

# Standing Committee of Analysts

## The Identification of Volatile Organic Compounds in Raw and Potable Waters by Gas Chromatography-Mass Spectrometry

Methods for the Examination of Waters and Associated Materials

July 2019

# **The Identification of Volatile Organic Compounds Raw and Potable Waters by Gas Chromatography-Mass Spectrometry**

## **Methods for the Examination of Waters and Associated Materials**

This booklet contains two techniques for the identification of volatile organic compounds in waters

Method A using purge and trap sample introduction Gas Chromatography-Mass Spectrometry (P/T GCMS)

Method B using headspace sample introduction into Gas Chromatography-Mass Spectrometry (H/S GCMS)

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.

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## 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.

Rob Carter  
*Secretary*  
August 2018

## 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 Identification of Volatile Organic Compounds Raw and Potable Waters by Gas Chromatography-Mass Spectrometry

## 1 Introduction

Identification of unknown volatile compounds is often required during investigation into suspected pollution and/or taste and odour events.

The techniques described in this booklet may be used in conjunction with semi-volatile and metal scan methods to provide a rapid response to water quality teams in the event of customer complaints or other potential incidents that could affect the quality of drinking water.

A positive identification using any of these methods could help to pinpoint the source of any contamination. A negative result however may not affect the actions taken by water quality teams to remove the source of contamination, e.g. for a taste or odour complaint, mains flushing or other appropriate techniques will still be carried out even if the analysis cannot identify the source.

The methods are designed only as screening tools to attempt to identify any volatile compounds that should not be present in the water samples.

Purge and Trap GCMS and Headspace GCMS are widely accepted techniques for monitoring volatiles in water but they do have limitations.

These methods perform well for non-polar organics and detection limits of  $1\mu\text{gL}^{-1}$  or less can readily be achieved.

Polar compounds and those with high water solubility and boiling points above  $200^{\circ}\text{C}$  generally exhibit poorer purging and headspace partitioning efficiencies so expected detection limits can be significantly higher. These compounds can still be identified, albeit at elevated concentrations.

It should be noted that there can be overlap between VOC and SVOC methods in terms of compound ranges identified – e.g. trihalomethane compounds (THMs) and naphthalene for example can appear in both VOC and SVOC methods care should be taken to use the most appropriate method for the compound in question i.e. VOC method for THMs.

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 Sample stability

Samples should be analysed as soon as possible after sampling and in incident cases this is likely to be within 24 hours. Typical sample stability ranges between 3 and 7 days and this is very much compound specific. ISO 5667:3 2012 quotes sample stability for VOC compounds

as 7 days once pH has been adjusted to 1-2 using HCl, HNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub>. Samples should be stored at 3 ± 2°C prior to analysis.

### 3 Identification

#### 3.1 Manual library searching

Unknown compounds are tentatively identified by comparison with the NIST spectral reference library. It is important to use the most up to date version of the reference library wherever possible. A minimum search fit of 700-800 is used as the identification criteria, although in certain circumstances this may be overridden by an experienced analyst. In addition to searching the mass spectral library (e.g. NIST), a lab specific reference library containing copies of spectra and retention time data from certified standards can be used as an additional reference.

Visual inspection of the unknown and library searched spectra is essential to confirm assignments. Manual library searching is best suited to well-defined chromatographic peaks. Where close co-elutions are present then the use of spectral deconvolution software (see section 3.2) may yield better results.

The following general guidelines should be observed when carrying out library searches and identifying unknowns:

- The spectrum selected for library searching should ideally be averaged across the chromatographic peak.
- Background correction is a technique used to remove unwanted chemical background ions from a target spectrum to ensure that a more accurate library search can be run.
- Spectra should be automatically background corrected before carrying out the library search (by ensuring that background correct spectra is on in the software where applicable). Whilst this is sufficient for most occasions, in the case of co-eluting peaks it may be necessary to correct manually. In the case of single well defined peaks it is normal to select the spectrum to be used for background correction by averaging several scans in front of and behind the peak in question. Where co-elution of compounds is possible then the background spectra for correction may be taken from one side of the chromatographic peak if necessary.
- Reverse fit searches often yield more reliable results than a forward fit search, especially in “dirty” samples. Use a search result that gives a good combination of fits in preference to one that gives one very high fit and one low one, e.g. forward fit 750 and reverse fit 750 is more likely to give a correct identification than forward fit 500 and reverse fit 900.
- A search may identify an unknown as a compound that could not possibly elute in that region of the chromatogram, e.g. identification of a peak that elutes before benzene as hexadecanol is obviously incorrect. Use your knowledge of chromatography and some common sense.
- Chemicals within certain groups produce very similar mass spectra and without certified standards it may not be possible to identify the individual compounds. In these cases it is permissible to identify the peak as a particular type of compound, e.g. a terpene.
- If a number of similar compounds are present (e.g. a mixture of petroleum hydrocarbons such as kerosene) these may be grouped together and reported as (for

example) a mixture of C5 to C12 aliphatic hydrocarbons. The hydrocarbon range is obtained by comparison of retention times to a stored chromatogram containing all the n-alkanes from C5 to C12.

- The technique may also be used for the tentative identification of volatile hydrocarbon mixes e.g. petrol etc.
- Again, there may be instances where there is significant overlap between VOC and SVOC methods for complex mixtures (eg hydrocarbons). Use the preferred technique depending on the volatility of the compounds of interest.

### 3.2 Automated searching and the use of deconvolution software

Chemical contamination of both drinking and environmental water could pose a significant risk to the end-user. Vigilant monitoring is essential; but the number of chemicals that need to be monitored is increasing. Therefore, rapid methods capable of screening for very high numbers of chemicals at trace levels need to be established. Gas chromatography (GC) / Mass spectrometry (MS) is one technique that is widely applicable to the identification of unknown chemicals.

When performing GCMS analyses, all ions are detected during the entire chromatographic run (full-scan). The presence and ratios of these ions, called mass spectra, can be used to aid the identification of unknown chemicals. Complex sample matrices can often obstruct the identification of chemicals, resulting in poor quality library matches. Background subtraction can be a lengthy and time consuming process and is both matrix-and-operator dependent, which can lead to incorrect identifications. To improve the detectability of chemicals in complex matrices some type of deconvolution is required. In the case of GCMS the free software AMDIS is the most widely used deconvolution tool, other sources of deconvolution programs are available. Settings for AMDIS or any other deconvolution software should be optimised for the matrix and particular application.

Deconvolution is an automated process, capable of extracting pure component spectra from a complex mixture of components. The deconvolution process finds the peak apexes of all extracted ions and tracks the rate of rise and fall for each ion profile. These deconvoluted ions are grouped together as a component.

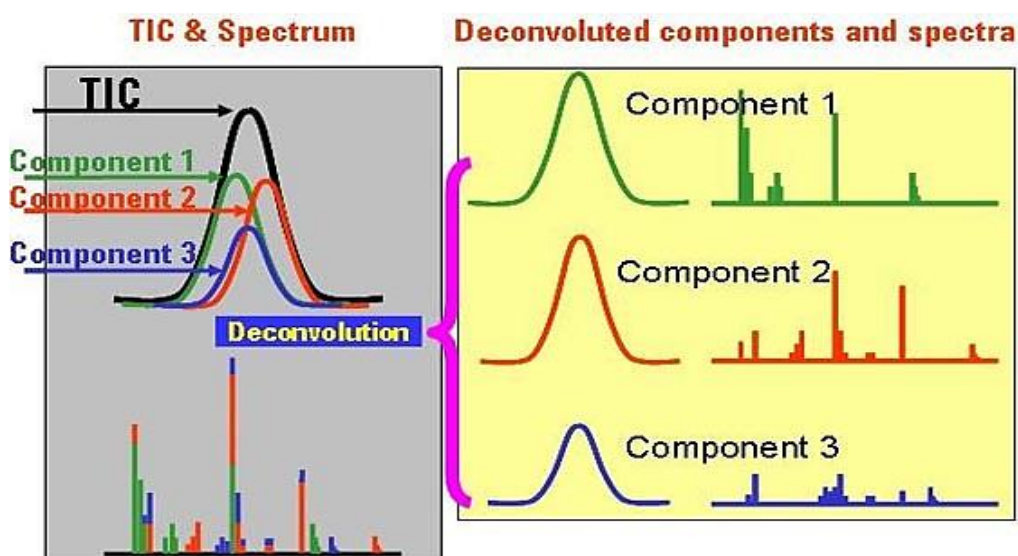


Figure 1. An illustration of mass spectral deconvolution process.



The matrix background or chemical noise is removed from the component spectrum. Now the spectrum is deconvoluted (cleaned) into a single component. Each individual component is then searched against a commercial or user-created database for identification.

By using deconvolution software you can reduce the analytical time required to detect unknowns by GCMS and dramatically increase the accuracy of identification.

#### 4 References

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## 5 Glossary

### **Blank**

The observed value when measurement is made on a sample identical to the sample of interest, but in the absence of the determinand. Analytical or calibration blanks are used to assess (and correct for) responses other than those caused by the calibration standards.

### **Calibration**

Comparison of responses derived from samples of known value with those from the samples under test.

### **Gas Chromatography (GC)**

Separation of thermally stable, volatile organic compounds from a complex mixture using an inert gas such as helium or nitrogen as the mobile phase and a liquid stationary phase usually supported on a silica based capillary column. The sample separates by differential partition of the analytes between the mobile and stationary phases, based on relative vapour pressure and solubility in the immobilized liquid stationary phase.

### **Headspace Analysis**

A technique whereby a test sample is heated in a sealed vial allowing volatile organic compounds to partition from the sample into the headspace above the sample. An equilibrium is reached between the VOCs in the sample and headspace and an aliquot of the headspace is injected into the analytical system.

### **Injection Standard**

A compound that is added in a constant amount to all samples and calibration standards after they have been extracted. It can then be used for calibration by plotting the ratio of the analyte signal to the injection standard signal as a function of the analyte concentration of the standards. This will correct for any loss of analyte during analysis.

### **Internal Standard**

A compound that is added in a constant amount to all samples and calibration standards before extraction. It can then be used for calibration by plotting the ratio of the analyte signal to the internal standard signal as a function of the analyte concentration of the standards. This will correct for any loss of analyte during sample preparation or analysis.

### **Limit of detection (LOD)**

The smallest concentration or quantity of a substance which can be expected (at a specified probability level) to be distinguishable (again at a given probability level) from the blank measurement.

## **Mass Selective Detector (MSD)**

Molecules are fragmented by a stream of electrons. The ionised fragments are then sorted by their mass to charge ratio ( $m/z$ ). The ions are then detected by an electron multiplier capable of registering the presence of charged particles. Results are displayed as spectra of the relative abundance as a function of the mass to charge ratio. Compounds will give a characteristic fragmentation pattern which can be used for identification.

## **Purge and Trap**

A technique whereby volatile organic compounds are stripped from a sample by purging with an inert gas. The VOCs are carried by the gas via a heated transferline to an adsorbant trap where they are concentrated prior to being thermally desorbed into the analytical system.

## **Reporting Limit (RPL)**

The smallest concentration or quantity of a substance that can be reported. Usually higher than the limit of detection to take in to account day to day variation in the method.

## **Retention Time (RT)**

The time taken for a particular compound to travel through the column to the detector. It is calculated as the time taken from injection to detection.

## **Spike**

A known quantity of determinand which is added to a sample, usually for the purpose of estimating the systematic error of an analytical system by means of a recovery calculation.

## **TIC**

Total Ion Chromatogram

## **VOC**

Volatile organic compound

## **A The Identification of Volatile Organic Compounds Raw and Potable Waters by Purge and Trap Gas Chromatography-Mass Spectrometry.**

### **A1 Performance characteristics of the method**

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<b>A1.1 Substances determined</b>	Volatile Organic Compounds in the range C1 to C12 (as n-alkanes) depending on polarity/water solubility.
<b>A1.2 Type of sample</b>	Raw waters (ground and surface), potable waters.
<b>A1.3 Basis of method</b>	Purge and Trap concentration, followed by capillary GC using MS detection. Library search of unknowns with approximate quantitation by comparison with an internal standard.
<b>A1.4 Range of application</b>	N/A - non-quantitative method.
<b>A1.5 Standard deviation</b>	N/A - non-quantitative method.
<b>A1.6 Limit of detection</b>	Typically around 0.1 to 1 µg L <sup>-1</sup> , although non-quantitative method and dependent on polarity.
<b>A1.7 Bias</b>	N/A non-quantitative method.

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### **A2 Principle**

An aliquot of sample is purged with helium to strip out any volatile components, which are subsequently collected on an adsorbent column (trap). The trap is heated to desorb the volatile components, which are swept by carrier gas on to a capillary GC column, separated by temperature programming and detected with the use of a mass spectrometer in full scan mode.

Standards containing known target VOC compounds are used to prove system suitability and verify the identification process. These standards may be used to provide estimates of quantitative results if required for target compounds and for unknowns quantitation can be based on the nearest internal standard but it must be stressed in these cases that this is semi-quantitative at best and takes no account of purge efficiencies etc.

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### **A3 Interferences**

Extreme care should be taken to minimise contamination of samples and blanks by solvents used in the laboratory. Without authentic standards it may not be possible to identify correct isomers of compounds.

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## **A4 Hazards**

Analysts using this method should familiarise themselves with the COSHH and risk assessments for this analysis. Skin contact or inhalation of all reagents and their solutions specified in this method should be avoided. Methanol is highly flammable; and should be handled away from sources of ignition.

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## **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. This is a particular issue with screening methods given the possibility of false positives being quoted. Reagents should be checked regularly. 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 Water - free from interference**

### **A5.2 Methanol – free from interference**

### **A5.3 General comments re Standard and Continuing Calibration Check (CCC) preparation**

All stock and intermediate standards should be stored in accordance to manufacturer's instructions. Intermediate and working standards are stored at  $3 \pm 2^\circ\text{C}$ .

Certified stock standards shall be purchased with certificates and records maintained showing date received, expiry date, opened date and date of disposal. Compounds covered are shown in appendix A1.

### **A5.4 200 mg L<sup>-1</sup> Volatile Organic Compounds Standard (Stable up to one month)**

This certified stock solution in methanol is for example available from Restek: Volatiles MegaMix with Gases (Catalogue No. 30603).

This standard is received in a 1mL sealed glass ampoule. After opening transfer the standard into a suitable vial, and assign a one month expiry to the opened vial (not exceeding the manufacturer's expiry).

### **A5.5 1000 mg L<sup>-1</sup> 1,3,5-Trichlorobenzene Standard (Stable up to one year)**

Certified 1,3,5-Trichlorobenzene solid is for example available from Sigma-Aldrich (Catalogue Number T54607). An expiry date of five years should be given to this compound. Weigh 100mg of 1,3,5-Trichlorobenzene. Transfer into a 100mL volumetric flask using methanol. Swirl the flask until completely dissolved, make up to the mark with methanol and mix well. Transfer into a labelled 44mL vial.

#### **A5.6 200 mg L<sup>-1</sup> 1,3,5-Trichlorobenzene Standard (Stable up to three months)**

To approximately 30mL of methanol in a 50mL volumetric flask, add 10mL of the 1000mg L<sup>-1</sup> solution using a bulb pipette, make up to volume with methanol and mix well. Transfer into a labelled 44mL vial.

#### **A5.7 5 mg L<sup>-1</sup> Intermediate Standard (Stable up to one month)**

To approximately 8mL of methanol in a 10mL volumetric flask add 250µL of both 200mg L<sup>-1</sup> VOC Standard and 200mg L<sup>-1</sup> 1,3,5-Trichlorobenzene Standard using a 250µL microsyringe. Make up to the mark with methanol and mix well. Transfer into a labelled 12mL vial.

Note other compounds of interest such as methyl tertiary butyl ether CAS 1634-04-4 (MTBE), ethyl tertiary butyl ether CAS 637-92-3 (ETBE), and tertiary amyl methyl ether CAS 994-05-8 (TAME) etc may be included in calibration standards as required

#### **A5.8 Working Standards & CCCs (prepare every 2 weeks)**

Fill the required number of 250mL Duran bottles (previously baked out at 130 ± 20 °C for a minimum of 1 hour) with 250mL of organic free water using a 250mL measuring cylinder. Then cool bottles and water for a minimum of 1 hour in a fridge at 3 ± 2°C

Spike two bottles with 50µL and 150µL of both 200mg L<sup>-1</sup> VOC Standard and 200mg L<sup>-1</sup> 1,3,5-Trichlorobenzene Standard, using 50µL and 250µL microsyringes, to give Working Standards 4 and 5 respectively. Inject the 200mg L<sup>-1</sup> standards below the water surface and swirl to mix.

Spike three bottles with 50µL, 250µL and 500µL of the 5mg L<sup>-1</sup> Intermediate Standard, using 50µL, 250µL and 500µL microsyringes as appropriate, to give Working Standards 1 to 3 respectively. Inject the intermediate standard below the water surface and swirl to mix.

Spike the required number of bottles with 1000µL of the 5mg L<sup>-1</sup> Intermediate Standard using a 500µL microsyringe to give the CCC. Inject the intermediate standard below the water surface and swirl to mix.

All Working Standards and CCCs should be transferred to labelled 44mL vials within one hour of preparation.

Working Standard	Std 1	Std 2	Std 3	Std 4	Std 5	CCC
Spiking Solution Type	5 mg L <sup>-1</sup> Int Cal	5 mg L <sup>-1</sup> Int Cal	5 mg L <sup>-1</sup> Int Cal	200 mg L <sup>-1</sup> Cal VOC & 1,3,5-TCB	200 mg L <sup>-1</sup> Cal VOC & 1,3,5-TCB	5 mg L <sup>-1</sup> Int Cal
Volume of Spiking Solution Added to 250mL of Water	50µL	250µL	500µL	50µL	150µL	1000µL
Component Concentrations	1µg L <sup>-1</sup>	5 µg L <sup>-1</sup>	10 µg L <sup>-1</sup>	40 µg L <sup>-1</sup>	120 µg L <sup>-1</sup>	20 µg L <sup>-1</sup>

#### **A5.9 Internal Standards (Stable up to one month)**

EPA8260 Internal Standard Mix, 2000mg L<sup>-1</sup> of each component, (pentafluorobenzene, 1,4-difluorobenzene, chlorobenzene-d5 and 1,4-dichlorobenzene-d4) is available for example from Ultra (Catalogue Number STM-341N). This standard is received in 1mL sealed glass ampoules. After opening transfer the standard into a suitable vial, and assign a 1 month expiry to the opened vial (not exceeding the manufacturer's expiry).

#### **A5.10 Surrogate Standards (Stable up to one month)**

EPA8260 Surrogate Standard Mix, 2000mg L<sup>-1</sup> of each component (dibromofluoromethane, toluene-d8 and 4-bromofluorobenzene), is available for example from Ultra (Catalogue Number STM-330N). This standard is received in 1mL sealed glass ampoules. After opening transfer the standard into a suitable vial, and assign a 1 month expiry to the opened vial (not exceeding the manufacturer's expiry).

#### **A5.11 25 mg L<sup>-1</sup> Internal and Surrogate Standard Mix (Stable up to six months)**

To approximately 8mL of methanol in a 10mL volumetric flask add 125µL of each of the above internal and surrogate stock solutions using a 250µL microsyringe, make up to volume with methanol and mix. Transfer to the internal standard vessel on the purge and trap system. Prime the internal standard before use.

#### **A5.12 Sodium thiosulphate solution (18 g L<sup>-1</sup>) (Stable up to 12 months)**

Dissolve 9 g of sodium thiosulphate pentahydrate in approximately 450 mL of ultra-pure water. Mix well. Make to 500 mL with ultra-pure water. Mix well.

## **A6 Apparatus**

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

### **A6.1 Purge and Trap Gas Chromatograph/Mass Spectrometer**

Atomx Purge & Trap autosampler, and concentrator fitted with a Supelco Vocab 3000 trap fitted to Agilent 7890A GC and 220 Ion Trap MSD fitted with a Restex Rtx-VMS column, 20m x 0.18mm ID, 1µm film thickness

### **A6.2 Analytical balance with valid calibration status**

### **A6.3 Grade B or better volumetric flasks – 10mL, 50mL, 100mL**

### **A6.4 Grade B or better bulb pipette – 10mL**

### **A6.5 Grade B or better measuring cylinder – 250mL**

### **A6.6 Microsyringes with valid calibration status - 50µL, 250µL, 500µL**

### **A6.7 Autopipettes with valid calibration status – 40-200µL, 200-1000µL, 2-10mL**

### **A6.8 Storage vials e.g. 1.5mL capillary amber glass bottles**

### **A6.9 Oven set at $130 \pm 20^{\circ}\text{C}$ with valid calibration status**

### **A6.10 Fridge set at $3 \pm 2^{\circ}\text{C}$ with valid calibration status**

### **A6.11 Freezer set as required by manufacturer's instructions**

### **A6.12 250mL glass Duran bottles with Teflon lined caps**

### **A6.13 44mL sample collection vials, with PTFE lined septa and containing 44µL $18 \text{ g L}^{-1}$ sodium thiosulphate solution.**

### **A6.14 44mL vials for standard preparation/storage, with PTFE lined septa**

### **A6.15 Cooled water bath for autosampler vial tray**

### **A6.16 Digital thermometer with valid calibration status**



**A6.2** The following instrument conditions have been used and found to be satisfactory.

**A6.2.1 Purge and Trap conditions**

Method Type – Water

Instrument - Atomx

Comments -Default parameters suggested for use when using a 5mL sample volume and a #9 trap or Vocarb 3000 (k) trap

<b>Purge</b>	
Valve Oven Temp	140°C
Transfer Line Temp	140°C
Sample Mount Temp	90°C
Water Heater Temp	90°C
Sample Vial Temp	20°C
Sample Equilibrate Time	0.00 min
Standby Flow	10 mL min <sup>-1</sup>
Purge Ready Temp	40°C
Condensate Ready Temp	43°C
Presweep Time	0.25 min
Prime Sample Fill Volume	3.0 mL
Sample Volume	5.0 mL
Sweep Sample Time	0.25 min
Sweep Sample Flow	100 mL min <sup>-1</sup>
Sparge Vessel Heater	Off
Sparge Vessel Temp	20°C
Prepurge Time	0.00 min
Prepurge Flow	0 mL min <sup>-1</sup>
Purge Time	8.00 min
Purge Flow	50 mL min <sup>-1</sup>
Purge Temp	20°C
Condensate Purge Temp	20°C
Dry Purge Time	0.5 min
Dry Purge Flow	100 mL min <sup>-1</sup>
Dry Purge Temp	20°C

<b>Desorb</b>	
Methanol Needle Rinse	Off
Methanol Needle Rinse Volume	3.0 mL
Water Needle Rinse Volume	10.0 mL
Sweep Needle Time	0.25 min
Desorb Preheat Temp	245°C
GC Start Signal	Start of Desorb
Desorb Time	2.00 min
Drain Flow	300mL min <sup>-1</sup>
Desorb Temp	250°C

<b>Bake</b>	
Methanol Glass Rinse	Off
Number of Methanol Glass Rinses	1
Methanol Glass Rinse Volume	30 mL
Number of Water Bake Rinses	3
Water Bake Rinse Volume	9.0mL
Bake Rinse Sweep Time	0.25 min
Bake Rinses Sweep Volume	100 mL min <sup>-1</sup>
Bake Time	2.00 min
Bake Flow	200 mL min <sup>-1</sup>
Bake Temp	280°C
Condensate Bake Temp	200°C

<b>Cryo</b>	
Focus Temp	-150°C
Inject Time	1.00 min
Inject Temp	180°C
Standby Temp	100°C

## A6.2.2 GC conditions

Parameter	Value
GC Column	RTX-VMS column, 20m x 0.18mm ID, 1 $\mu$ m film thickness
Oven equilibration Time	0.5 min
Max Temperature	240°C
Slow Fan	Disabled
Oven Program	50°C for 3 min then 20°C min <sup>-1</sup> to 220°C for 2.5 min
Run Time	14 min
Front SS Inlet He Mode	Split
Heater	On 220°C
Pressure	On 26.18 psi
Total Flow	On 42.3 mL min <sup>-1</sup>
Septum Purge Flow	On 2 mL min <sup>-1</sup>
Gas Saver	Off
Split Ratio	30:1
Split Flow	39 mL min <sup>-1</sup>

### A6.2.3 MS conditions

Ion trap conditions (quad conditions provided in method B) you can mix/match

Parameter	Value		
Transfer Line Temp	220°C		
Manifold Temp	80°C		
Trap Temp	150°C		
<b>Segment 1</b>			
Emission Current	10 microamps		
Mass Defect	0 mmu per 100u		
Count Threshold	1 counts		
Multiplier Offset	0 V		
Cal Gas	OFF		
Scan Time	1 sec		
Segment Start Time	0.00 min		
Segment End time	1.20 min		
Segment Low Mass	40 m/z		
Segment High Mass	650 m/z		
Ionisation Mode	None		
Ion Preparation Technique	None		
<b>Segment 2</b>			
Emission Current	10 microamps		
Mass Defect	0 mmu per 100u		
Count Threshold	1 counts		
Multiplier Offset	OFF		
Cal Gas	1 sec		
Scan Time	0.45 sec		
Segment Start Time	1.20 min		
Segment End time	12.00 min		
Segment Low Mass	35 m/z		
Segment High Mass	300 m/z		
Ionisation Mode	EI AGC		
Ion Preparation Technique	None		
<b>EI Auto Mode</b>			
Max ionisation Time	25000 µsec		
Target TIC	20001 counts		
Prescan Ionisation Time	100 µsec		
Background Mass	34 m/z		
RF Dump Value	350 m/z		
<b>Scan Segment</b>	<b>Mass range</b>	<b>Ion Storage Level</b>	<b>Ion Time Factor</b>
1	10 to 99	34.0 m/z	100%
2	100 to 249	34.0 m/z	100%
3	250 to 399	34.0 m/z	100%
4	400 to 650	34.0 m/z	100%

## **A7 Sample collection and preservation**

Samples should be collected directly into 44mL sample collection vials filling completely to leave no headspace. Two sample vials should be filled per sample. If analysis cannot be performed on receipt, samples should be stored at  $3 \pm 2^{\circ}\text{C}$ . See section 2 for information on sample stability.

## **A8 Analytical Procedure**

### **A8.1 Sample Preparation**

**A8.1.1** For samples of known low VOC concentrations e.g. water supply samples, river water, etc., no sample preparation is required and sample vials may be placed directly into the autosampler. Note the P/T system automatically adds 2uL of internal and surrogate standard to each 5 mL sample aliquot before purging.

**A8.1.2** For unknown samples, samples with large amounts of suspended solids, or known highly contaminated samples, a dilution maybe required. Appearance, odour or previous knowledge of the sample determines the dilution factor. Sample dilutions are prepared directly into 44mL vials using previously cooled (between  $3 \pm 2^{\circ}\text{C}$ ) dilution water, ensuring that the sample is mixed adequately and that the vials are completely full i.e. zero headspace.

### **A8.2 Calibration (Target Compounds)**

**A8.2.1** Perform a multipoint calibration of the instrument using the standards prepared in A5.8. This calibration is valid for targeted analysis methods ran on the instrumentation and need not be run at each incidence of unknowns analysis, however a CCC should be run both before and after samples as a system suitability check to ensure that all target compounds are identified correctly.

**A8.2.2** Appropriate system suitability checks should be carried out for example, the response (peak area) and peak asymmetry of the 1,4-Difluorobenzene internal standard in the CCC should be checked to see that they are within the established limits.

### **A8.3 Analysis of results**

**A8.3.1** Unknown compounds are tentatively identified by comparison with the mass spectral reference library following guidelines described in sections 3.1 and 3.2

**A8.3.2** For non-target compounds, the peak is either automatically integrated and semi-quantified by the instrument software or manually integrated and semi-quantified against the nearest internal standard using the calculation in A9.

**A8.3.3** Surrogate recoveries should be used to assess the applicability of the method to each sample matrix.

## A9 Calculation

Semi-quantitative results for target compounds can be calculated using the following:-

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

Semi-quantitative results for non-target compounds can be calculated using the following although users must be aware of the limitations of the method as described in A2:-

$$\text{Concentration } \mu\text{g L}^{-1} = \frac{\text{Area of compound peak (total ion count)} \times \text{concentration of internal standard } \mu\text{g L}^{-1}}{\text{Area of designated or nearest internal standard peak (total ion count)}}$$

and the internal standard concentration is  $10\mu\text{g L}^{-1}$

## Appendix A1 –Target Compounds – RTC Megamix

Compound	Chemical Abstract Service Number	Typical Retention Time (min) (See Figure A1)
Dichlorodifluoromethane	75-71-8	0.938
Chloromethane	74-87-3	1.008
Vinyl Chloride	75-01-4	1.037
Trichlorofluoromethane	75-69-4	1.239
1,1-Dichloroethene	75-35-4	1.436
Dichloromethane	75-09-2	1.684
trans-1,2-Dichloroethene	156-60-5	1.753
1,1-Dichloroethane	75-34-3	2.077
cis-1,2-Dichloroethene	156-59-2	2.409
2,2-Dichloropropane	594-20-7	2.481
Bromochloromethane	74-97-5	2.551
Chloroform	67-66-3	2.603
Carbon Tetrachloride	56-23-5	2.690
1,1,1-Trichloroethane	71-55-6	2.754
1,1-Dichloropropene	563-58-6	2.852
Benzene	71-43-2	3.076
1,2-Dichloroethane	107-06-2	3.273
Trichloroethene	79-01-6	3.588
Dibromomethane	74-95-3	3.952
1,2-Dichloropropane	78-87-5	4.040
Dichlorobromomethane	75-27-4	4.101
cis-1,3-Dichloropropene	10061-01-5	4.621
Toluene	108-88-3	4.802
Tetrachloroethene	127-18-4	5.086
trans-1,3-Dichloropropene	10061-02-6	5.150
1,1,2-Trichloroethane	79-00-5	5.270
Dibromochloromethane	124-48-1	5.392
1,3-Dichloropropane	142-28-9	5.472
1,2-Dibromoethane	106-93-4	5.556
Chlorobenzene	108-90-7	5.967
Ethyl Benzene	100-41-4	6.006
1,1,1,2-Tetrachloroethane	630-20-6	6.025

## Appendix A1 –Target Compounds continued

Compound	Chemical Abstract Service Number	Typical Retention Time (min)(see Figure A1)
m + p-Xylene	108-38-3 / 106-42-3	6.124
o-Xylene	95-47-6	6.443
Bromoform	75-25-2	6.486
Styrene	100-42-5	6.488
Isopropyl Benzene	98-82-8	6.688
Bromobenzene	108-86-1	6.951
n-Propylbenzene	103-65-1	7.003
1,1,2,2-Tetrachloroethane	630-20-6	6.025
2-Chlorotoluene	95-49-8	7.102
1,2,3-Trichloropropane	96-18-4	7.155
1,3,5-Trimethylbenzene	108-67-8	7.162
4-Chlorotoluene	106-43-4	7.231
tert-Butylbenzene	98-06-6	7.393
1,2,4-Trimethylbenzene	95-63-6	7.451
sec-Butylbenzene	135-98-8	7.528
4-Isopropyltoluene	99-87-6	7.648
1,3-Dichlorobenzene	541-73-1	7.669
1,4-Dichlorobenzene	106-46-7	7.741
n-Butylbenzene	104-51-8	7.968
1,2-Dichlorobenzene	95-50-1	8.056
1,2-Dibromo-3-Chloropropane	96-12-8	8.679
1,3,5-Trichlorobenzene <sup>(1)</sup>	108-70-3	8.702
Hexachlorobutadiene	87-68-3	9.189
1,2,4-Trichlorobenzene	120-82-1	9.203
Naphthalene	91-20-3	9.455
1,2,3-Trichlorobenzene	87-61-6	9.594

Note<sup>1</sup> 1,3,5-TCB is not present in the megamix but prepared separately as in section 5

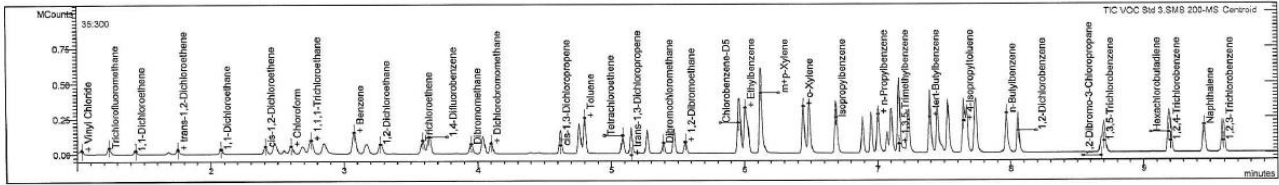
# Figure A1 Typical Chromatogram Target Suite Calibration Standard

## 10µg L<sup>-1</sup> Standard

Print Date: 09 Apr 2018 14:16:00  
 O030 Target Compounds

Sample Report for voc std 3.sms

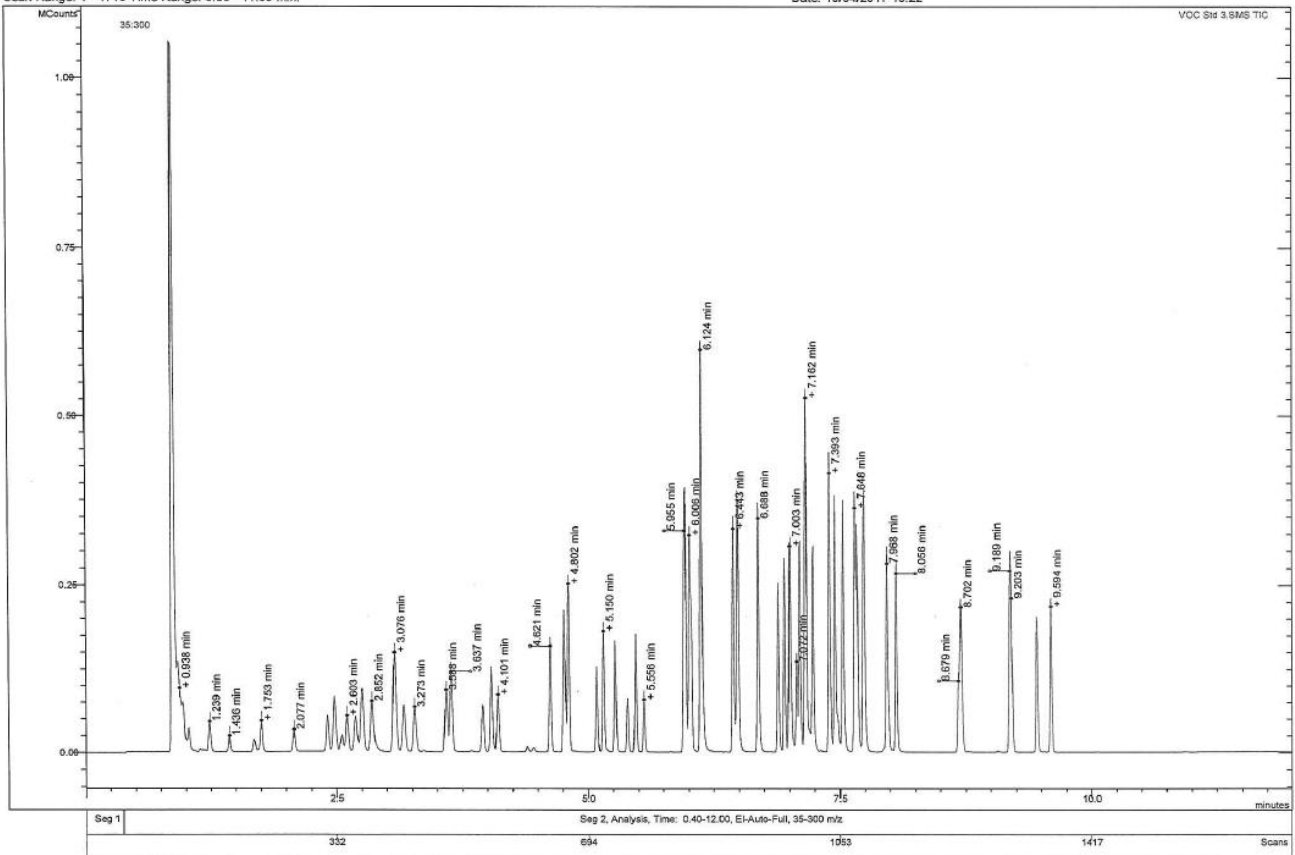
Sample ID:	VOC Std 3	Multiplier:	1.000000	Divisor:	1.000000
Inj. Sample Notes:	None	Acquisition Date:	10/04/2017 16:22	Data File:	...peatability/voc std 3.sms
Method:	...ityrepeatability.mth				



### Chromatogram Plot

File: c:\agilent\ms\data\2017\_thms\raw\_data\scans\repeatability\voc std 3.sms  
 Sample: VOC Std 3  
 Scan Range: 1 - 1710 Time Range: 0.00 - 11.99 min.

Operator: Steve D  
 Date: 10/04/2017 16:22





**B The Identification of Volatile Organic Compounds Raw and Potable Waters by Headspace Gas Chromatography-Mass Spectrometry**

**B1 Performance Characteristics of the Method**

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<b>B1.1</b>	<b>Substances determined</b>	Various Volatile Organic Compounds in the range C1 to C12 (as n-alkanes) depending upon boiling points and equilibration with its headspace vapour at 70°C.
<b>B1.2</b>	<b>Types of Sample</b>	Raw waters (ground and surface), potable waters.
<b>B1.3</b>	<b>Basis of method</b>	Sample placed in a septum vial and allowed to equilibrate with its headspace vapour at 70°C. A sample of the vapour is injected using a headspace sampler into a capillary GC with MS detection. Library search of unknowns with approximate quantitation by comparison with an internal standard.
<b>B1.4</b>	<b>Range of application</b>	N/A - non-quantitative method
<b>B1.5</b>	<b>Calibration curves</b>	For "Target SIM Analytes" - Typically Quadratic Regression or Linear Repr, Force (0, 0) with Equal weight or Inverse of Conc weight depending on target analyte
<b>B1.6</b>	<b>Internal standards used</b>	Pentafluorobenzene (363-72-4), 1,4-Difluorobenzene (540-36-3), Chlorobenzene-D5 (3114-55-4), 1,4-Dichlorobenzene-D4 (3855-82-1), 1,2-Dichloroethane-D4 (17060-07-0), Dibromofluoromethane (1868-53-7), Toluene-D8 (2037-26-5), 1-bromo-4-fluorobenzene (460-00-4)
<b>B1.7</b>	<b>Standard deviation and Bias</b>	N/A - non-quantitative method.
<b>B1.8</b>	<b>Limit of detection</b>	Typically around 0.25 to 1µg L <sup>-1</sup>

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## **B2 Principle**

15mL of sample is placed in a 20mL headspace vial containing 3 to 4 g of sodium sulphate and spiked with 75µL of internal standard solution and immediately capped. The vial is heated in a headspace sampler and allowed to equilibrate with its headspace vapour at 70°C for 17 minutes. A sample of the vapour is injected from the headspace sampler into a capillary GC column separated by temperature programming and detected with the use of mass spectrometer run in SIM / full scan mode.

Standards containing known target VOC compounds are used to prove system suitability and verify the identification process. These standards may be used to provide estimates of quantitative results if required for target compounds and for unknowns quantitation can be based on the nearest internal standard but it must be stressed in these cases that this is semi-quantitative at best.

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## **B3 Interferences**

Any compound, which is present in the air of the environment, and is trapped in the headspace vial, and has similar gas chromatographic and mass spectrometric properties to a compound of interest may cause interference. Extreme care should be taken to minimise contamination of samples and blanks by solvents used in the laboratory i.e. dichloromethane (DCM) and the choice of reagents is key. Without authentic standards it may not be possible to identify correct isomers of compounds.

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## **B4 Hazards**

Analysts using this method should familiarise themselves with the COSHH and risk assessments for this analysis. Skin contact or inhalation of all reagents and their solutions specified in this method should be avoided. Methanol is highly flammable; and should be handled away from sources of ignition.

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## **B5 Reagents**

All reagents should be of sufficient purity that they do not give rise to interfering peaks or raised background levels during the analysis. Procedural blanks should be run with each batch of samples analysed.

**B5.1 Water** - free from interference

**B5.2 Methanol** - free from interference

**B5.3 Sodium Sulphate anhydrous**

Muffled in furnace at  $500 \pm 20^{\circ}\text{C}$  for approx. 4 hours and transferred to a suitable container stored desiccator when cool enough. The batch is labelled with a 1 month expiry date.

**B5.4 MTBE (methyl tertiary butyl ether) CAS 1634-04-4**

For MTBE, a neat reference material is purchased (e.g. Sigma Aldrich) and a 2 year or manufacturer's expiry applied, whichever is sooner. Storage in accordance with the manufacturer's direction.

An individual stock solution is then produced to a concentration of  $4000 \text{ mg L}^{-1}$ .

**B5.5 General comments re Standard preparation**

All stock and intermediate standards should be stored in a freezer.

Certified stock standards shall be purchased with certificates and records maintained showing date received, expiry date, opened date and date of disposal.

Compounds covered by the targeted SIM analysis are shown in appendix B1

**B5.6  $200 \text{ mg L}^{-1}$  Volatile Organic Compounds Standard**

This certified stock solution in methanol is available for example from Restek: Volatiles MegaMix with Gases (Catalogue No. 30603)

This standard is received in a 1mL sealed glass ampoule. After opening transfer the standard into a suitable vial, and assign a one month expiry to the opened vial (not exceeding the manufacturer's expiry)

**B5.7  $4000 \text{ mg L}^{-1}$  MTBE Stock solution.**

Assuming a density of 0.741 and a purity of  $\geq 99.0\%$ , accurately spike  $270\mu\text{L}$  of MTBE into approx. 30mL methanol in a 50mL volumetric flask and make up to volume with methanol and mix well. Transfer to a labelled amber glass vial or bottle, with a 6 month expiry.

**B5.8  $6 \text{ mg L}^{-1}$  High Standard solution.**

Spike  $600\mu\text{L}$  of Volatile MegaMix (B5.6) and  $30\mu\text{L}$  of MTBE Stock solution (B5.7) into approximately 10mL methanol in a 20mL volumetric flask and make up to the mark with methanol and mix well. Transfer to a labelled amber glass vial or bottle, with a 1 month expiry.

**B5.9  $0.75 \text{ mg L}^{-1}$  Low Standard solution.**

Spike  $2500\mu\text{L}$  of the High Standard solution (B5.8) into approx. 10mL methanol in a 20mL volumetric flask and make up to the mark with methanol and mix well. Transfer to a labelled amber glass vial or bottle, with a 1 month expiry.

**B5.10 Internal and Surrogate Standards**

An internal standard mix (for example Restek, 8260 Internal Standard Mix, catalogue # 30074) at 2500mg L<sup>-1</sup> and surrogate mix (Restek, 8260A Surrogate Mix, catalogue # 30240) at 2500 mg L<sup>-1</sup> are purchased and a 1 year, or manufacturers expiry is applied, whichever is sooner.

**B5.11 6 mg L<sup>-1</sup> Internal and Surrogate Standard Mix**

Spike 120µL of internal standard mix and 120µL of surrogate mix into approx. 30mL of methanol in a 50mL volumetric flask and make up to the mark with methanol and mix well. Transfer to a labelled amber glass vial or bottle, with a 1 month expiry.

**B5.12 Working Daily Standards (Prepare daily or with each batch of samples run).**

Calibration standards 1 to 5 are run at the start of each batch of samples, in order to calibrate the instrument for the SIM target compounds. These can also be used as system verification check standards and to verify instrument performance.

Calibration standards are prepared by adding approx. 3 to 4g of sodium sulphate to a 20mL headspace vial, adding 15mL of 'Blank' water and capping immediately.

Inject the intermediate standards, as shown in table, below the water surface and swirl to mix.

All Working Standards are prepared daily or with each batch of samples run.

Calibration Level	Volume of High Cal solution (µL) [5.8]	Volume of low Cal solution (µL) [5.9]	Resultant concentration µgL <sup>-1</sup>
Cal 5	50	-	20
Cal 4	25	-	10
Cal 3	12.5	-	5
Cal 2	-	20	1
Cal 1	-	10	0.5

A blank water vial is also prepared as above, without the addition of any calibration standard solutions.

To each vial in the batch, spike 75µL of Internal Standard Mix (B5.11), giving an internal standard and surrogate concentration of 30µg L<sup>-1</sup> in vial. (Note this stage can be automated by use of dual rail autosampler system after capping - if performed manually this can be done before capping the vial.)

## **B6 Apparatus**

Apparatus should be free from contamination before use. Glassware should be washed, rinsed with dilute acid followed by deionised water and allowed to dry.

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

### **B6.1 GC/MS with headspace auto sampler**

HP7890 Gas Chromatograph fitted with 5975 mass selective detector and a GERSTEL MPS2 XL dual rail auto sampler / headspace unit are suitable for the analysis. The following column is suitable for the analysis:  
DB-624 30m x 0.25mm id x 1.4µm film thickness

**B6.2** Analytical balance with valid calibration status

**B6.3** Grade B or better volumetric flasks – 20mL, 50mL

**B6.4** Micro syringes with valid calibration status - 10µL, 25µL, 50µL, 100µL, 250µL, 500µL

**B6.5** 10mL auto-pipette with valid calibration status and disposable tips

**B6.6** 20mL headspace vials and magnetic screw caps with septum

**B6.7** Vial trays

**B6.8** Spark proof freezer set at a suitable temperature, according to manufacturer guidance.

**B6.9** Spark proof refrigerator typically set at  $5 \pm 3^{\circ}\text{C}$

**B6.10** Appropriate amber glass storage vials or bottles, with PTFE lined cap – no headspace

**B6.11** Muffle Furnace set at  $500 \pm 20^{\circ}\text{C}$

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

#### B6.12 Gerstel MPS and Headspace Parameters

Parameter	Value
Incub Temp	70°C
Incub Time	17 min
Agitate Speed	750 rpm
Agitate on Time	2 sec
Agitate off Time	1 sec
Syringe Temp	90°C
Syringe Fill Speed	250 $\mu\text{L sec}^{-1}$
Pull Up Del	0 sec
Injection Volume	1000 $\mu\text{L}$

Parameter	Value
Inject To	GC Inlet
Inject Speed	600 $\mu\text{L sec}^{-1}$
Pre Inj Del	0 sec
Post Inj Del	0 sec
Syringe Flushing	0
Extractions per Vial	1
GC Runtime	9 min
Helium Pressure	14 psi

#### B6.13 GC conditions.

Parameter	Value
Column	DB-624 30m x 0.25mm id x 1.4 $\mu\text{m}$ film thickness
Injector Temp	175°C
Injection Mode	Split (10:1) 20 mL $\text{min}^{-1}$
Flow Mode	Constant Flow (2 mL $\text{min}^{-1}$ )
Septum purge	ON (3 mL $\text{min}^{-1}$ )
Gas Saver	ON (15 mL $\text{min}^{-1}$ after 5 min)
Injection Liner	4mm tapered with glass wool
Carrier Gas	Helium at approximately 16 psi
Initial Oven Temp	35°C
Initial Time	0.50 min
Level 1 Rate	20°C $\text{min}^{-1}$
Level 1 Final Temp	160°C
Level 1 Time	0.00 min
Level 2 Rate	30°C $\text{min}^{-1}$
Level 2 Final Temp	190°C
Level 2 Final Time	0.00 min
Level 2 Rate	60°C $\text{min}^{-1}$
Level 2 Final Temp	240°C
Level 2 Final Time	1.00 min

**B6.14** MS condition (SIM/Scan).

<b>Parameter</b>	<b>Value</b>
<b>Scan Parameters</b>	
Start Time	0.50 min
Start Mass	35 amu
End Mass	300 amu
Threshold	150
Sampling Rate	2 <sup>3</sup>
Scan Rate	2.83 scans sec <sup>-1</sup>
<b>SIM Parameters</b>	
Solvent Delay	0.50 min
EMV mode	Gain Factor
Gain Factor	5.00 (subject to change as electron multiplier ages)
MS Source Temp	230°C
MS Quad Temp	150°C
<b>Group 1</b>	
Start Time	0.50 min
Resolution	Low
Ions in group (dwell time)	50(5), 52(5), 62(5), 64(5), 66(5), 85(5), 87(5), 94(5), 96(5), 101(5), 103(5)
<b>Group 2</b>	
Start Time	1.35 min
Resolution	Low
Ions in group (dwell time)	49(10), 57(10), 61(10), 63(10), 65(10), 73(10), 84(10), 96(10)
<b>Group 3</b>	
Start Time	2.20 min
Resolution	Low
Ions in group (dwell time)	49(10), 61(10), 62(10), 75(10), 77(10), 78(10), 83(10), 85(10), 96(10), 97(10), 98(10), 99(10), 110(10), 111(10), 114(10), 117(10), 119(10), 130(10), 168(10), 192(10)
<b>Group 4</b>	
Start Time	2.83 min
Resolution	Low
Ions in group (dwell time)	63(10), 76(10), 83(10), 85(10), 88(10), 93(10), 95(10), 114(10), 130(10), 174(10)
<b>Group 5</b>	
Start Time	3.50 min
Resolution	Low
Ions in group (dwell time)	61(10), 75(10), 76(10), 83(10), 91(10), 92(10), 97(10), 98(10), 99(10), 100(10), 110(10), 166(10)
<b>Group 6</b>	
Start Time	4.05 min
Resolution	Low
Ions in group (dwell time)	76(10), 78(10), 83(10), 97(10), 99(10), 107(10), 109(10), 127(10), 129(10), 131(10), 166(10)

<b>Group 7</b>	
Start Time	4.50 min
Resolution	Low
Ions in group (dwell time)	77(10), 82(10), 91(10), 104(10), 106(10), 112(10), 117(10), 131(10)
<b>Group 8</b>	
Start Time	5.00 min
Resolution	Low
Ions in group (dwell time)	75(10), 78(10), 83(10), 85(10), 91(10), 95(10), 104(10), 105(10), 106(10), 110(10), 120(10), 126(10), 134(10), 156(10), 158(10), 173(10), 174(10), 175(10)
<b>Group 9</b>	
Start Time	5.85 min
Resolution	Low
Ions in group (dwell time)	91(20), 105(20), 119(20), 120(20), 134(20)
<b>Group 10</b>	
Start Time	6.10 min
Resolution	Low
Ions in group (dwell time)	75(10), 91(10), 105(10), 111(10), 119(10), 128(10), 129(10), 134(10), 146(10), 157(10), 180(10), 182(10), 225(10), 260(10)

Note: Dwell times are in ms.

Compound order of elution, approximate retention times, MS ions.

## **B7 Sample Collection and Preservation**

Vials are received in 40mL amber glass capped vials with sodium thiosulphate preservative filled completely to leave no headspace. If a sample is seen to possess a significant headspace, then an appropriate analyst's comment must be assigned to the sample. Two sample vials should be filled per sample. If analysis cannot be performed on receipt, samples should be stored at  $3 \pm 2^{\circ}\text{C}$ . See section 2 for information on sample stability.

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## **B8 Analytical Procedure and Sample Preparation**

- B8.1** Place approx. 3 – 4 g of sodium sulphate in a 20mL headspace vial.
- B8.2** Add 15mL of sample from a sampling vial into the headspace vial using an auto-pipette. The vial is then immediately capped.
- B8.3** To the headspace vial, spike 75 $\mu\text{L}$  of the Internal standard solution (B5.11), below the water sample surface and swirl to mix. (Note this stage can be automated by use of dual rail autosampler system - if performed manually this can be done at stage B8.2 before capping.)



- B8.4** Prepare analytical blanks and calibrations as per B5.12
- B8.5** Setup the instrument sequence to incorporate all blanks, standards and samples and run.
- B8.6** Perform a multipoint calibration of the instrument using the standards prepared. This calibration is valid for the targeted compounds.
- B8.7** Results are generated from both the targeted SIM and non-targeted SCAN instrument data as per section B9 and reported.
- 

## **B9 Calculation**

Quantitative results for known target compounds can be calculated using the following:-

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

This calculation is performed by the instrument software (i.e. MS Chemstation) from the SIM chromatogram data.

Semi-quantitative results for non-target compounds can be calculated from the SCAN chromatogram, using the following although users must be aware of the limitations of the method as described in B3.

This should be achieved by comparison of responses between the non-target compound and the nearest internal standard peak i.e.

$$\text{Concentration } \mu\text{g L}^{-1} = \frac{(\text{response component in sample})}{(\text{response internal standard in sample})} \times (30 (\mu\text{g L}^{-1}))$$

This should be completed for each sample and any peaks showing significance should be identified in the chromatogram visually by the analyst and an approximate concentration determined.

## Appendix B1 –Target SIM Compounds – Retention Times and Ions

Compound	Approx. Retention Time (min)	Fragment Ion ( $m/z$ )
<i>Pentafluorobenzene (IS)</i>	2.527	168, 99
Dichlorodifluoromethane	0.725	85, 87
Chloromethane	0.802	50, 52
Vinyl Chloride	0.872	62, 64
Chloroethane	1.081	64, 66
Bromomethane	1.039	96, 94
Trichlorofluoromethane	1.206	101, 103
1,1-Dichloroethene	1.447	96, 61
Dichloromethane	1.667	84, 49
MTBE	1.800	73, 57
trans-1,2-Dichloroethene	1.800	96, 61
1,1-Dichloroethane	1.998	63, 65
cis-1,2-Dichloroethene	2.265	96, 61
2,2-Dichloropropane	2.265	77, 97
Chloroform	2.424	83, 85
Bromochloromethane	2.386	130, 49
Dibromofluoromethane (Surr)	2.498	111, 192
1,1,1-Trichloroethane	2.517	97, 61
1,1-Dichloropropene	2.592	110, 75
Carbon Tetrachloride	2.601	117, 119
1,2-Dichloroethane	2.714	62, 98
<i>1,4-Difluorobenzene (IS)</i>	2.899	114, 88
Benzene	2.704	78, 77
1,2-Dichloropropane	3.161	63, 76
Trichloroethene	3.038	130, 95
Dibromomethane	3.223	174, 93
Bromodichloromethane	3.308	83, 85
cis-1,3-Dichloropropene	3.562	75, 110
Toluene-d8 (Surr)	3.717	98, 100
Toluene	3.755	91, 92
trans-1,3-Dichloropropene	3.886	75, 110
1,1,2-Trichloroethane	4.002	97, 83, 99
<i>Chlorobenzene-d5 (IS)</i>	4.605	117, 82
1,3-Dichloropropane	4.100	76, 78
Tetrachloroethene	4.085	166, 131
Dibromochloromethane	4.240	129, 127
1,2-Dibromoethane	4.313	107, 109
Chlorobenzene	4.627	112, 77
1,1,1,2-Tetrachloroethane	4.677	131, 117
Ethyl Benzene	4.698	91, 106
m,p-Xylene	4.777	91, 106
o-Xylene	5.031	91, 106
Styrene	5.049	104, 78

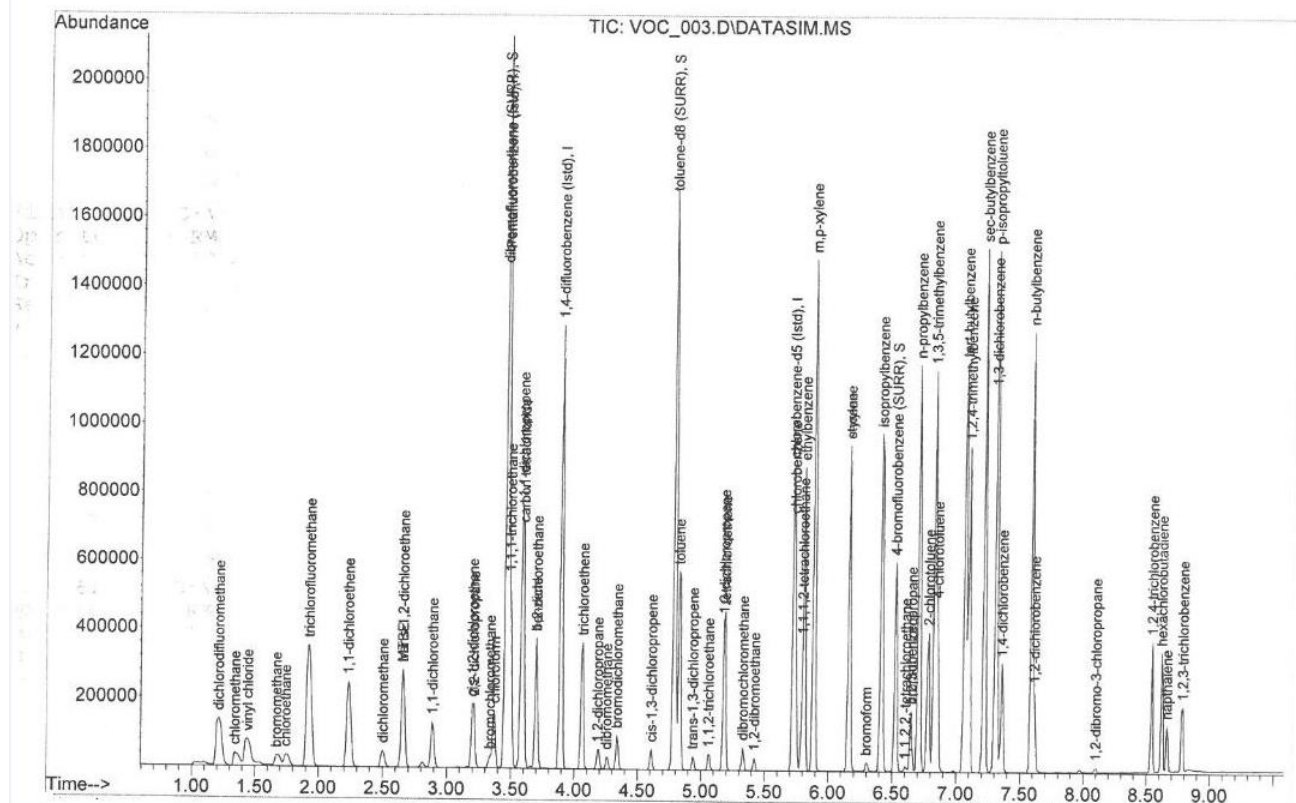
Bromoform	5.166	173, 175
Isopropylbenzene	5.292	105, 120
1,1,2,2-Tetrachloroethane	5.499	83, 85
4-Bromofluorobenzene (Surr)	5.391	174, 95
1,2,3-Trichloropropane	5.525	110, 75
n-Propylbenzene	5.920	91, 120
Bromobenzene	5.490	156, 158
2-Chlorotoluene	5.624	91, 126
1,3,5-Trimethylbenzene	5.696	105, 120
4-Chlorotoluene	5.705	91, 126
tert-Butylbenzene	5.928	134, 119
1,2,4-Trimethylbenzene	5.958	105, 120
sec-Butylbenzene	6.081	105, 134
p-Isopropyltoluene	6.187	119, 134
1,3-Dichlorobenzene	6.145	146, 111
1,4-Dichlorobenzene	6.213	146, 111
n-Butylbenzene	6.484	91, 134
1,2-Dichlorobenzene	6.475	146, 111
1,2-Dibromo-3-chloropropane	7.043	157, 75
1,2,4-Trichlorobenzene	7.593	180, 182
Hexachlorobutadiene	7.703	225, 260
Naphthalene	7.745	128, 129
1,2,3-Trichlorobenzene	7.889	180, 182

Order of elution remains the same but retention times vary with instrument maintenance.

# Figure B1 Typical Chromatogram Target Suite Calibration Standard

## 10µg L<sup>-1</sup> Standard

File : D:\MSCHEM\Data\VOCs\170710\_51075\VOC\_003.D  
 Operator : RM  
 Acquired : 10 Jul 2017 10:42 using AcqMethod VOCs.M  
 Instrument : VOCPrepStation  
 Sample Name: VOC Cal 4  
 Misc Info :  
 Vial Number: 8



## 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.

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