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

Methods for the Examination of Waters and Associated Materials

June 2021

The determination of Unknown Semi Volatile Organic Compounds in Raw and Potable Waters by Gas Chromatography – Mass Spectrometry (2019)

Methods for the Examination of Waters and Associated Materials

This booklet contains a method for the determination of unknown semi volatile organic compounds in raw and potable waters by Gas Chromatography - Mass Spectrometry.

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

1 Introduction

Identification of unknown semi-volatile compounds (SVOCs) 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 volatile (VOC), Liquid Chromatorgraphy-Mass Spectrometry (LCMS) 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 semi volatile compounds that should not be present in the water samples.

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 1 and 14 days and this is very much compound specific. Samples should be stored at 5±3ºC prior to analysis. Information on sample stability can be found in SCA Bluebook 261 (The Stability and Preservation of Waters) and US EPA SW-846, Chapter 4.

3 Identification of Unknown Compounds

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 criteria 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 coelutions 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 backround 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 100 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 C12 to C20 aliphatic hydrocarbons. The hydrocarbon range is obtained by comparison of retention times to a stored chromatogram containing all the even numbered n-alkanes from C10 to C40.

- The technique may also be used for the tentative identification of hydrocarbon mixes e.g. petrol, kerosene, diesel 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.

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.

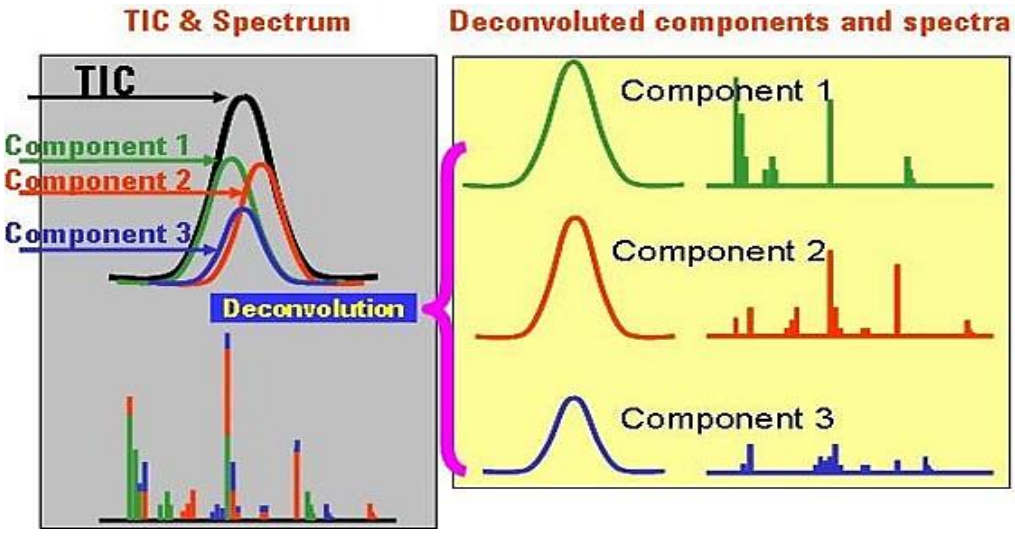


Figure 1. An illustration of mass spectral deconvolution process.

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

Water Quality — Sampling**,** Part 3: Preservation and handling of water samples (ISO 5667-3:2012)

United States Environmental Protection Agency. SW-846 Test Method 8270d, Revision 5 July 2014, Semivolatile Organic Compounds by Gas chromatography/Mass Spectrometry

SCA Bluebook 261, The Stability and Preservation of Waters, 2018.

United States Environmental Protection Agency. SW-846 Chapter 4, Revision 5 July 2014

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 standards 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.

Internal Standard (see method A)
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.

Injection Standard (see Appendix 1)
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.

Note:- The use of either internal or injection standards for screening methods can be used to estimate the concentration of unknowns in a sample but are only ever at best, semi-quantitative with no ability to recovery correct during extraction or accurately estimate response factors during mass spectrometry detection.

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 sorted by their mass to charge ratio (m/z). The ions are then detected by an electron multipler 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.

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.

Solid Phase Extraction (SPE)
A sample preparation technique which uses the affinity of solutes dissolved or suspended in a liquid for a solid through which the sample is passed. The analytes of interest in the sample are retained on the stationary phase. They are then removed from the solid phase by rinsing with an appropriate eluent.

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.

Total Ion Chromatogram (TIC)
A plot of the total ion current vs. retention time obtained from a chromatography experiment with mass detection. The total ion current chromatogram monitors a very large window often of several hundred mass-to-charge units.

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

A1 Performance characteristics of the method

A1.1	Substances determined	Any compound that is extracted from the sample by dichloromethane, is amenable to gas chromatography and whose mass spectra is available in the mass spectral library (e.g. NIST).
A1.2	Type of sample	Raw waters (ground and surface), potable waters.
A1.3	Basis of method	Unknown and target compounds are extracted from samples using liquid/liquid extraction using dichloromethane as the extraction solvent and are analysed using gas chromatography with a mass spectrometer operating in scan mode.
A1.4	Range of application	Typically linear upto 1.0 µg L^{-1} for target compounds. The range may be extended by dilution.
A1.5	Standard deviation	Not applicable.
A1.6	Limit of detection	Typically 0.1µg L^{-1} for 1000ml of sample.
A1.7	Bias	Not applicable.

A2 Principle

The sample is extracted with dichloromethane using a liquid-liquid extraction technique under neutral and acidic conditions. The dichloromethane extract is dried using anhydrous sodium sulphate or dry disk membrane before being evaporated down to 1 mL. Unknown and target compounds are determined by GC with a mass spectrometer operating in scan mode.

Unknown compounds are identified by comparing their mass spectra to those contained in a specialist Mass Spectral Library (e.g. National Institute of Standards and Technology, NIST). An estimation of the amount of the compound present is made by comparing the peak response of the unknown to that of the nearest eluting internal standard. These values are reported as µg L^{-1} equivalent of x (where x is the chosen internal standard).

The following categories of compounds will not be detected by this screening method:

(a) Compounds that are too volatile and are lost in the concentration stage.
(b) Compounds that are too volatile to be separated from the extracting solvent (Dichloromethane) in the gas chromatography stage.
(c) Compounds that lack sufficient volatility to pass through a capillary GC column within a reasonable timescale.
(d) Compounds that are thermally unstable and break down in the high temperature inlet of the GC.
(e) Compounds that polymerise under the high temperature of the GC inlet.
(f) Compounds of molecular weight outside the scan range of the method (m/z <35 to >550). The range can be expanded but must be within the capability of the instrument.
(g) Compounds not extractable in the chosen solvent.
(h) Compounds not extractable at the chosen pH range.

A3 Interferences

Care should be taken to ensure the reagents are as free as possible from contamination. They should be stored in glass containers to prevent leaching of contaminants from plastic containers. Solvents should be of a high purity and tested to ensure they contain minimal levels of contaminants.

A4 Hazards

Standards containing semi volatile compounds are harmful / toxic and should be treated with the appropriate care, although in most laboratories they are obtained as a dilute standard in a common solvent.

- Acetone is an irritant and flammable.
- Dichloromethane is toxic.
- Sodium sulphate is an irritant.
- Hydrochloric acid is corrosive.
- All reagents must be handled with care, safety data sheets consulted and the appropriate control measures implemented.

Waste solvents should be discarded according to documented procedures.

A5 Reagents

All reagents should be of analytical grade quality and distilled or deionised water should be used throughout.

A5.1 Acetone.

A5.2 Dichloromethane.

A5.3 Water.

A5.4 Hydrochloric acid 20% w/v.

A5.5 Sodium sulphate (anhydrous). Dry at 500 ± 50°C for a minimum of 4 hours in a muffle furnace. Allow to cool in a desiccator prior to use. This solid should be stored in a sealed glass bottle at ambient temperature for up to 3 months.

A5.6 1N Sodium hydroxide solution

A5.7 Calibration stock solution – SVOC Mega Mix (Restek) at 500 to 1000mg L^{-1} in dichloromethane or suitable equivalent. The mixture contains 76 semi volatile compounds, see appendix 3 for list of the target compounds.

The solution should be stored according to manufacturer's instructions.

It is advisable to analyse an Analytical Quality Control sample to demonstrate the ongoing performance of the method. A small selection of target compounds from key analytical groups may be selected for this purpose. AQC sample stock standard solutions should be obtained, preferably from a different supplier or at least separate lot number.

A5.8 Working calibration standard solution (1000-2000 µg L^{-1}) – Partially fill a 25 mL volumetric flask with acetone and add 50 µL of the stock solution. Make up to the mark with acetone and mix by inversion. This solution may be stored at 5 ± 3°C for up to 1 month.

A5.9 Stock injection standard solution – SV Internal Standards Mix, 2000 mg L^{-1} in Dichloromethane or suitable equivalent.

Contains; 1,4-Dichlorobenzene-D4, Acenaphthene-D10, Chrysene-D12, Naphthalene-D8, Perylene-D12 and Phenanthrene-D10.

The solution may be available commercially and should be stored according to manufacturer's instructions.

A5.10 Working internal standard solution (20 mg L^{-1}) – Partially fill a 25 mL volumetric flask with acetone and add 250 µL of stock internal standard solution. Make up to the mark with acetone and mix thoroughly by inversion. This solution may be stored at 5 ± 3ºC for up to 3 months.

A5.11 Blank
A procedural blank is analysed with every batch of samples. 1000 mL of a suitable bottled or tap water is transferred to a labelled 1 Litre clear glass bottle. This sample should be prepared on the day of use.

A5.12 Calibration standard solutions – For example, for a four point calibration, prepare a series of four 1 litre clear glass bottles. Label them Cal 1, Cal 2, Cal 3 and Cal 4, and add 1000 mL of deionised water to each bottle. Using the table below, add the relevant amount of spiking solution to each bottle.

Standard	Concentration µg L^{-1}	Amount of calibration spiking solution (µL)
Cal 1	0	0
Cal 2	0.2	100
Cal 3	0.5	250
Cal 4	1.0	500

Note:- these concentrations are based on a 2000 mg L^{-1} standard and may vary.

These solutions should be prepared on the day of use.

A6 Apparatus

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

A6.1 Muffle Furnace capable of being set to 500 ± 50°C

A6.2 2 Litre glass separating funnel.

A6.3 Blow-down apparatus. Any device capable of being set at 25 ± 3°C and can direct a gentle stream of nitrogen or air on to the extract. Higher temperatures may be used but should be evaluated due to the potential to lose a greater amount of volatile compounds.

A6.4 Bottle Roller capable of up to 180 rpm.

A6.5 Evaporating tubes with 1 mL end point.

A6.6 Funnel for sodium sulphate or Dry Disk filter apparatus and Dry Disk membranes.

A6.7 GC MS system capable of operating in scan mode and an appropriate data station. This method was set up on an Agilent GC MS system and the conditions listed below, other systems are available but the suitability of the equipment should be evaluated.

Columns:	HP-5MS Ultra-inert, 30 m x 0.25 mm, 0.25 µm, Agilent (19091S-433UI), or suitable equivalent.
Carrier gas:	Helium, constant flow at 1.2 ml per minute.
Injection volume:	2 µL
Inlet:	Split/Splitless operating in pulsed Splitless mode
Inlet temperature:	250°C
Injection pulse pressure:	25 psi until 0.4 minutes
Purge flow to split vent:	60 mL min^{-1} at 1 minute.
Temperature programmes:	
Oven:	Initial temperature at 35 °C for 5 minutes, then

	5 °C per minute to 150 °C, then 10 °C per minute to 300 °C and hold for 5 minutes
Run time:	48 minutes

MS Instrument conditions:

Source Temperature:	230°C
Quad Temperature	150°C
Transfer Line Temperature:	280°C
Acquisition mode:	Scan
Scan Range:	35-550 amu.
Scan rate:	2.83 scans sec^{-1}

Internal Standards:

Compound	Typical RT	Quantifier (m/z)
1,4 Dichlorobenzene d4	6.00	150
Naphthalene d8	7.60	136
Acenaphthene d10	9.80	162
Phenanthrene d10	11.70	188
Chrysene d12	15.50	240
Perylene d12	18.20	264

A7 Sample collection and preparation

Samples may be taken in 1 Litre amber glass bottles with caps fitted with a PTFE liner. It is recommended that the samples are solvent extracted as soon as possible after being taken, however, they may be stored for up to 14 days in glass bottles at 5 ± 3°C. The sample extracts are stable for up to 40 days when stored at 5 ± 3°C, see US EPA SW-846 Chapter 4. Individual stability data is provided in SCA Bluebook 261.

A8 Analytical procedure

A8.1 Rinse all glassware with dichloromethane before commencing this procedure.

A8.2 Sample is inverted to mix and sufficient sample is removed from the bottle to allow the solvent to be added. The bottle is then weighed and the weight recorded. Approximately 50mL of dichloromethane and 25µL of internal standard are added to the bottle using a dispenser. Care must be taken not to discard any non-homogeneous contents prior to weighing.

A8.3 The sample is then placed on a bottle roller for 30 minutes at 180 rpm.

A8.4 The sample is transferred to a 2 L separating funnel and left to stand until the solvent layer has settled to the bottom.

A8.5 Place a filter paper in a glass funnel and fill it with anhydrous sodium sulphate. Rinse funnel and sodium sulphate with dichloromethane and discard the rinsings. Pass

the solvent layer slowly through the sodium sulphate and collect it in a labelled evaporation tube. Alternatively use a sintered glass column or Dry Disk filter.

A8.6 Return the sample to the bottle, add 1.0mL of the 20% w/v hydrochloric acid and approximately 50mL of dichloromethane and repeat steps A8.3 to A8.5. Note: an improved recovery may be achieved for some compounds with a further extraction under alkaline conditions (pH 10). The pH can be adjusted by the addition of 1N sodium hydroxide.

A8.7 Rinse the sodium sulphate with approximately 20 mL of dichloromethane to ensure all contents are removed. This washing is added to the labelled evaporation tube.

A8.8 The evaporation tube is then placed into a concentration unit (e.g. Turbovap) at 25±3°C, where the dichloromethane is gradually evaporated under a gentle flow of nitrogen.

A8.9 When the volume of the extract has been reduced to just below 1 mL, remove the tube from the Turbovap. Make the extract up to the 1 mL graduation mark on the evaporation tube with dichloromethane.

A8.10 The contents of the evaporation tube are then transferred using a Pasteur pipette to a labelled auto sampler vial.

A8.11 After every sample, the separating funnel, funnel and evaporation tube are thoroughly cleaned with water, followed by successive rinses with acetone and dichloromethane.

A8.12 Prepare the blank and calibration standards using the entire procedure as described in sections A8.1 – A8.11.

A8.13 Set up the GCMS system according to manufacturer's instructions. Using the four calibration solutions, construct a calibration graph of response versus amount of component, monitoring the ions referred to in Appendix 3 for the target compounds.

A8.14 Analyse the sample extract and from the calibration graph, obtain the amount, Av, of target compounds in the vial and then calculate the concentration, Cs, of target compounds in the sample. If the response exceeds the calibration range, the analysis may be repeated using a smaller amount of sample and making the volume to 1000 ml with water.

A9 Calculation

From the calibration graph determine the amount, Av, of component in the vial and determine the concentration, Cs, in the sample using the equation:

$$Cs = Av \times (1000/Vs)$$

Cs is the concentration (µg L^{-1}) of the compound in the sample;
Av is the amount (µg L^{-1}) of the compound in the vial obtained from the graph; and

Vs is the sample volume taken (see section A8.2).

Estimating the amount of an unknown compound using internal standard equivalence.

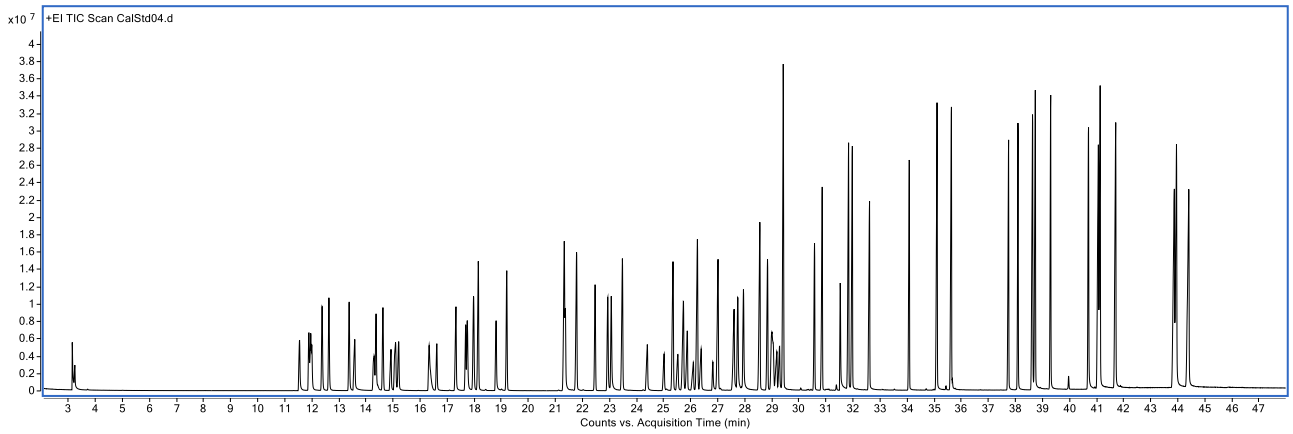
An estimation of the amount of an unknown compound is calculated by comparing its peak response to that of the nearest eluting Internal Standard taken from the total ion chromatograph (TIC). The following calculation will give a value in µg L^{-1} equivalence of x (where x is the chosen internal standard):

$$\frac{\text{Response of compound in sample}}{\text{Response of Internal Standard in sample}} \times \text{Concentration of Internal Standard in sample.}$$

A10 Performance data

It is possible to validate the procedure by carrying out a matrix spike recovery exercise looking at sub sets of target compounds from different chemical groups. The target compounds listed in US EPA method 8270d is recommended as a good starting point.

Figure A1 Typical chromatogram of target compounds
(Concentration of 1.0µg L^{-1} extracted standard)



Appendix 1 Alternative extraction using solid phase extraction.

A1-1 Principle

500mL of sample is passed through a conditioned C18/ENV+ solid phase extraction cartridge. The cartridge is dried under vacuum and the analytes are eluted from the cartridge with dichloromethane and internal standard added. The extract is then ready for gas chromatography (GC) with mass spectrometric (MS) detection operating in scan mode.

A1-2 Reagents

All reagents should be of analytical grade quality and distilled or deionised water should be used throughout.

Dichloromethane

Methanol

Acetone

Formic acid (98/100%)

A1-3 Apparatus

In addition to normal laboratory glassware (grade B or better) the following will be required.

SPE cartridges – For example, 6 mL, 400 mg C18/ENV+ cartridges, or suitable equivalent.

Vacuum manifold.

Glass vials.

Vortex mixer.

Blow-down apparatus. Any device capable of being set at 25 ± 3°C and can direct a gentle stream of nitrogen or air on to the extract.

A1-4 Analytical procedure

Allow the samples to reach room temperature before proceeding.

See method A for details of standards, blanks and AQC.

For each blank, AQC, sample and standard, condition a labelled SPE cartridge by passing approximately 5 mL of methanol through the cartridge under gravity. Do not allow the meniscus of the solvent to go below the level of the cartridge packing material. Discard the washings. Repeat this process with two further washes of methanol.

Repeat the previous step using three 5mL aliquots of distilled water.

Transfer 500mL of sample to a labelled, pre cleaned 500mL amber glass bottle and add 5ml of methanol and 100µL of formic acid.

Use a transfer line to connect the sample to the appropriately labelled SPE cartridge. Apply the vacuum and allow the sample to flow through the cartridge at approximately 10ml per minute. When all of the sample has passed through the cartridge, use 5 mL of deionised water to rinse the sample bottle, and allow it to pass through the cartridge.

Dry the cartridge, this process should take about 60 minutes when applying a vacuum or passing nitrogen through the cartridge. Ensure the cartridge is thoroughly dry before continuing, the packing will return to a light brown colour and become more fluid.

Add 2 mL of dichloromethane to each SPE cartridge. Allow the dichloromethane to soak into the cartridge packing material for about 10 minutes. Continue the elution under gravity, collecting the eluate in a test tube or other suitable container. Note: other solvents such as acetone and methanol may aid the extraction of more polar compounds)

Add a further 2 mL of dichloromethane collecting the eluate in the same test tube. Use a syringe to push out any residual solvent from the cartridge.

The test tubes are placed into a concentrator (e.g. Turbovap LV) at 25°C, where the dichloromethane is gradually evaporated under a stream of nitrogren. Reduce the extract to just below 1 mL.

Add working injection standard solution and mix.

Transfer the extract to a suitably labelled auto sampler vial, make up to 1 mL with dichloromethane and cap ready for analysis.

Appendix 2 – Solid samples

It is possible to use the screening procedure for solid samples. In these cases an appropriate portion of the sample should be taken and sonicated in dichloromethane. The solvent extract can then be analysed with the same GC MS instrument parameters and mass spectral library as those used for the water samples.

Appendix 3 – 8270 Target Compound List

Compound	CAS Number	Typical retention time (min)	Target ion (m/z)	Qualifier ions (m/z)
Pyridine	110-86-1	3.55	79	52,51
n-Nitrosodimethylamine	65-75-9	3.60	74	42,43
Aniline	62-53-3	8.95	93	66,65
Phenol	108-95-2	9.15	94	65,39
Bis(2-chloroethyl)ether	111-44-4	9.28	93	63,95
2-Chlorophenol	95-57-8	9.24	128	130,64
1,3-Dichlorobenzene	541-73-1	9.68	146	148,111
1,4-Dichlorobenzene	106-46-7	9.88	146	148,111
1,2-Dichlorobenzene	95-50-1	10.53	146	148,111
Benzyl alcohol	100-51-6	10.62	79	108,107
2,2'-Oxybis(1-chloropropane)	108-60-1	11.26	45	121,41
2-Methylphenol	95-48-7	11.28	108	107,79
Hexachloroethane	67-72-1	11.64	201	117,166
N-Nitroso-di-n-propylamine	621-64-7	11.82	70	43,130
3+4-Methyl phenol	108-39-4/106-44-5	11.90	107	108,77
Nitrobenzene	98-95-3	12.14	123	77,51
Isophorone	78-59-1	13.18	82	138
2-Nitrophenol	88-75-5	13.44	139	65,109
2,4-Dimethylphenol	105-67-9	14.00	122	107,77
Bis(2-chloroethoxy)methane	111-91-1	14.39	93	63,95
2,4-Dichlorophenol	120-83-2	14.48	162	164,98
1,2,4-Trichlorobenzene	120-82-1	14.74	180	145,109
Naphthalene	91-20-3	14.91	128	102
4-Chloroaniline	106-47-8	15.50	127	65,92
Hexachlorobutadiene	87-68-3	15.91	225	190,260
4-Chloro-3-methylphenol	59-50-7	17.95	107	77,144
1-Methylnaphthalene	90-12-0	18.00	141	115
2-Methylnaphthalene	91-57-6	18.45	141	115
Hexachlorocyclopentadiene	77-47-4	19.11	237	272,95
2,4,6-Trichlorophenol	88-06-2	19.57	196	97,132
2,4,5-Trichlorophenol	95-95-4	19.71	196	97,132
2-Chloronaphthalene	91-58-7	20.12	162	127

2-Nitroaniline	88-74-4	21.00	138	65,92
1,3-Dinitrobenzene	99-65-0	21.61	168	75,50
Acenaphthylene	208-96-8	21.98	152	76
1,4-Dinitrobenzene	100-25-4	22.11	168	75,50
Dimethyl phthalate	131-11-3	22.30	163	77,92
2,6-Dinitrotoluene	606-20-2	22.45	165	63,89
1,2-Dinitrobenzene	528-29-0	22.60	168	50,63
Acenaphthene	83-32-9	22.88	153	76,154
3-Nitroaniline	99-09-2	22.96	138	65,92
2,4-Dintrophenol	51-28-5	23.40	184	63,107
Dibenzofuran	132-64-9	23.63	168	139
4-Nitrophenol	100-02-7	24.20	139	65,109
2,4-Dinitrotoluene	121-14-2	24.16	165	89,63
2,3,4,6-Tetrachlorophenol	58-90-2	24.34	232	131,194
2,3,4,5-Tetrachlorophenol	935-95-5	24.54	232	131,166
Fluorene	86.73-7	25.11	166	165,82
4-Chlorophenyl phenyl ether	7005-72-3	25.37	204	141
Diethyl phthalate	84-66-2	25.50	149	177
4-Nitroaniline	100-01-6	25.61	138	65,108
Diphenylamine	122-39-4	25.91	169	167,168
4,6-Dinitro-2-methylphenol	534-52-1	25.74	198	51,121
Azobenzene	103-33-3	25.92	77	51,182
4-Bromophenyl phenylether	101-55-3	27.04	248	141,77
Hexachlorobenzene	118-74-1	27.32	284	142,249
Pentachlorophenol	87-86-5	27.97	266	165,268
Phenanthrene	85.01-8	28.28	178	176,152
Anthracene	120-12-7	28.41	178	176,152
Carbazole	86-74-8	29.03	167	139,83
Di-n-butyl phthalate	84-74-2	30.46	149	150,76
Fluoranthene	206-44-0	31.51	202	200,101
Pyrene	129-00-0	32.05	202	200,101
Benzylbutylphthalate	85-68-7	34.14	149	91,206
Bis(2-ethylhexyl) adipate	103-23-1	34.47	129	57,112
Benzo (a) anthracene	56-55-3	35.05	228	226,114
Chrysene	218-01-9	35.15	228	226,114
Bis(2-ethylhexyl) phthalate	117-81-7	35.70	149	167,279
Di-n-octylphthalate	117-84-0	37.08	149	150,279
Benzo (b) fluoranthene	205-99-2	37.48	252	250,126
Benzo (k) fluoranthene	207-08-9	37.55	252	250,126
Benzo (a) pyrene	50-32-8	38.14	252	250,126
Indeno(1,2,3-cd)pyrene	193-39-5	40.40	276	277,138
Dibenzo(a,h)anthracene	53-70-3	40.48	278	276,139
Benzo(g,h,i)perylene	191-24-2	41.00	276	277,138

Appendix 4

List of Known Contaminants

No.	Compound	Approx R.T.	CAS Number	LRI Value	Source(s) of contaminant
1	2,2-Dimethoxybutane	5.66	3453-99-4		
2	3-Penten-2-one, 4-methyl	6.95	141-79-7		
3	Amylene hydrate	7.26	75-85-4	665.9	DCM
4	3-Methylbutan-2-one	7.55	563-80-4	677.0	reaction between amylene stabiliser and water
6	2-Chloro-2-methylbutane	7.67	594-36-5	681.6	DCM
7	t-Amyl methyl ether	7.92	994-05-8	691.3	DCM
9	Pent-3-en-2-ol	8.16	1569-50-2	700.7	reaction between amylene stabiliser and water
10	3-Methyl-3-chlorobut-1-ene	8.28	2190-48-9	722.6	reaction between amylene stabiliser and HOCl
12	Dichlorobromomethane	8.73	75-27-4	722.7	naturally present in drinking water
13	t-Amyl ethyl ether	8.97	919-94-8	732.2	DCM
14	2-Methyl-3-Bromo-2-Butanol	9.64	2588-77-4		reaction between amylene stabiliser & HOBr
15	2-Methylpentanal	9.64	123-15-9	757.9	DCM
16	Toluene	9.93	108-88-3	770.0	DCM
17	1-Methylethylbenzene (Cumene)	10.60	98-82-8		DCM
18	1,1-Dimethyl-2-chloropropan-1-ol	11.06	N/A	813.2	reaction between amylene stabiliser and HOCl
19	1-α-Pinene	11.25	7785-70-8		DCM
20	4-Hydroxy-4-methylpentan-2-one	11.81	123-42-2	845.3	reaction betwen water and acetone
21	Unknown compound, possibly isomer of heptanol; $C_7H_{16}O$ – **45, 57, 56, 83**	12.42	N/A		DCM
22	α-Methylstyrene	12.49	98-83-9		DCM
23	Unknown compound, possibly isomer of heptanol; $C_7H_{16}O$ – **45, 43, 41, 57**	12.55	N/A		DCM
24	Unknown compound, possibly isomer of heptanol; $C_7H_{16}O$ – **59, 87, 43, 45**	12.94	N/A		DCM
25	o-Xylene	13.15	95-47-6	896.3	DCM
26	2-(Ethoxyethoxy)ethanol	15.60	111-90-0	1001.2	DCM
27	Δ3-Carene	15.84	13466-78-9	1012.8	DCM
28	2-Ethylhexan-1-ol	16.24	104-76-7	1029.6	DCM

29	α-Cumyl alcohol	17.51	617-94-7	1089.9	
30	Dodec-1-ene	19.46	112-41-4	1192.2	DCM
31	Benzothiazole	20.38	95-16-9	1239.4	DCM
32	1-Hydroxy-2,4,4-trimethylpentan-3-yl isobutyrate (Texanol A)	22.44	74367-33-2	1356.4	Paint coalescent
33	3-Hydroxy-2,4,4-trimethylpentyl isobutyrate (Texanol B)	22.80	74367-34-3	1378.1	Paint coalescent
34	Tetradec-1-ene	22.99	1120-36-1	1392.0	DCM
35	Sulphur- hexa	23.41	13798-23-7	1499.0	
36	Propanoic acid , 2-methyl-,1(1,1-dimethylethyl)-2-methyl-1,3-propanediyl	24.09	74381-40-1		Plasticiser
37	2,4-Di-tert-butylphenol	24.82	96-76-4	1508.5	trace in DCM, observed when concentrated
38	N,N-Dihexyl-1-hexamine	28.12	102-86-3	1729.9	Glassware
39	Sulphur- octa	29.52	10544-50-0	1998.0	
40	Di-n-butylphthalate	31.10	84-74-2	1959.8	DCM
41	Octadeca-(9Z)-enamide	35.60	301-02-0	2375.0	Slip agent from plastic
42	Bis-(2-Ethylhexyl)phthalate	37.34	117-81-7	2535.4	
43	Docosa-(13Z)-enamide	39.76	112-84-5	2785.0	Slip agent from plastic
44	Squalene	39.98	111-02-4	2817.3	DCM
45	Unknown compound, similar to Irganox 1076 – **57, 219, 531, 43**	55.88	N/A	3593.8	Glassware

Note:- RT based on a 60m 0.32mm 0.25um ZB5 (inc 2.5m renention gap)

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