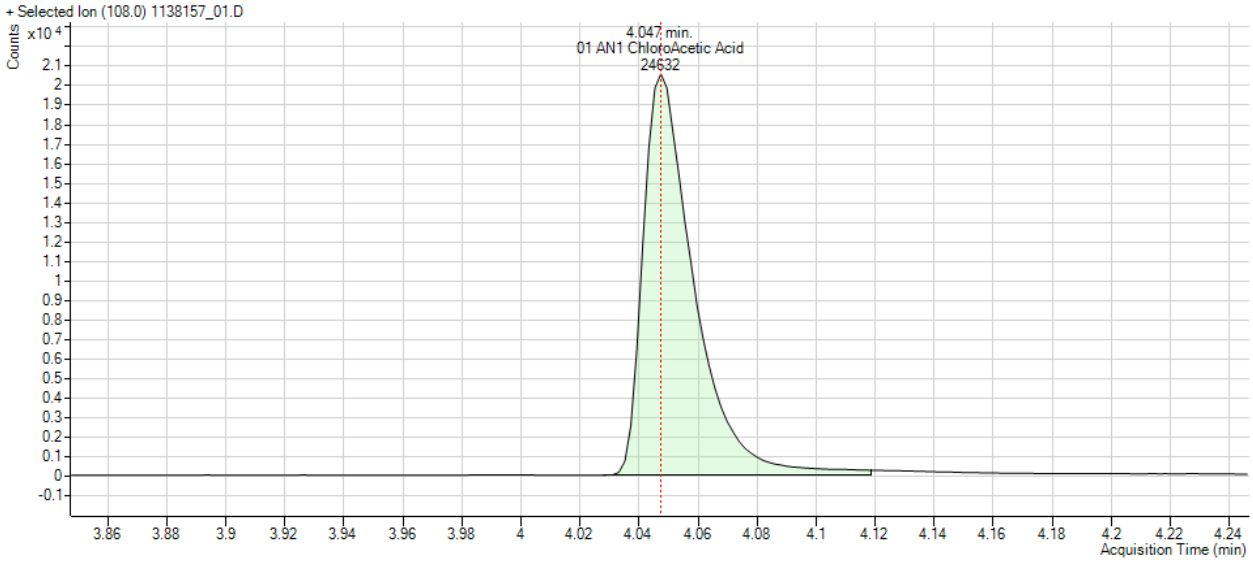
$$\text{Concentration } (\mu g\ L^{-1}) = \frac{(\text{response component in sample})/(\text{response internal std. in sample})}{(\text{response component in standard})/(\text{response internal std. in standard})} \times \text{Concentration of std } (\mu g\ L^{-1})$$

Figure A1 Typical chromatograms

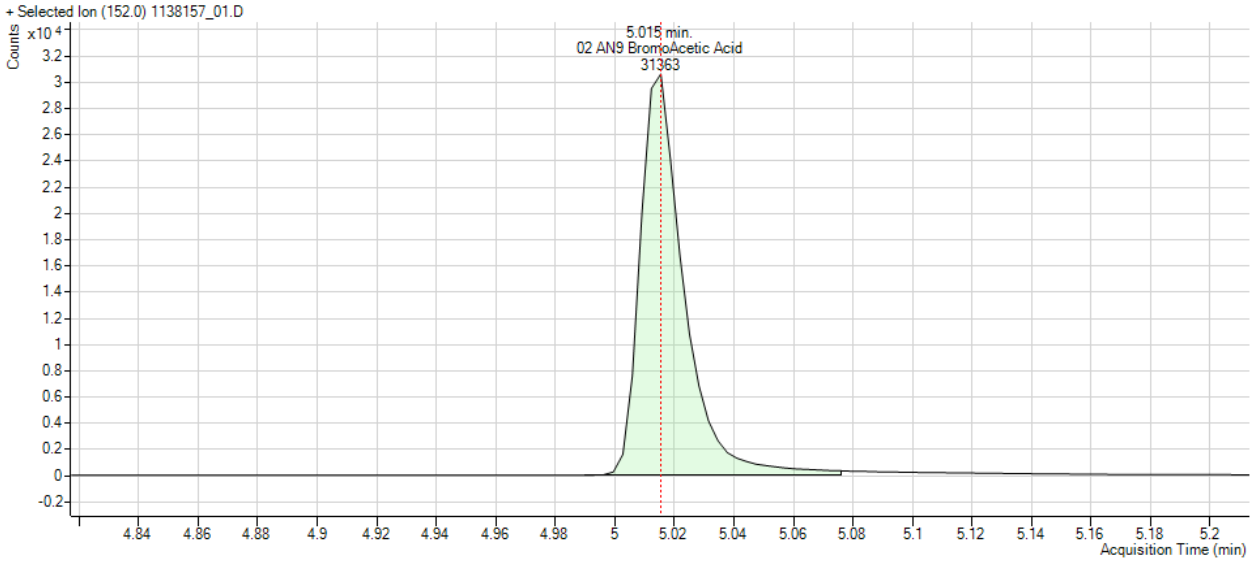
125µgL^{-1} Calibration Standard, Extracted Ions



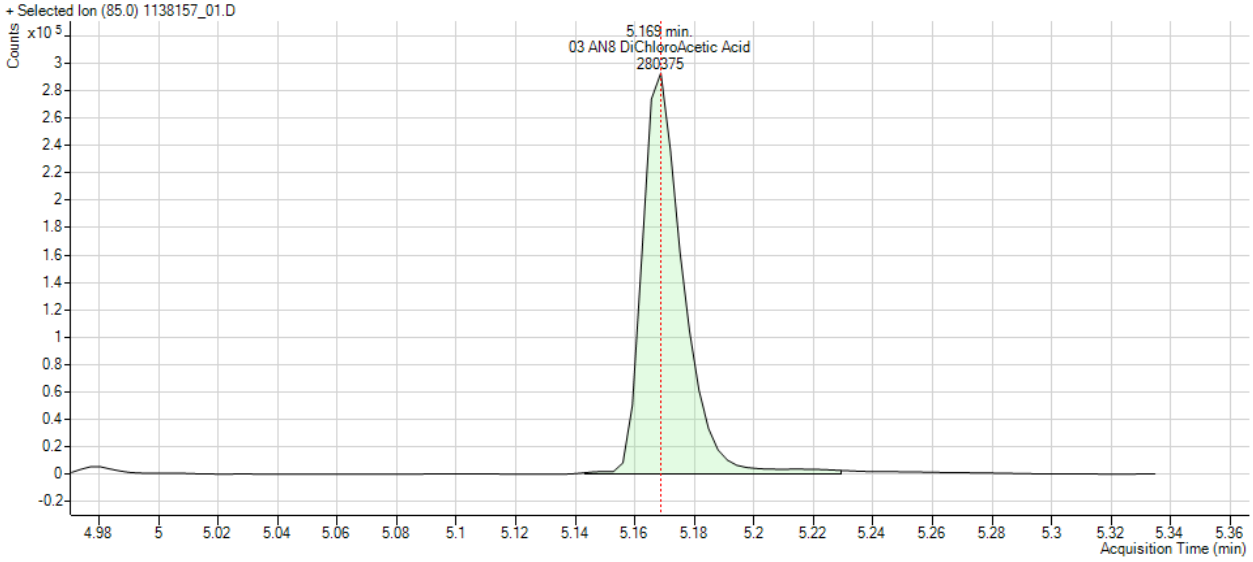
MCAA, 125µg L^{-1}



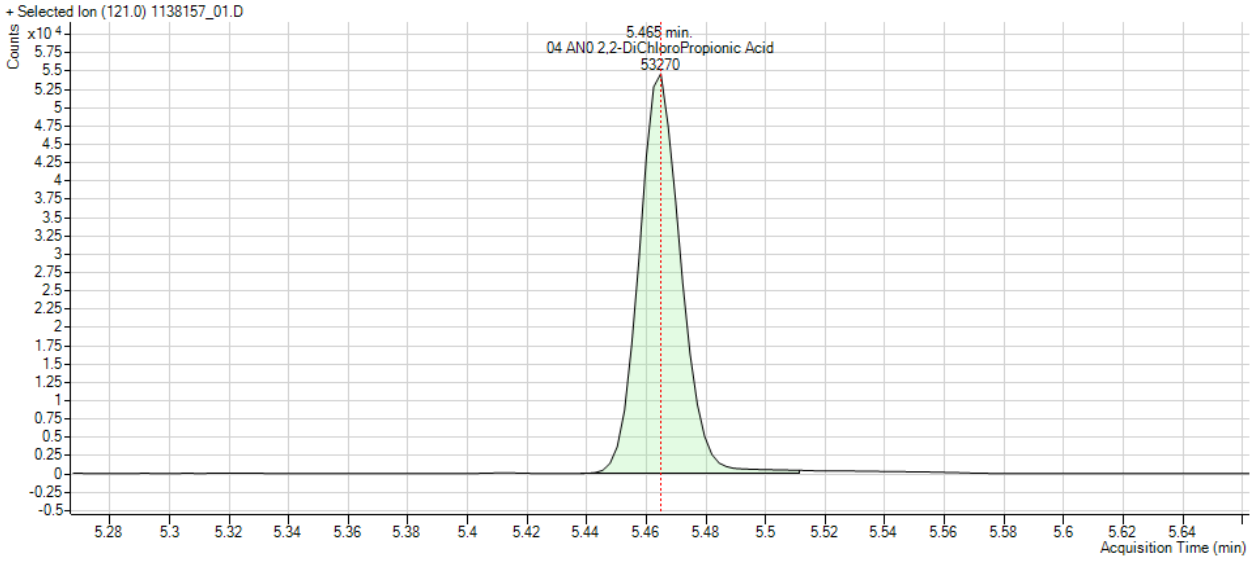
MBAA, 125µg L^{-1}



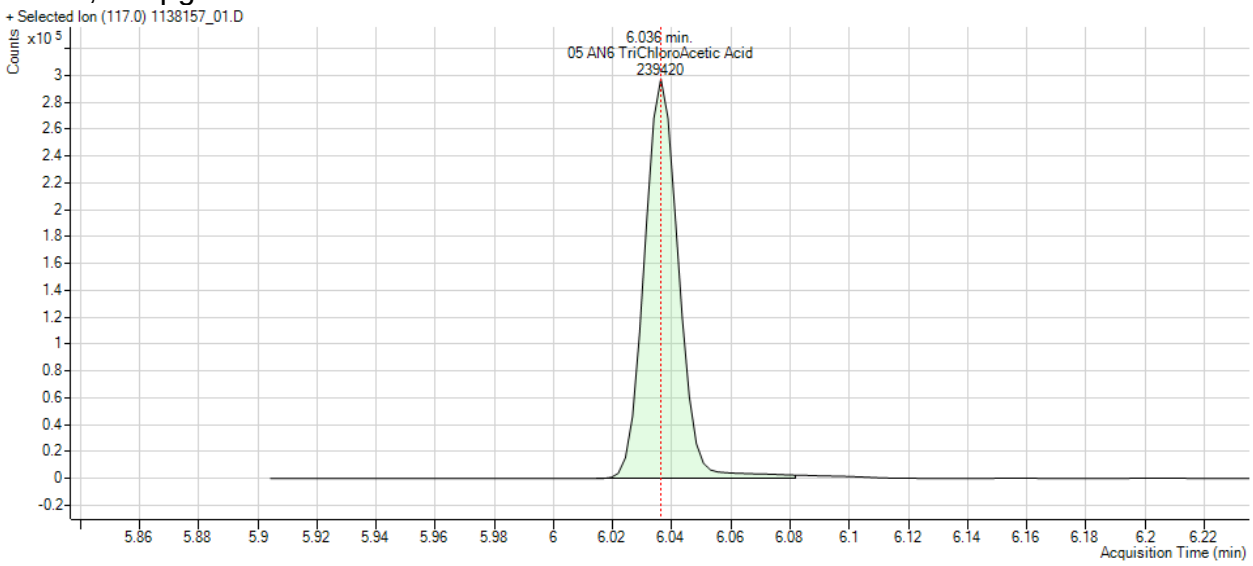
DCAA, 125µg L^{-1}



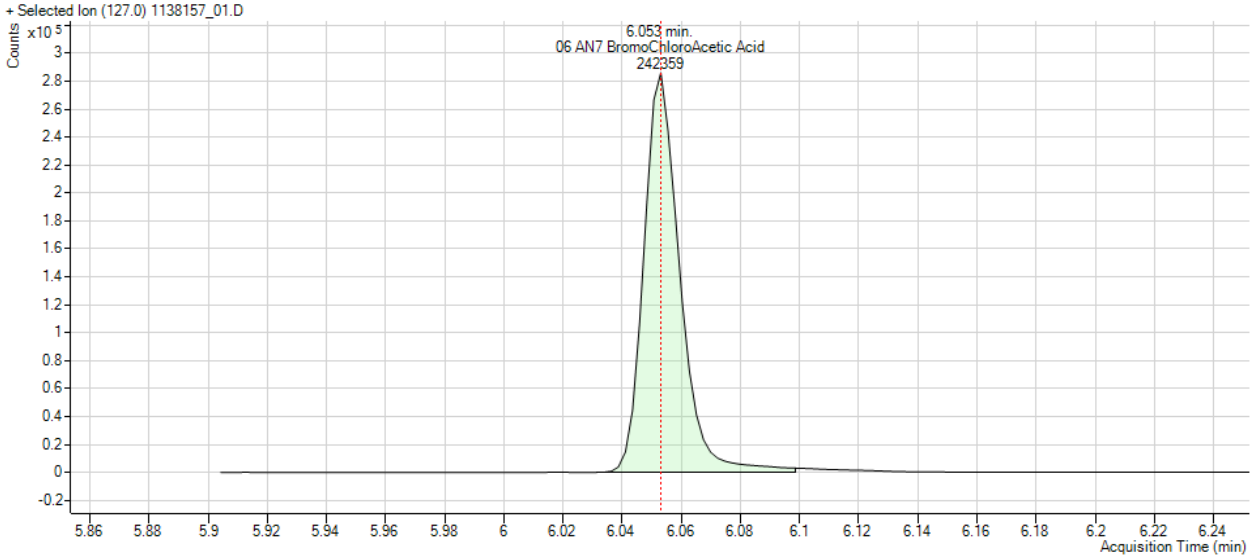
Dalapon, 125µg L^{-1}



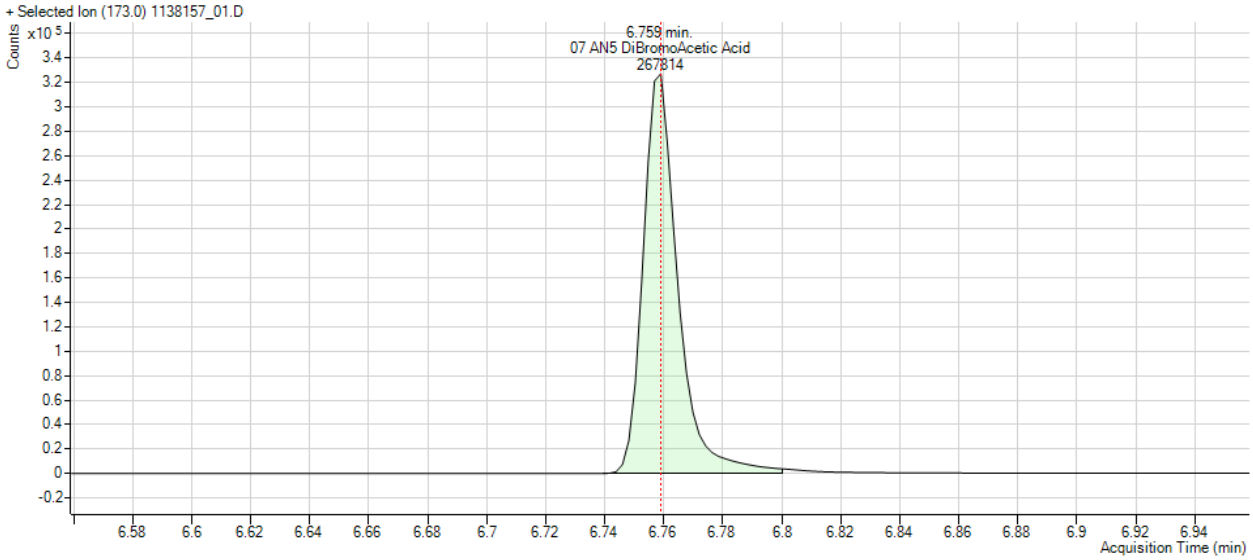
TCAA, 125µg L^{-1}



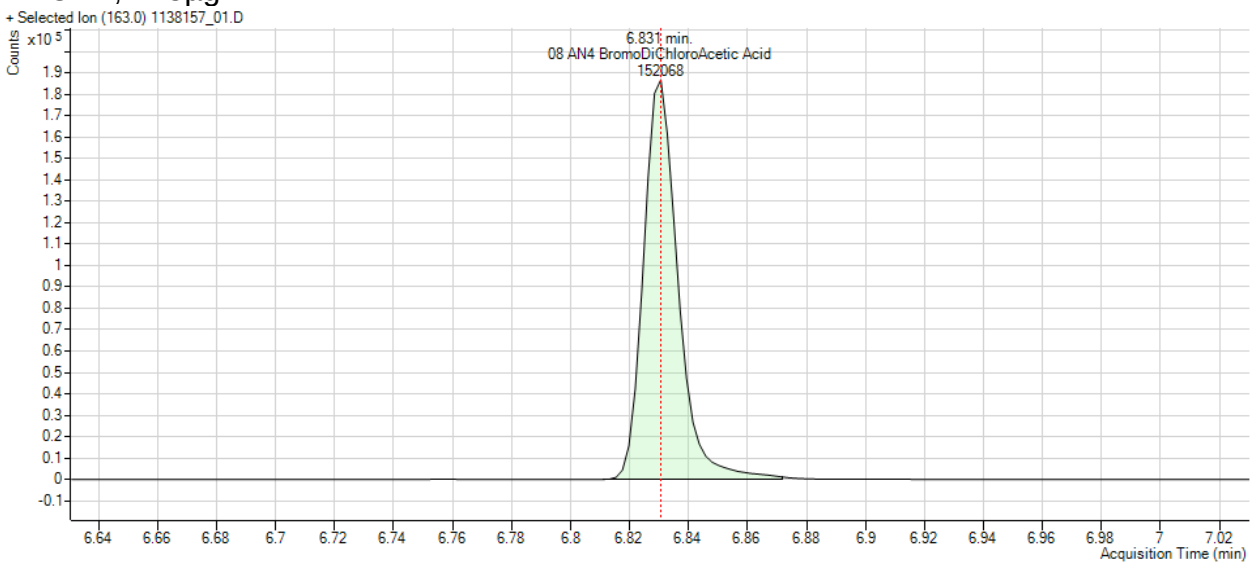
BCAA, 125µg L^{-1}



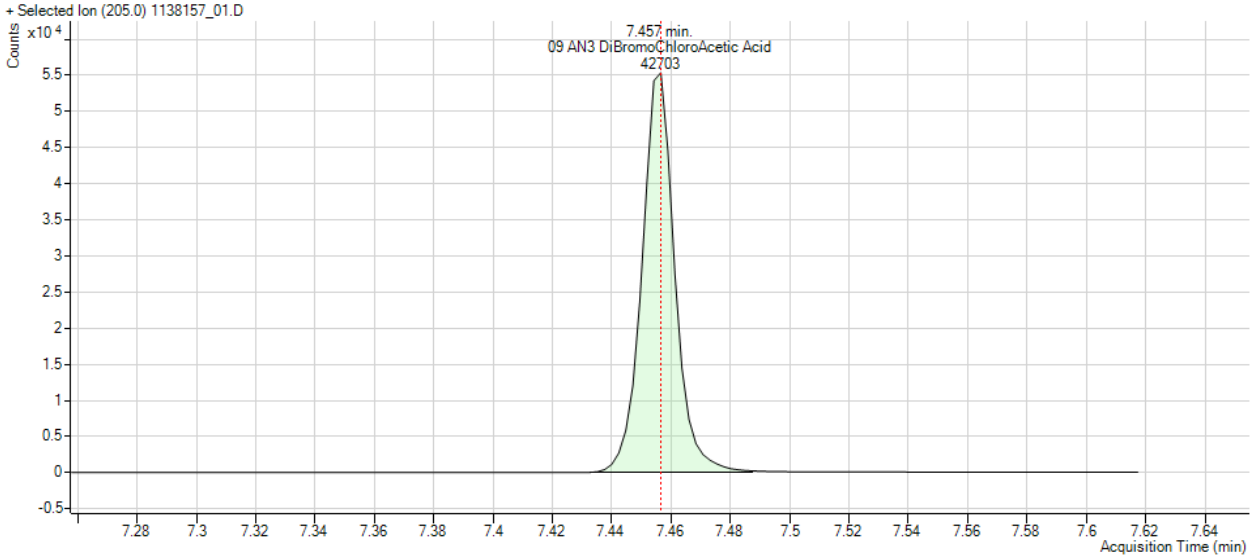
DBAA, 125µg L^{-1}



BDCAA, 125µg L^{-1}



DBCAA, 125µg L^{-1}



TBAA, 125µg L^{-1}

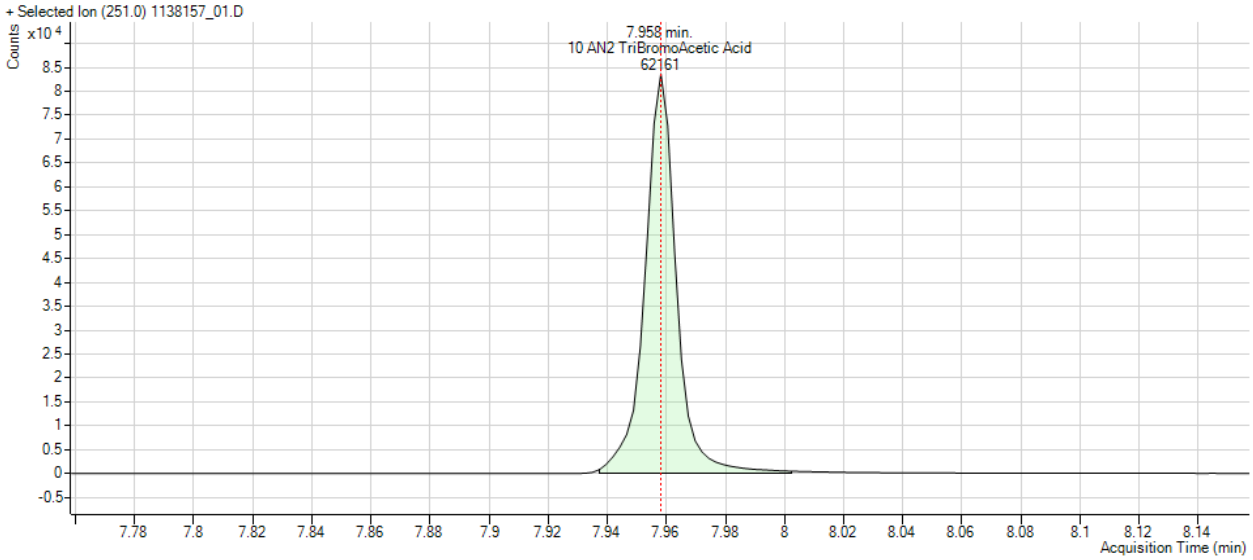


Table A1 Method performance data

Analyte	LOQ µg L^{-1}	Direct Standards				Banwell Treated Water (Medium Hardness)		
		Low Standard, 25 µg L^{-1}		High Standard, 100 µg L^{-1}		80% Spike, 100 µg L^{-1}		
		Bias	RSD	Bias	RSD	Recovery	RSD	Uncert
MCAA	0.6	-2.4%	1.7%	0.4%	1.9%	100.6%	2.0%	± 4.5%
MBAA	0.5	-2.8%	2.2%	0.5%	1.9%	100.9%	1.5%	± 4.0%
DCAA	0.6	-2.8%	2.4%	0.6%	1.7%	100.6%	3.2%	± 7.0%
Dalapon	0.6	-2.6%	3.3%	0.9%	2.0%	100.2%	2.1%	± 4.5%
TCAA	0.3	-2.3%	2.9%	1.1%	1.6%	99.8%	1.9%	± 4.0%
BCAA	0.4	-2.4%	1.4%	1.2%	0.9%	100.3%	1.9%	± 4.1%
DBAA	0.4	-5.2%	4.0%	1.4%	1.1%	102.3%	2.5%	± 7.2%
BDCAA	0.5	-5.6%	6.8%	4.4%	4.4%	105.1%	4.7%	± 14.6%
DBCAA	0.8	-2.5%	9.1%	3.4%	5.7%	103.5%	5.5%	± 14.4%
TBAA	1.1	0.3%	10.6%	3.3%	7.0%	105.1%	6.1%	± 17.4%

Method performance data provided by ALS Wakefield.

B The Determination of Haloacetic Acids in Raw and Potable Waters by Direct Injection Liquid Chromatography Tandem Mass Spectrometry

B1 Performance characteristics of the method

B1.1	**Substances determined**	Monochloroacetic acid (MCAA), Dichloroacetic acid (DCAA), Trichloroacetic acid (TCAA), Monobromoacetic acid (MBAA), Dibromoacetic acid (DBAA), Bromodichloroacetic acid (BDCAA), Dibromochloroacetic acid (DBCAA), Bromochloroacetic acid (BCAA), Tribromoacetic acid (TBAA)
B1.2	**Type of sample**	Raw waters, drinking waters and process waters.
B1.3	**Basis of method**	Samples are acidified prior to analysis on a liquid chromatography with mass spectrometric detection by direct aqueous injection.
B1.4	**Range of application**	Typically, up to 100μgL^{-1}
B1.5	**Standard deviation**	Data in Table B1.
B1.6	**Limit of quantitation**	Typically, 0.5μgL^{-1}, based on low level (2μgL^{-1}) standard solutions.
B1.7	**Bias**	Data in Table B1.

B2 Principle

The sample, after dilution if required, is acidified and internal standard is added. The sample is transferred to a vial and injected on the LC system and the analytes are eluted on to the analytical column using a gradient LC method and detected by LC mass spectrometric detection.

B3 Interferences

Any co-extracted material which has a LC retention time similar to any of the above analytes and which gives a detector response at the MRMs will interfere. However, none are known at the $^{m}/_{z}$ values selected.

B4 Hazards

Skin contact or inhalation of all reagents and their solutions specified in this method should be avoided. Methanol and Acetone are highly flammable; these solvents should be handled away from sources of ignition. Haloacetic acids are toxic and suspected carcinogens.

Formic acid is corrosive. See Safety Data Sheet (SDS) provided by the chemical manufacturer/supplier.

B4.1 Methanol, CH_3OH, CAS No. 67-56-1

B4.2 Methyl tert-butyl ether (MTBE), $(CH_3)_3CCH_3$, CAS No. 1634-04-4

B4.3 Certified Reference Materials

B4.4 Formic acid, CH_2O_2, CAS No. 64-18-6

B4.5 Syringes

Adequate care should be taken when handling syringes in order to avoid injecting one-self. Damaged and broken syringes should be disposed of in a safe manner, preferably to a “sharps” canister.

B5 Reagents

All reagents should be of sufficient purity that they do not give rise to interferences during the analysis and distilled, deionised or similar grade water should be used throughout. A procedural blank should be run with each batch of samples to check for interferences. All solutions should be mixed well prior to use.

B5.1 Water, LCMS grade, or deionised

B5.2 Acetone, AR grade

B5.3 Methanol LCMS grade

B5.4 Methyl tert-butyl ether (MTBE), LCMS grade

B5.5 Formic acid, LCMS grade

B5.6 Sodium thiosulfate Solution 1% w/v sodium thiosulfate solution (24mg L^{-1}) AR Grade

B5.7 Mixed haloacetic acid calibration stock solution, 1000mg L^{-1}

This standard is bought in as a custom mix containing all 9 HAAs.

B5.8 Mixed calibration intermediate solution, 10mg L^{-1}

Add 500µL of mixed haloacetic acid calibration stock solution to 50mL volumetric flask and make to volume with MTBE. The solution may be stored between 1-5°C and has an expiry date of 6 months.

B5.9 Mixed haloacetic acid AQC stock solution, 2000mg L^{-1}

This standard is bought in as a custom mix containing all 9 HAAs.

B5.10 Mixed AQC intermediate solution, 10mg L^{-1}

Add 250µL of mixed haloacetic acid AQC stock solution to 50mL volumetric flask and make to volume with MTBE. The solution may be stored between 1-5°C and has an expiry date of 6 months.

B5.11 Internal standard stock solution, 400mg L^{-1}

Weigh 40mg of the desired pure internal standard compound and transfer into a 100mL volumetric flask dissolve and make to mark with MTBE. The solution should be stored between 1-5°C and have an expiry date of 12 months.
3 Internal Standard Stocks are used: MCAA $^{13}C_2$, MBAA $^{13}C_1$, TCAA $^{13}C_1$.

B5.12 Internal standard intermediate solution, 20mg L^{-1}

Add 2500µL of each internal standard stock solution into a 50mL volumetric flask and make to volume with MTBE. The solution may be stored between 1-5°C and has an expiry date of 6 months.

B5.13 Internal standard working solution, 1mg L^{-1}

Add 2500µL of internal standard intermediate solution into a 50mL volumetric flask and make to volume with MTBE. The solution may be stored between 1-5°C and has an expiry date of 6 months.

B5.14 Calibration standards

Prepare by adding the required amounts of intermediate calibration solution in the table below to the designated volumetric flasks and fill with HPLC grade water. Transfer to 40mL sample vials and label.

Calibration Standard	Calibration intermediate solution to add (µL)	Volumetric flask volume (mL)	Concentration ($\mu g L^{-1}$)
Cal 1	20	100	2
Cal 2	50	100	5
Cal 3	200	100	20
Cal 4	250	50	50
Cal 5	400	50	80
Cal 6	500	50	100
Cal 7	0	NA	0

B5.15 AQC working solution, 80µg L^{-1}

Add 400µL of AQC intermediate solution to a 50mL volumetric flask, fill with relevant matrix water and transfer to 40mL sample vial. Treat as a sample from this point.

B5.16 0.2M EDTA Solution

Weigh 37.2g of Ethylenediaminetetraacetic acid disodium dehydrate salt (AR Grade) and dissolve into a 500mL volumetric flask into HPLC Grade water, make up to the mark. The solution may be stored at room temperature and has an expiry date of 6 months.

B6 Apparatus

In addition to normal laboratory glassware and apparatus the following may be required.

B6.1 Amber glass sample bottles - 40mL capacity with PTFE-lined screw plastic cap, containing 100ul of 1% w/v sodium thiosulfate solution (24mg L^{-1}) or equivalent.

B6.2 Refrigerator and freezer, set at 1-5°C and less than -17°C, with valid calibration status.

B6.3 Analytical Balance, four decimal place, for the preparation of stock solutions.

B6.4 Auto-pipette with valid calibration status, 100-1000µL capacity.

B6.5 Measuring Syringes, various sizes.

B6.6 Volumetric Flasks, glass, various sizes.

B6.7 Measuring Cylinder, 1000mL capacity.

B6.8 Reagent Bottles, amber glass, 50mL and caps.

B6.9 Pasteur pipettes, glass, disposable.

B6.10 Auto-sampler vials, amber glass, 2mL capacity, snap-capped and snap-caps with septa.

B6.11 Liquid Chromatograph/Mass Spectrometer

A high performance liquid chromatograph triple quadrupole mass spectrometer system fitted with a binary pump and column oven connected to a triple quadrupole mass spectrometer capable of unit mass resolution and operating in MRM mode, with an appropriate data station, e.g. Agilent, 1200 series liquid chromatograph and 6460 triple quadrupole mass spectrometer

The following instrument conditions have been used and found to be satisfactory.

B6.11.1 Typical Operating Conditions for the Liquid Chromatograph

HPLC ACQUISITION PARAMETERS				
Analytical Column	Phenomenex Luna C18 150x2.1mm			
Column Temperature	45°C			
Injection Volume	40 uL*			
Binary Pump	Agilent 1260 Infinity Series			
Mobile Phase A	Water, HPLC grade, 0.05% formic acid			
Mobile Phase B	90% Methanol, HPLC grade:10% Water, HPLC grade, 0.05% formic acid			
Gradient Program Timetable				
	Time (minutes)	**A (%)**	**B (%)**	**Flow rate (mL minute^{-1})**
Initial	0.00	97.0	3.0	0.300
1	2.00	50.0	50.0	0.300
2	3.50	3.0	97.0	0.300
3	7.50	97.0	3.0	0.300
4	11.00	97.0	3.0	0.300

* note that injection volume is dependent on the sensitivity of the mass spectrometer and required LOD/LOQ. Injecting more than 40uL may cause peak shape to be degraded.

B6.11.2 Typical Operating Conditions for the Mass Spectrometer

MS ACQUISITION PARAMETERS	
Acquisition parameters	ESI mode, neg ionization polarity; MRM mode
Drying gas	Nitrogen
Drying gas temperature	150°C
Drying gas flow	8 L minute^{-1}
Nebulizer pressure	60 psi
Nebulizer voltage	0 V

LC-MS/MS MRM transitions				
Compound Name	Mode	Expected retention time (minutes)	Quantitative Transition (m/z)	Qualifier Transitions (m/z)
DCAA	Negative ESI	1.95	127.0>83.0	129.0>85.0
MCAA $^{13}C_2$ (ISTD)	Negative ESI	2.01	95.0>35.0	
MCAA	Negative ESI	2.01	93.0>35.0	95.0>37.0
BCAA	Negative ESI	2.11	172.8>128.9	170.8>126.8
MBAA $^{13}C_1$ (ISTD)	Negative ESI	2.30	138.0>79.0	
MBAA	Negative ESI	2.30	137.0>79.0	139.0>81.0
DBAA	Negative ESI	2.34	217.0>173.0	215.0>171.0
TCAA $^{13}C_1$ (ISTD)	Negative ESI	3.25	161.8>116.9	
TCAA	Negative ESI	3.25	162.8>118.9	160.8>116.9
BDCAA	Negative ESI	3.63	163.0>81.0	161.0>79.0
CDBAA	Negative ESI	4.15	207.0>79.0	209.0>81.0
TBAA	Negative ESI	4.80	250.7>78.7	252.7>80.7

B7 Sample collection and preservation

Samples are taken in 40mL amber glass vials with caps (lined with PTFE) containing sodium thiosulfate. See B6.1.

B8 Analytical procedure

B8.1 Prepare calibration standards and AQCs as listed B5.14 and B5.15.

B8.2 Add 100µL of formic acid and 200µL of 0.2M EDTA solution to all samples and standards in the 40mL vials and shake. Transfer 1mL to individual 2mL amber vials and add 100µL of working internal standard solution.

B8.3 Set up LC and MS as above. Run test injection standard (Cal 5) to check system suitability.

B8.4 Run calibration standards and construct a calibration graph of response versus amount for each analyte.

B8.5 Analyse sample extracts and from the calibration graph calculate amount of the analyte in the sample.

B9 Calculation

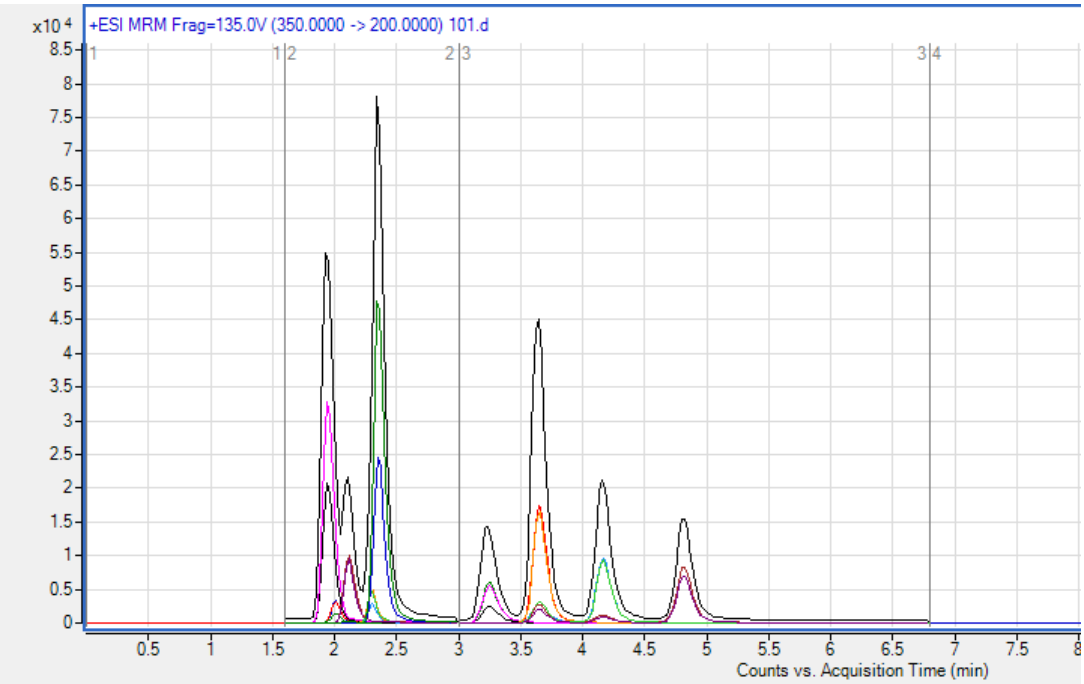
The concentration of each analyte is given by an internal standard procedure:-

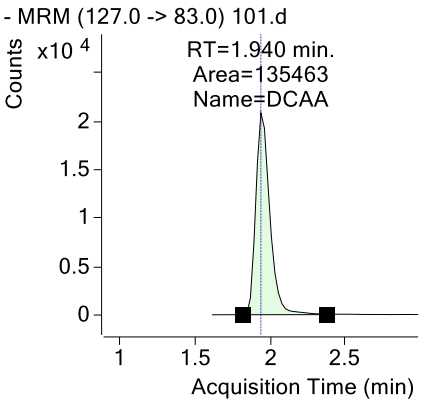
$$\mathbf{C} = \frac{\mathbf{A}.\mathbf{ISstd}.\mathbf{Cstd}}{\mathbf{Astd}.\mathbf{IS}}\ \mu gL^{-1}$$

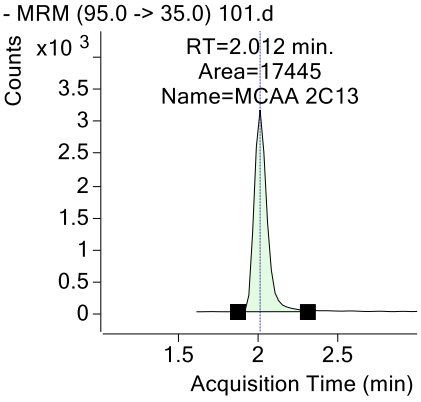
A = peak area in sample
Astd= peak area in standard
IS = peak area of internal standard in sample
ISstd = peak area of IS in standard
Cstd = concentration of analyte in standard, (μgL^{-1})

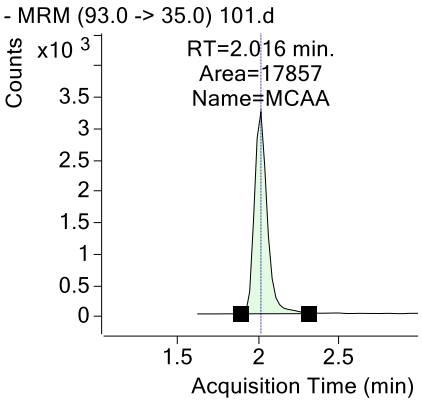
Figure B1 Typical Chromatogram

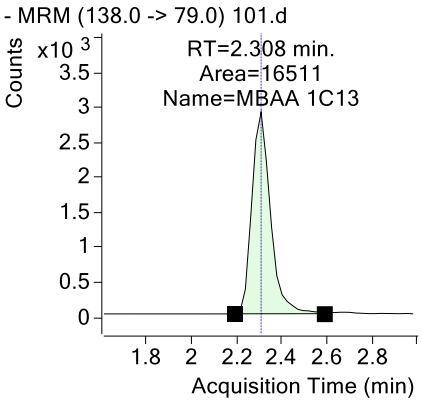
100ugL^{-1} Standard

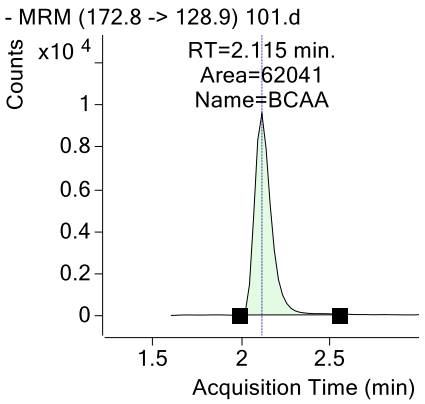


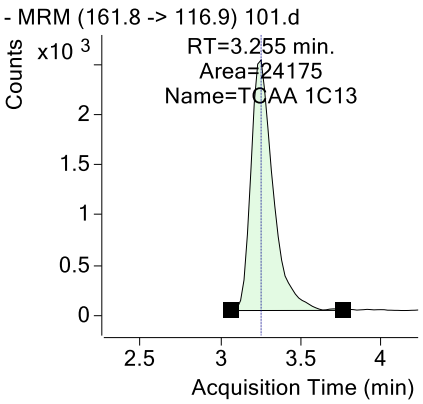


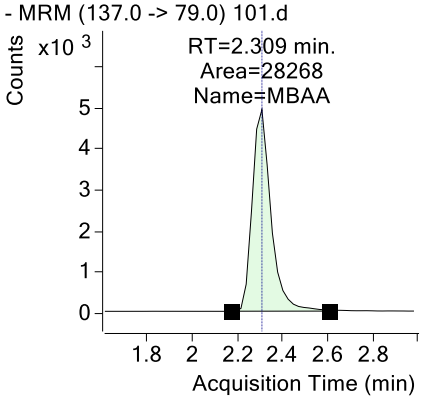


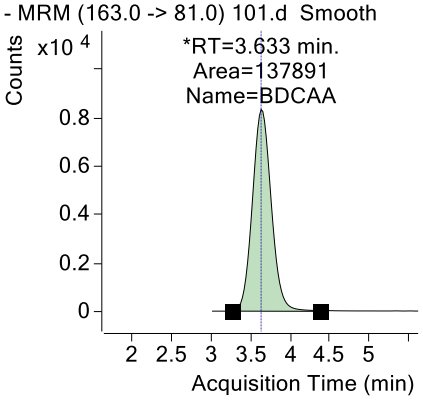


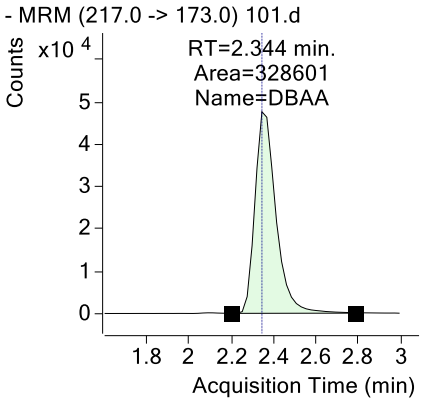


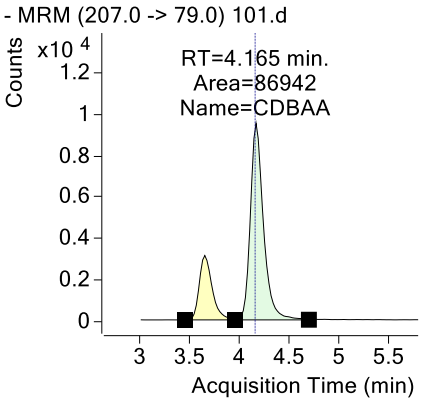

- MRM (172.8 -> 128.9) 101.d
Counts
x10 4
RT=2.115 min.
Area=62041
Name=BCAA
Acquisition Time (min)

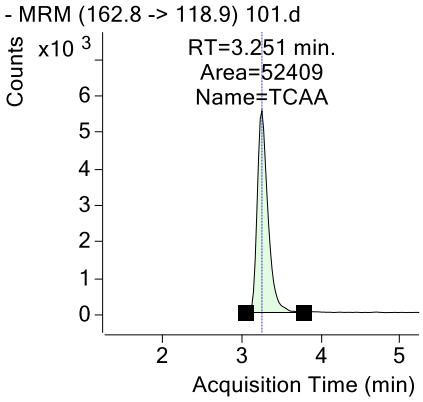

- MRM (161.8 -> 116.9) 101.d
Counts
x10 3
RT=3.255 min.
Area=24175
Name=TCAA 1C13
Acquisition Time (min)


- MRM (137.0 -> 79.0) 101.d
Counts
x10 3
RT=2.309 min.
Area=28268
Name=MBAA
Acquisition Time (min)


- MRM (163.0 -> 81.0) 101.d Smooth
Counts
x10 4
*RT=3.633 min.
Area=137891
Name=BDCAA
Acquisition Time (min)


- MRM (217.0 -> 173.0) 101.d
Counts
x10 4
RT=2.344 min.
Area=328601
Name=DBAA
Acquisition Time (min)


- MRM (207.0 -> 79.0) 101.d
Counts
x10 4
RT=4.165 min.
Area=86942
Name=CDBAA
Acquisition Time (min)


- MRM (162.8 -> 118.9) 101.d
Counts
x10 3
RT=3.251 min.
Area=52409
Name=TCAA
Acquisition Time (min)

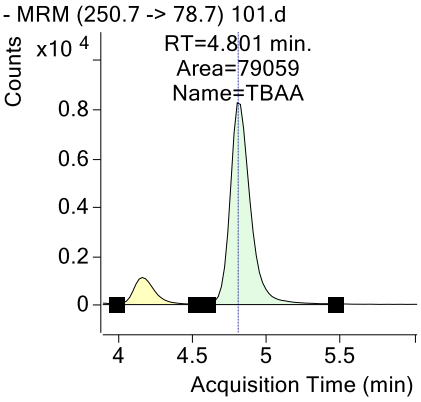

- MRM (250.7 -> 78.7) 101.d
Counts
x10 4
RT=4.801 min.
Area=79059
Name=TBAA
Acquisition Time (min)

Table B1 Method performance data

LOQs (μgL^{-1})

	MCAA	DCAA	TCAA	MBAA	DBAA	TBAA	BCAA	BDCAA	DBCAA
Raw Ground Water	1.9	0.9	1.2	1.8	0.8	1.1	1.4	1.0	1.4
Final Water from ground source	1.8	1.2	1.2	2.5	1.0	1.4	1.8	1.4	2.1
Raw surface water	1.6	1.0	1.7	2.9	2.2	1.1	1.3	1.5	1.9
Final Water from surface source	2.5	1.7	2.1	1.5	1.9	1.3	1.9	1.5	1.3

Precision (%RSD) at $80\mu gL^{-1}$

	MCAA	DCAA	TCAA	MBAA	DBAA	TBAA	BCAA	BDCAA	DBCAA
Raw Ground Water	3.30	3.02	2.19	4.65	4.88	5.24	3.12	5.13	4.50
Final Water from ground source	2.91	3.07	2.08	8.39	4.31	5.84	3.45	3.45	5.67
Raw surface water	2.41	2.75	1.97	3.24	7.63	5.45	3.73	6.29	5.25
Final Water from surface source	3.37	2.74	2.94	7.13	5.23	5.68	3.83	4.67	7.35

Uncertainty of measurement (%)

	MCAA	DCAA	TCAA	MBAA	DBAA	TBAA	BCAA	BDCAA	DBCAA
Raw Ground Water	11.83	13.34	9.86	14.33	17.56	15.05	22.40	21.91	15.09
Final Water from ground source	11.77	12.84	9.38	19.43	18.72	15.66	20.50	22.87	17.52
Raw surface water	10.85	12.26	9.50	13.32	20.83	15.16	15.88	22.92	15.95
Final Water from surface source	11.76	10.81	10.35	17.14	17.96	15.54	15.41	17.20	19.11

Recovery (%) at 80µgL-1

	MCAA	DCAA	TCAA	MBAA	DBAA	TBAA	BCAA	BDCAA	DBCAA
Raw Ground Water	101.3	104.03	101.69	101.86	99.73	101.2	101.5	102.72	102.06
Final Water from ground source	101.7	103.6	100.91	97.26	96.01	100.7	101.33	101.51	102.63
Raw surface water	100.55	103.31	101.31	102.64	99.33	100.25	101.9	103.33	102.72
Final Water from surface source	100.28	101.61	101.28	100.42	99.89	99.88	102.05	102.32	103.72

Method performance data provided by United Utilities Laboratory, Warrington.

Address for correspondence

However well procedures may be tested, there is always the possibility of discovering hitherto unknown problems. Analysts with such information are requested to contact the Secretary of the Standing Committee of Analysts at the address given below. In addition, if users wish to receive advanced notice of forthcoming publications, please contact the Secretary.

Secretary
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Environment Agency (National Laboratory Service)
56 Town Green Street
Rothley
Leicestershire
LE7 7NW
www.environment-agency.gov.uk/nls

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