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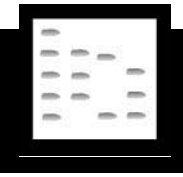
VOLATILE ORGANIC COMPOUNDS IN WATER: GAS CHROMATOGRAPHY



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Introduction

An important class of substances for which it is increasingly necessary to analyse in environmental waters comprises a wide range of volatile organic compounds (VOC). These include aromatics such as methylbenzene (toluene) and the dimethylbenzenes (xylenes), and the environmentally persistent halogenated solvents such as tetrachloromethane and trichloroethene. Many of these compounds are finding their way onto national and international lists of proscribed or regulated compounds, and as a result there is a requirement for robust methods of analysis to monitor both the environment itself and potential sources of discharge to it.

In the aqueous environment, there are a number of sample types that an analyst may be required to examine, each presenting their own problems and challenges and requiring slightly different analytical solutions. Drinking waters, for example, are a relatively straightforward matrix, often with a clearly defined quality standard imposed, such as the requirements of the European Union Drinking Water Directive (see Further Reading). River waters and marine waters may also be required to meet exacting environmental quality standards (EQS), which are frequently much lower than those set for drinking waters where the presence of haloforms, for example, is an accepted by-product of the disinfection process. Monitoring of wastewater effluents is fundamental to environmental quality management, since these are

a major source of VOCs in the environment. Such effluents are frequently complex mixtures of many different compounds present in a wide range of concentrations, and as such offer special challenges to the analyst.

Quantitative analytical methods must therefore offer good precision and accuracy and be able to withstand the rigorous inspection required by the legislative environment, in order to demonstrate satisfactory compliance with the regulations.

This article discusses some of the methods available for the analysis of VOCs in these matrices and is illustrated with examples taken from routine drinking water and wastewater quality analysis. The chromatograms are reproduced here by courtesy of North West Water Laboratory Services.

Sampling Techniques

The first stage of any analysis, whether carried out in the field or remotely in the laboratory, is the collection of a representative sample and the preservation of that sample intact until it reaches the analyst. Without doubt the best approach is to sample straight into the container to be used for the analysis, but this may present logistical problems with handling either very small containers or carrying out precise measurements of volume. It is easy enough to do this in a clean, well-equipped laboratory, but it becomes a much more challenging task on a cold, wet river bank or windswept beach!

The problem is that with the analytes being so volatile, their concentration in the matrix can change significantly between sampling and analysis if the sample is not correctly taken. One method widely used with good results is to use a pre-cleaned screw-cap septum vial, made from borosilicate glass and of around 20 or 40 mL capacity. The vial is rinsed several times with the sample before being filled so that the meniscus stands proud of the brim. A thick septum faced with polytetrafluoroethylene (PTFE) is then slipped sideways over the top of the vial, ensuring that no air bubble remains trapped within, and the septum cap is then firmly screwed down, sealing the sample in the vial. A vial with a leaking seal will obviously cause sample to be lost, but will also allow preferential evaporation of VOCs. Similarly, a vial containing an air bubble will also damage sample integrity by allowing dissolved VOCs to equilibrate between the aqueous and vapour phases. Any subsequent sample taken from the vial for analysis will therefore contain a *lower* concentration of VOCs than the original.

Use of a septum will allow the withdrawal of a subsample from the vial, using a syringe and an air bleed needle, without opening it and risking the possible loss of volatiles. Similarly, a suitable extraction solvent may be added by a displacement technique. Some laboratories use these approaches; others will open the vial and rapidly transfer the required volume to another closed container. Either way, taking further subsamples should be avoided, as the concentration of VOC in the sample will already have begun to change. Further information on sample collection is to be found in a 1987 HMSO publication.

Table 1 Common options for the analysis of VOCs

Introduction	*Separation*	*Detection*
Solvent extraction		FID
Direct aqueous injection		ECD
Headspace	GC	MS
Purge-and-trap		ELCD
		PID

Note: FID, flame ionization detector; ECD, electron-capture detector; MS, mass spectrometry; ELCD, electrolytic conductivity detector; PID, photoionization detector.

Methods of Analysis

Modern capillary gas chromatography (GC) lends itself particularly well to the low-level analysis of VOCs, offering a good separation of the analytes and high sensitivity. There is a variety of sample introduction techniques in common use and a wide choice of columns is available to the analyst. Several different detector systems can be used, dependent on the analytes and the sensitivity and specificity required.

The actual method of analysis chosen will depend on several factors. These include the analytes themselves, the sample matrix, the resources available to the analyst and the level of confidence required in the results. For example, an analyst interested in a rough-and-ready assessment of the presence of aromatic solvents at levels in excess of 1 mg L^{-1} might choose to use direct aqueous injection (DAI) with a flame ionization detector (FID) as the simplest way of obtaining the information required. Conversely, an analyst investigating a complex industrial wastewater and providing evidence for prosecuting an illegal discharge may prefer the precision of a headspace sample introduction technique and the confirmatory information which may be obtained by using a mass spectrometer (MS) as a detector. The commonest options are set out in **Table 1**.

Sample Introduction Techniques 1: Solvent Extraction

Solvent extraction is a useful technique for dealing with relatively clean samples, such as drinking waters

Table 2 Solvent extraction performance data for selected compounds

Compound	*Recovery (%)*	*RSD (%)*	*LOD ($\mu g\ L^{-1}$)*
Trichloromethane[a]	85	6.1	0.19
Tetrachloromethane[a]	79	11.7	0.009
Tetrachloroethene[a]	104	3.1	0.012
Benzene[b]	105	nd	1.58
Methylbenzene[b]	99	nd	0.13

[a]Chlorinated compounds determined at a concentration of 2.5 $\mu g\ L^{-1}$ (tetrachloroethene 5 $\mu g\ L^{-1}$) with four degrees of freedom. 20 mL sample extracted with 2.5 mL petroleum ether 30–40°C. Analysis by packed column GC-ECD. From HMSO (1987).

[b]Aromatic compounds determined at a concentration of 10 $\mu g\ L^{-1}$. 1 L sample extracted with 10 mL pentane, cleaned up with florisil and concentrated to 1 mL. Analysis by 50 m × 0.2 mm OV-1 capillary column with FID. From HMSO (1987). RSD, relative standard deviation; LOD, limit of detection; nd, not determined.

or high-quality river waters. The pentane or hexane extraction solvent may be added to the sample vial by displacement, as described above, and the vial is then shaken or rolled for up to 30 min. A sample of the solvent may then be withdrawn – again without opening the vial – and analysed by GC using conventional sample inlet techniques such as split/splitless or on-column injection. Typical sample/solvent ratios of between 5 : 1 and 20 : 1 give some sample preconcentration, but the injection volume of around 1–2 μL restricts ultimate sensitivity.

The technique is well-suited to the analysis of chlorinated hydrocarbons, using an electron-capture detector (ECD), but may also be used in conjunction with most other types of detector, including mass spectrometers. Its main drawback is the time and effort required to carry out the extraction. Some performance data are listed in **Table 2**.

Sample Introduction Techniques 2: Direct Aqueous Injection

Perhaps the simplest of all sample introduction techniques, direct aqueous injection has been the subject of several papers. It has a number of advantages, not the least of which is convenience: samples collected in the manner described above require no further handling between collection and final analysis. As the name of the technique suggests, a 1 μL aliquot of sample is taken from the vial and injected directly into the instrument, using either an on-column or split/splitless injector.

This technique has been applied to the analysis of trihalomethanes and is said to be reliable and offers good precision and recoveries. Recoveries of 100% and peak area standard deviations of between 1.9 and 5.2% with approximately 14 degrees of freedom at the 10–100 $\mu g\ L^{-1}$ level for the four chlorine- and bromine-containing trihalomethanes have been quoted. This compares with recoveries of between 60 and 90% for pentane extraction. The technique has been shown to be applicable to other chlorinated hydrocarbons, including 1,1,1-trichloroethane and tetrachloromethane.

The technique certainly works well with small numbers of samples, but experience in a laboratory handling upwards of 30 analyses daily suggests that the robustness of the analytical system becomes an important factor. Passing relatively large quantities of water vapour through an ECD shortens its useful life, and therefore the alternative inlet techniques described here are to be preferred where large numbers of samples are involved.

Another potential problem with the technique is that there is no initial clean-up of the sample and it is therefore only appropriate for relatively clean samples such as drinking waters. With other sample matrices there is a risk that significant quantities of nonvolatiles (including inorganic salts) can build up at the front of the column, reducing its life; similarly, the presence of less-volatile contaminants remaining on the column may interfere with subsequent analyses.

Despite this, DAI may be used successfully where a minimum effort, rough screening method is required, e.g. for an industrial wastewater. The use of an FID allows other, nonhalogenated compounds such as aromatics to be detected and estimated at milligram per litre levels. This analysis may be sufficient to meet some needs, but could also be used as a pre-screening technique to identify appropriate dilution factors for headspace or purge-and-trap analysis. An example of a chromatogram of a standard solution of aromatic compounds in water is shown in **Figure 1**.

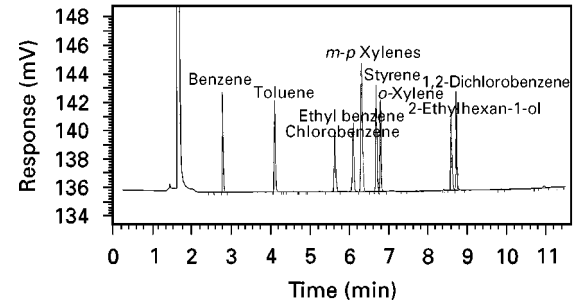

Figure 1 Aromatic compounds in water by DAI. Conditions: 1 μL injection; injector temperature 230°C; 30 m × 0.25 mm DB-1 column; temperature program 70°C, hold 2 min → 90°C at 20°C min^{-1} → 260°C at 35°C min^{-1}, hold 5 min; FID temperature 280°C. Chromatogram shown is from a standard solution in water containing 10 mg L^{-1} each compound.

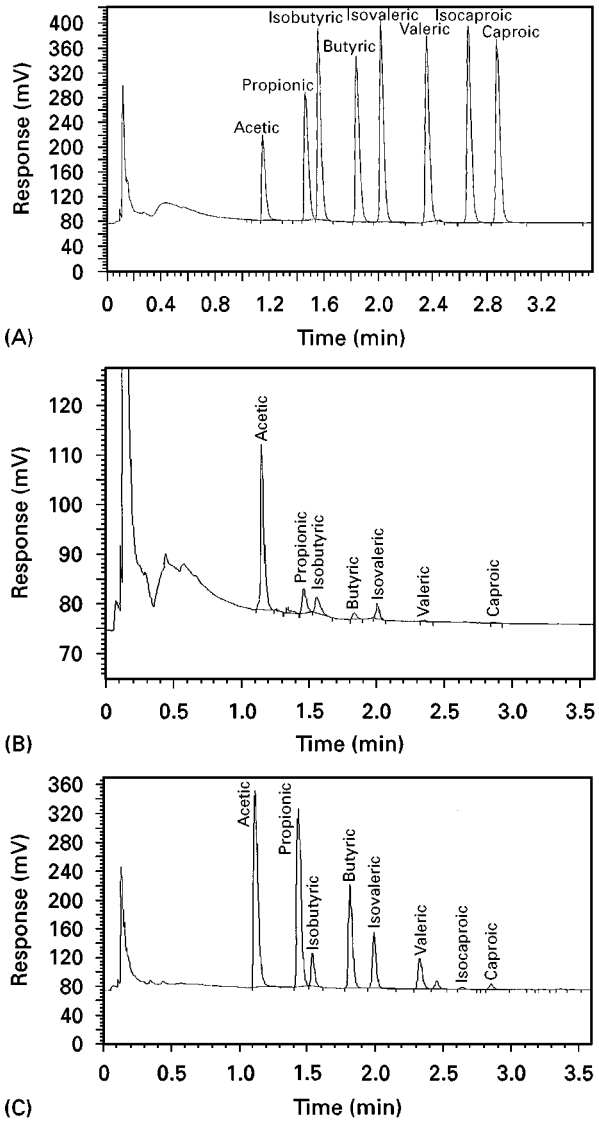

Figure 2 Analysis of VFA in sewage sludge supernatant water by DAI. Conditions: 1 μL 20 : 1 split injection; injector temperature 250°C; 12 m × 0.53 mm BP-21 column; temperature program 60°C → 250°C at 20°C min^{-1}, hold 3 min; carrier gas, nitrogen 3 mL min^{-1}; FID temperature 300°C. (A) Chromatogram shown is from a standard solution in water containing approximately 800 mg L^{-1} each compound. (B) VFA in digested sludge. Acetic acid concentration 100 mg L^{-1}; others < 10 mg L^{-1}. (C) VFA in a partially digested sludge. Acetic acid concentration approximately 800 mg L^{-1}.

Difficult-to-extract analytes such as alcohols, ketones or volatile fatty acids (VFA) may also be estimated by this technique (**Figure 2**). A specific application is the analysis of VFA in sewage sludge, the results of which are used to monitor the performance of sludge digesters in wastewater treatment plants. Samples of sludge are centrifuged and the supernatant water filtered through a 1 μm membrane, in order to prevent particulate matter blocking either the injection syringe needle or the capillary column itself. Acidified with phosphoric or formic acid, the samples are then analysed by direct aqueous injection GC-FID. The analytical range required of the application is typically 1–1000 mg L^{-1} for each compound, although ethanoic (acetic) acid will predominate in samples from a stable digester.

A simple packed column application of direct aqueous injection is the analysis of methane in water. A 1 μL sample is injected directly onto a 1 m Chromosorb™ 101 column for isothermal analysis at 70°C, with an FID. Calibration is normally carried out using a standard gas mixture.

Sample Introduction Techniques 3: Headspace Analysis

Headspace analysis is a clean, reliable method of introducing volatile analytes to a GC column, and is especially useful where complicated matrices such as industrial wastewaters containing many other contaminants must be analysed. Involving the analysis of just the *vapour* above a sample of water, the method provides instant clean-up by ensuring that only volatile materials are introduced into the GC sample inlet, resulting in a clean chromatogram and enchanced column life.

The technique is a practical application of Henry's law, which states that 'the vapour pressure of a solute is proportional to the amount of solute present in a solution at equilibrium with its vapour'. Thus if the concentration of an analyte in the vapour phase can be measured, it can be correlated by a suitable calibration with its concentration in the sample.

The two methods of introducing samples to the GC are known as *static* and *dynamic* headspace. In the former, the vapour in equilibrium with the sample in a vial is analysed, usually at an elevated temperature; in the latter the vapour is first enriched by actively purging the sample with an inert gas.

Given that the solubility of gases decreases with increasing temperature, raising the temperature of the sample will favour the vaporization of the analytes, enriching the headspace, and this effect is used to enhance analyte recovery. It does mean, however, that temperature must be rigorously controlled both during analysis and from sample to sample, if reproducibility is to be assured.

Static headspace Samples may be collected for this analysis in two ways. A vial can be filled as described previously, or a fixed amount (typically 5–10 mL) of sample may be accurately measured and sealed – with an internal standard, if one is to be used – in a vial of about 20–25 mL capacity, which is to be used for the

analysis. The latter option would allow the sample to be presented to the instrument unopened, minimizing the requirement for sample preparation in the laboratory, but practical considerations in the field mean that the former is often preferred.

Sealed in its headspace vial, the sample is placed in a thermostatted heater and allowed to equilibrate with the air space above it. Some headspace sampling devices will also agitate the sample to accelerate this equilibration. Once equilibrium is established, the vial is pressurized with carrier gas passing through a sampling needle penetrating the septum. On reaching the required pressure, the flow is reversed, carrying sample vapour to the GC inlet. The volume transferred is controlled either by reversing the flow for a fixed time or by the use of a sample loop. The liquid sample therefore does not come into contact with any part of the GC itself.

Calibration of the system is carried out by preparing standard solutions of the analytes of interest in water, and treating them in exactly the same way as samples, sealing the same volume in a vial and subjecting them to the whole procedure described above. Key to the process is consistency: each sample and standard must be treated exactly alike, and automated headspace samplers facilitate this. In order to achieve reproducible results, it is not even necessary for the samples to achieve equilibrium; providing they are consistently treated, i.e. by equilibrating at exactly the same temperature and for the same length of time, reproducibility is assured.

A suitable internal standard can be added to the headspace vial before sealing and then used either directly to calibrate the individual analysis or to aid an external calibration process.

The technique has a good linear range and sensitivity and provides a robust and reliable method of introducing both clean and dirty water samples to a GC with very little sample preparation (**Table 3**). As might be expected, attainable recoveries measured against standard solutions are close to 100% and interferences and column degradation are minimized. It may be used with any detector type, including mass spectrometers. An example of the analysis of trihalomethanes and chlorinated hydrocarbons in drinking water is shown in **Figure 3**.

Table 3 Headspace performance data for selected compounds

Compound	*Recovery (%)*	*RSD (%)*	*LOD ($\mu g\,L^{-1}$)*
Trichloromethane	99.95	3.4	1.42
Tetrachloromethane	98.30	4.18	0.04
Tetrachloroethene	96.84	4.43	0.44

Data determined at a concentration of 122 $\mu g\,L^{-1}$ (trichloromethane); 3 $\mu g\,L^{-1}$ (tetrachloromethane); and 10 $\mu g\,L^{-1}$ (tetrachloroethene) with approximately 17 degrees of freedom. 5 mL sample equilibrated for 5 min at 80°C. Analysis by 30 m × 0.53 mm DB-624 capillary column GC-ECD. Data provided by North West Water Laboratory Services.

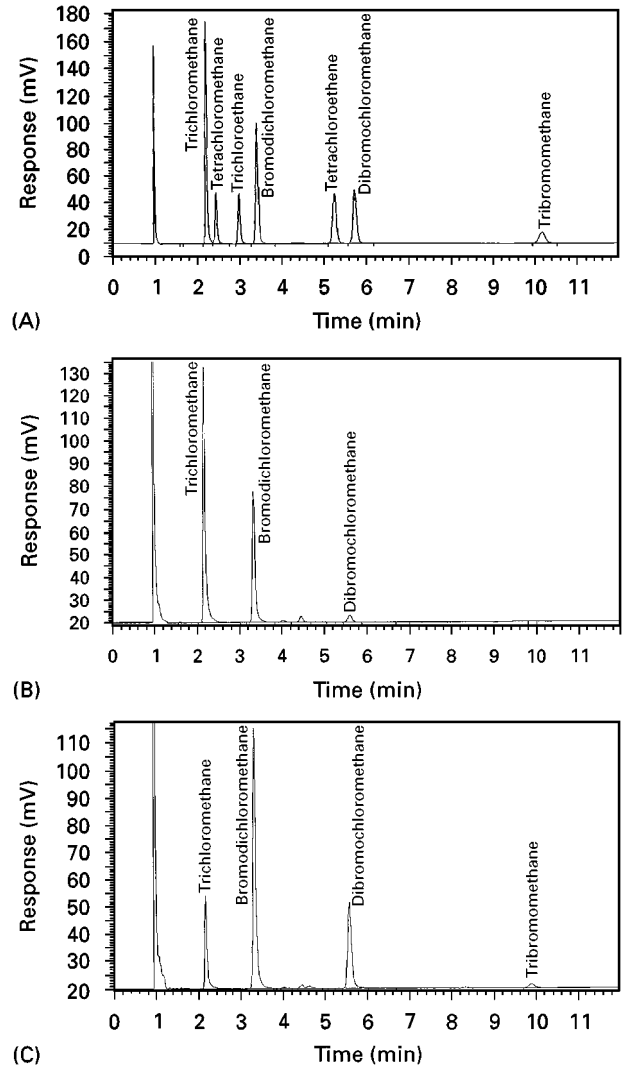

Figure 3 Analysis of trihalomethanes and chlorinated hydrocarbons in drinking water by headspace GC-ECD. Conditions: 5 mL sample, equilibrated for 10 min; 30 m × 0.53 mm DB-624 column; isothermal at 80°C. ECD temperature 250°C; carrier gas: nitrogen 7.5 mL min^{-1}. (A) Chromatogram shown is from a standard solution in water containing 91.5 $\mu g\,L^{-1}$ tricholoromethane (highest concentration component) and 2 $\mu g\,L^{-1}$ tetrachloromethane (lowest). (B) Trihalomethanes in drinking water derived from a surface source. Concentrations: trichloromethane 63 $\mu g\,L^{-1}$; bromodichloromethane 7 $\mu g\,L^{-1}$; dibromochloromethane 1 $\mu g\,L^{-1}$. Note the almost total absence of other chlorinated hydrocarbons. (C) Trihalomethanes in blended drinking water derived from surface and underground sources. Concentrations: trichloromethane 18 $\mu g\,L^{-1}$; bromodichloromethane 12 $\mu g\,L^{-1}$; dibromochloromethane 2 $\mu g\,L^{-1}$; tribromomethane < 2 $\mu g\,L^{-1}$. Note the reduced concentration of chlorinated compounds and the increase in brominated compounds.

Absolute recoveries are dependent on equilibration time and temperature. Increasing the equilibration time to the point where the sample and its vapour are fully equilibrated will maximize recovery; raising the temperature will increase the partial pressure of volatile compounds in the headspace. Systems typically operate at temperatures of up to 80°C: any higher and the increased vapour pressure of the water matrix itself interferes, negating the benefits.

One drawback is the inability to reanalyse samples, because once a vial has been subsampled, the integrity of the sample itself is destroyed and equilibration with the new headspace will alter the composition of the sample. This means that a subsequent repeat analysis cannot be carried out if confirmation of a result is required: a fresh sample must be collected. Although this may present a problem to the environmental analyst, a technique known as 'multiple headspace extraction' (MHE) has been described (see Further Reading) where a sample is equilibrated with successive volumes of gas. Analysis of each successive headspace volume will allow the distribution of the analytes to be determined, providing a measure of an important physical property. Headspace analysis has been used for this purpose almost since it was first developed.

The extrapolation of MHE data to the 'zero equilibration' level provides a measure of the original concentration of an analyte. This may be particularly useful in situations where for some reason it is not possible to calibrate the analytical system with either the analyte or matrix of interest, or where an 'absolute' recovery must be determined.

Dynamic headspace Dynamic headspace or purge-and-trap sampling is an effective way of achieving high sensitivity in the analysis of VOC. This is particularly important in the analysis of environmental samples for comparison with stringent EQS, which frequently test the limits of analytical methodology.

Unlike static headspace, where the sample is simply allowed to equilibrate, in purge-and-trap the sample is purged with an inert gas (usually helium) in order to drive the volatiles out into the vapour phase. The vapour is then caught in a cold trap or adsorbed on an appropriate support before being thermally desorbed and passed to the GC inlet. The method retains the advantage of the headspace technique in terms of presenting a clean sample to the GC, but potentially offers much greater sensitivity (**Table 4**).

Whilst the technique has the ability to improve sensitivity, the overall range of an analysis may not be increased, since this is dependent on the dynamic range of the detector. This means that with the general tendency to analyse suites of compounds together, those compounds for which low limits of detection are required can be analysed satisfactorily, but those present in higher concentrations in the same sample may well exceed the range of the detector! For example, purge-and-trap GC-MS analysis of some drinking waters easily achieves the required limit of detection of 0.3 $\mu g\,L^{-1}$ for tetrachloromethane, but exceeds the linear range of the detector for the trichloromethane present in a much higher concentration.

Table 4 Purge-and-trap performance data for selected compounds

Compound	*Recovery (%)*	*RSD (%)*	*LOD ($\mu g\,L^{-1}$)*
Trichloromethane	94.10	3.80	0.002
Tetrachloromethane	nd	nd	0.004
Tetrachloroethene	98.80	1.30	0.005
1,2-Dichlorobenzene	77.70	8.50	0.020
Methylbenzene	99.11	0.77	0.001
1,2-Dimethylbenzene	98.38	1.46	0.004

Recovery and RSD data determined at a concentration of 4 $\mu g\,L^{-1}$ with approximately two degrees of freedom. 25 mL sample purged at 35°C with helium, 50 mL min^{-1} for 10 min. Analysis by packed column GC-FID. From Driss and Bouguerra (1991). LOD, limit of detection. 5 mL sample purged with helium, 40 mL min^{-1} for 2 min. Analysis by 60 m × 0.53 mm DB-624 capillary column GC with electrolytic conductivity detector and photoionization detector. From Mehran, Nickelsen, Golkar and Cooper (1990) *Journal of High Resolution Chromatography* 13: 429–433.

The optimization of a purge-and-trap method has been examined and both purge gas volume and temperature have a significant effect on analyte recovery. Keeping the purge gas flow rate constant, but extending the purge time from 10 to 20 min, greatly enhanced the recoveries of all the analytes examined, although the recoveries of compounds with a higher solubility in water (e.g. tribromomethane) were still poor. Difficulties have been reported with the use of very short purge times: 1 min gave rise to reproducibility problems due to the mode of operation of the equipment, whereas 2 min resulted in an acceptable performance and a much faster method. Extended purge times may risk compromising recoveries of highly volatile compounds, since these can be purged efficiently in a short time. Recovery is then dependent on the efficacy of the trap in retaining them until the chromatographic separation is ready to begin.

Elevated temperatures also speed recovery. Results obtained from purging for 20 min at 25°C have been found to be comparable with those from a 10-min purge at 40°C. The disadvantage of using a higher temperature is that more water vapour is carried over into the analytical system. Without effective control

Table 5 Effect of purge time and temperature on recovery of selected compounds

Compound	*Recovery (%)*			
	10 min purge	*20 min purge*	*30°C*	*40°C*
Trichloromethane	78.06	91.81	82.01	87.63
1,2-Dichloroethane	60.55	88.10	62.48	64.75
Tetrachloroethene	98.03	99.10	97.94	100
1,2-Dichlorobenzene	59.86	66.82	60.94	65.41
Methylbenzene	85.73	93.12	88.63	94.05
1,2-Dimethylbenzene	81.86	84.28	84.99	89.66

Data determined at a concentration of 4 $\mu g\ L^{-1}$ with approximately two degrees of freedom. 25 mL sample purged with helium, 50 mL min^{-1} 10/20-min purge data determined at 25°C. Temperature data determined with a purge time of 10 min. Analysis by packed column GC-FID. From Driss and Bouguerra (1991).

this will interfere with the analysis – particularly with moisture-sensitive equipment such as ECD or mass spectrometers. For this reason, purge temperatures significantly greater than 40°C are not widely used. **Table 5** shows the effect of purge time and temperature on the recovery of selected compounds.

Waters containing detergents or other foaming agents may prove difficult to analyse effectively by this technique. It is, however, suitable for use with most types of detector.

Matrix Modification

The use of matrix modifiers is common practice in water analysis, and they are often used to enhance the performance of some methods for the analysis of VOC – in particular the headspace and purge-and-trap methods. The addition of modifiers such as sodium chloride or sodium sulfate to samples prior to analysis will – by modifying the activity coefficient of the VOC solutes and the vapour pressure of the solvent – enhance the relative concentration of the analyte in the headspace above the sample. This effect is most noticeable for the less soluble or less volatile compounds such as the dimethylbenzenes or the dichlorobenzenes, although it may be of limited use with other compounds, such as trichloromethane, where recoveries may readily be optimized by temperature control.

Table 6 Effect of ionic strength on recovery of selected compounds

Compound	*Purging efficiency*		
	0% NaCl	*10% NaCl*	*20% NaCl*
Trichloromethane	83.63	93.98	98.52
1,2-Dichloroethane	63.2	67.97	76.17
Benzene	90.12	97.22	99.50
1,3-Dichlorobenzene	72.45	81.59	91.5
1,2-Dimethylbenzene	86.43	96.72	98.91

Purge-and-trap recovery data determined at a temperature of 35°C. From Driss and Bouguerra (1991).

Although the effect may be used to improve the performance of a method, it is important to remember that the samples themselves may be subject to some variability. **Table 6** provides the evidence to show why a seawater sample could not be analysed using a method set up and calibrated for use with drinking water, or vice versa: the performance of the method will differ significantly between the two matrices. For the same reason, it is important that the ionic strength of both samples and standards is consistent. If there is any doubt then an excess of salt (e.g. around 2 g mL^{-1}) should be added to all samples and standards to ensure consistency.

Analytical Columns

Today, most applications for VOC analysis use capillary columns, the length and film thickness of which will depend on the complexity of the analysis. Up to about 20 compounds can be satisfactorily resolved by a 25–30 m column in about 10 min, whereas a 50–60 m column is more appropriate for samples containing 60 or more analytes, taking 30 min to 1 h to achieve an acceptable separation.

Although the superior resolution of the capillary column means that most separations can be achieved using 'standard' nonpolar or moderately polar phases such as DB-1 from J & W or BP-5 from SGE, there is an increasing number of columns tailored for specific analyses. These include J & W's DB-624 phase, designed to substitute for the packed column specified in US Environmental Protection Agency (US EPA) method 624, for purgeable organic compounds. Such columns are designed to optimize the separation and the time required for the analysis of the compounds of interest.

The direct aqueous injection technique requires the use of bonded-phase columns to ensure that the water passing through it does not destroy the column.

Detectors

Perhaps the commonest detectors used for VOC analysis in the environmental industry are the ECD and the mass spectrometer, primarily because of the keen interest in levels of organochlorine compounds in the environment. However, the FID also finds application in the analysis of hydrocarbons – including aromatics – providing reliable detection and sensitivity down to around 100 μg L^{-1} without sample pre-concentration. It may also be used with mixtures of hydrocarbons and some chlorinated solvents, and although limits of detection for the latter are relatively high, the robustness of the detector may make it an appropriate choice for the analysis of an industrial wastewater, for example. As previously described, the FID can be used for the analysis of relatively high concentrations of VOCs by the direct aqueous injection technique.

Where low levels of halogenated solvents are to be determined, by far the best option is to use an ECD, which has a high specificity and sensitivity for many halogenated compounds. This will work with all of the sample introduction techniques previously described, although complex industrial wastewaters may contain compounds that contaminate the detector. In such cases, selective introduction techniques such as headspace or purge-and-trap are to be preferred, as these will eliminate or substantially reduce the contaminants introduced to the system.

When a wide-ranging screen coupled with specificity and reasonable sensitivity is required, then a mass spectrometer may be used. Small bench-top instruments are increasingly found in environmental laboratories, and many are employed in just this kind of activity, coupled to headspace GC systems. Such a configuration provides a good response to a variety of compound classes, is robust enough to handle samples of badly contaminated industrial wastewaters, and yet has sufficient sensitivity to analyse clean river waters to the levels required by most EQS. Additionally, the ability to produce a recognizable mass spectrum lends confidence to the identification of analytes. This is of particular importance when collecting evidence for the prosecution of an illegal discharge. Examples of analysis of chlorinated and aromatic hydrocarbons by headspace GC-MS are shown in **Figure 4**.

Other detector types in use, particularly in the USA, include the electrolytic conductivity detector (ELCD) and the photoionization detector (PID) specified in some EPA methods. The latter can be up to a hundred times more sensitive than a FID when used for the analysis of some aromatic compounds, but in contrast to both the ECD and ELCD it will not detect the lighter haloalkanes such as those found in drinking water. The convenience the ECD offers over the ELCD coupled with the greater specificity and sensitivity of the PID relative to the FID means that a useful application for the detectors in tandem is the analysis of both halogenated and aromatic compounds in the same sample.

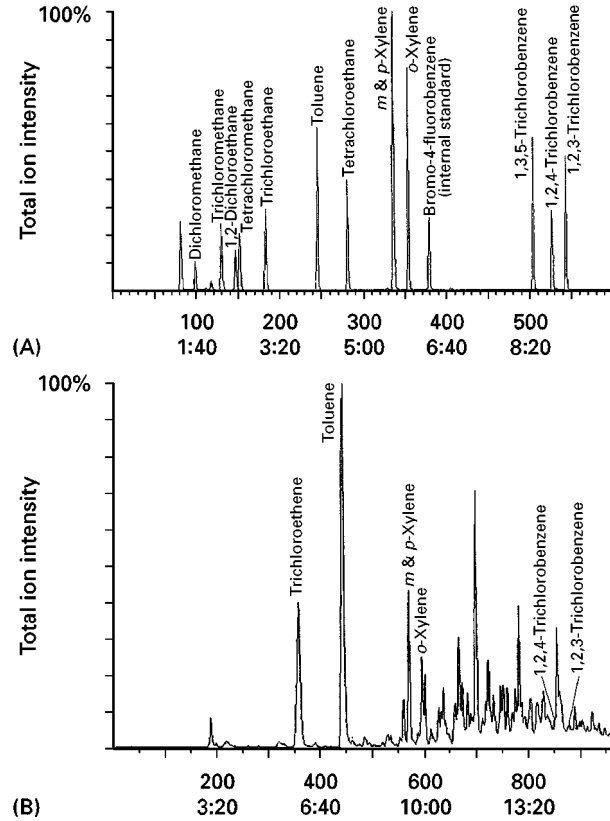

Figure 4 Analysis of VOCs by headspace GC-MS. Conditions: 5 mL sample, equilibrated for 10 min; 30 m × 0.25 mm DB-5MS column; temperature program 40°C, hold 5 min → 200°C at 15°C min^{-1} → 250°C at 50°C min^{-1}; carrier gas: helium 3 mL min^{-1}; Ion Trap™ detection, EI mode, 1 s scan, mass range 45–220 amu. (A) Chromatogram shown is from a 100 μg L^{-1} standard solution in water. (B) VOCs in trade effluent from a road haulier's premises. Conditions as above except carrier gas approximately 1.5 mL min^{-1}. Approximate concentrations: trichloroethene 1150 μg L^{-1}; toluene 1700 μg L^{-1}; *m*- and *p*-xylenes 500 μg L^{-1}; *o*-xylene 250 μg L^{-1}; 1,2,4-trichlorobenzene 20 μg L^{-1}; 1,2,3-trichlorobenzene 40 μg L^{-1}. Other compounds, including the internal standard, are also present, but cannot be seen on this scale.

Conclusion

This article has summarized the main methods of analysing for VOC in common use today and

has briefly described some of the advantages and disadvantages of each. It is hoped that the data illustrating the performance of the methods will assist readers in selecting an appropriate technique for their own application.

It is difficult to see where VOC analysis will go in the future, although possible developments include the more widespread application of automation to the dynamic headspace technique, enabling the unattended analysis of large batches of samples. Continued development of membrane and other direct inlet techniques for mass spectrometry and the shrinking size and price of MS-MS instruments may ultimately render the time-consuming chromatographic separation itself superfluous, offering the prospect of analysis in seconds rather than tens of minutes. However, for the time being the availability of suitable membranes permitting the migration of VOC restricts the application of this technique.

The increasing sensitivity of detection systems could well prove to be of little benefit to the analyst, as it may only serve to encourage the setting of even lower quality standards!

Whatever happens with the equipment and methodology that is employed, it is clear that continued growth in legislation controlling these substances in the environment will lead to an ever-increasing workload for the analytical laboratory.

See also: **II/Chromatography: Gas:** Column Technology; Detectors: General (Flame Ionization Detectors and Thermal Conductivity Detectors); Detectors: Mass Spectrometry; Detectors: Selective; Gas-Solid Gas Chromatography; Multidimensional Gas Chromatography; Sampling Systems; Theory of Gas Chromatography. **Extraction:** Analytical Extractions; Solid-Phase Extraction; Solid-Phase Microextraction. **III/Gas Analysis: Gas Chromatography.**

Further Reading

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