



**Technical Guidance Note
(Monitoring)**

M16

**Monitoring volatile organic compounds
in stack gas emissions**

**Environment Agency
Version 5
November 2016**

Purpose

This Technical Guidance Note (TGN) provides information about how we regulate emissions of volatile organic compounds (VOCs) to air from industrial processes. It defines what they are, why they are regulated, how we classify them, and provides an outline of the methods used to measure them.

Status of this document

This TGN may be subject to review and amendment following publication. The latest version of this note is available from www.mcerts.net

Record of changes

Version	Date	Change
5	Nov 2016	Removed information about monitoring methane
		1 – Added definition of VOCs from Industrial Emissions Directive
		9 – updated section on European methods
		References - Added link to website for access to " <i>The categorisation of Volatile Organic Compounds</i> "

Feedback

Any comments or suggested improvements to this TGN should be e-mailed to Rupert Standing at rupert.standing@environment-agency.gov.uk .

Contents

1. What are volatile organic compounds?	1
2. Why do we regulate VOCs?	1
3. How do we regulate VOCs?	1
4. How do we classify VOCs?	2
5. How do we specify the concentration of VOCs?	3
6. Techniques for monitoring TOC.....	3
7. Techniques for monitoring individual VOCs	4
8. Hierarchy of monitoring standards.....	7
9. European periodic monitoring methods	8
10. CEMs	8
Annex 1: Guidance on approach to measuring highly harmful, class A and class B VOCs	9
References.....	11

1. What are volatile organic compounds?

Volatile organic compounds (VOCs) are organic chemicals that have a significant vapour pressure at room temperature. If they are allowed to build up in the air, they can harm human health or damage the environment. VOCs come from many different classes of chemicals, including aliphatic, aromatic and halogenated hydrocarbons, aldehydes, ketones, esters, ethers, alcohols, acids and amines.

The Industrial Emissions Directive¹ defines VOCs as any organic compound, as well as the fraction of creosote, having at 293.15K, a vapour pressure of 0.01 kPa or more, or having a corresponding volatility under the particular conditions of use.

Many industrial processes emit VOCs. These include printing, surface coating, painting, manufacturing of chemicals, rubber fabrication, wood and plastic lamination or cleaning. However, besides industrial emissions of VOCs, households and road transport contribute a substantial fraction.

2. Why do we regulate VOCs?

We regulate VOCs from industrial processes to minimise the harm that they do. They can cause harm in the following ways:

- harming human health directly
- promoting ozone pollution at ground level
- damaging the ozone layer in the stratosphere
- contributing to global climate change
- causing offensive smells

Research has shown that certain VOCs are involved in the generation of photochemical oxidants, in particular ozone, in the lowest region of the atmosphere (the troposphere). VOCs are an important class of pollutants commonly found in the atmosphere at ground level in urban and industrial centres, and contribute to high levels of ozone there.

Most industrial processes that can emit large quantities of VOCs require an Environmental Permit to operate. Before the Permit is granted, we assess the likely impact of all its emissions, including VOCs. We will not issue a Permit unless we are confident that the way that the process is operated will not put human health at risk and will minimise the environmental impact.

3. How do we regulate VOCs?

VOCs from industrial processes are regulated under “The Environmental Permitting (England and Wales) Regulations” (EPR).

The EPR contain a comprehensive list of industrial processes that can cause pollution. They place a duty on us to issue an Environmental Permit to every organisation that operates a listed process. The permit must contain conditions that require the process operator to prevent or minimise pollution by the use of Best Available Techniques (BAT).

Industrial processes release VOCs from a defined emission point (for example, an exhaust flue from a paint spray booth). These are known as ‘point source emissions’.

Permits often control point source emissions by specifying emission limits. These may either state that the concentration of the pollutant must not exceed a certain value, or that the source must not release more than a certain mass of the pollutant over a defined period.

If the potential for environmental harm from the process is substantial, the operator will be required to measure the concentration of the pollutant continuously and stop processing as soon as he safely can, if the concentration exceeds the permitted value. If the potential for harm is lower, the requirement to measure the concentration is reduced to an appropriate level. It becomes, in effect, a check that the process is not changing gradually over a period of time.

4. How do we classify VOCs?

We classify VOCs according to their potential environmental harmfulness, so that an assessment can be made of the degree of control needed on their release from a process. We identify the following three classes of VOCs:

Highly harmful – such as benzene, vinyl chloride and 1,2 dichloroethane. They are substances that are known to be carcinogenic, mutagenic, toxic to reproduction, or very toxic by inhalation or ingestion. Emissions of these compounds must either be prevented or minimised by setting very low emission limits in permits. If a process could emit one or more highly harmful VOCs we would use the Environmental Permit to set an emission limit for each separate VOC.

Class A compounds – carry a lower, albeit significant risk. They are suspect carcinogens, or they contribute substantially to the creation of photochemical ozone, depletion of stratospheric ozone or global warming. They are considered as having a medium degree of harmfulness. Examples include acetaldehyde, aniline, benzyl chloride, carbon tetrachloride, ethyl acrylate, halons, maleic anhydride, 1,1,1-trichloroethane, trichloroethylene and trichlorotoluene.

Class B compounds – the remaining majority of VOCs are considered as having a lower degree of harmfulness. However, these VOCs are also regulated substances whose releases must be prevented or minimised. Examples include butane and ethyl acetate.

We have developed an index of VOCs², together with their classification. Industrial operators, regulators and monitoring contractors should use it to categorise VOCs.

The Environmental Permit specifies the monitoring method that should be used. When an industrial operator uses a monitoring contractor to carry out the monitoring, they should provide the contractor with a copy of the relevant part of the Permit. If the Permit refers to class A and class B VOCs, the industrial operator should tell the contractor, which VOCs are expected in the emission, so that they can plan the monitoring campaign accordingly. The operator should ensure that the contractor reports their results according to the requirements of the Permit. Further information is provided in Annex 1.

5. How do we specify the concentration of VOCs?

There are three commonly used ways of reporting the concentrations of VOCs:

- the concentration of individual VOCs
- the sum of the concentrations of specific, individual VOCs in a sample
- as total organic carbon (TOC), which is the concentration of organic carbon in the gas stream

The concentrations are expressed in milligrams per cubic metre (mg/m³).

6. Techniques for monitoring TOC

6.1 Flame ionisation detectors

Flame ionisation detector (FID) techniques work by a gas being passed into a measurement chamber, which uses a flame to create ions from the VOCs. More specifically, FID analysers make use of the chemi-ionisation of organically bound carbon atoms in a hydrogen flame to provide measurements. The measurement cell contains a pair of electrodes, which the instrument applies a voltage between. If there are ions present in the cell, then a current can pass between the electrodes. The ionisation current measured by the FID depends upon the number of carbon-hydrogen bonds of the organic compounds burning in the fuel gas flame and the ability with which these compounds ionise. The more ions present in the cell, the greater the current. As the abundance of ions within the cell depends on the concentration of the gas, then FID provides an effective means of measuring the concentrations of gases.

FIDs do not differentiate between different compounds since they respond to carbon-hydrogen bonds, rather than specific compounds. FIDs measure Total Organic Carbon (TOC).

The main strength of the FID is that it is a useful instrument for measuring total carbon in a gas stream. As a general rule, the response of a FID is mostly influenced by the number of carbon atoms in a sample. Furthermore, FIDs only respond to gaseous or vapour phase molecules which contain carbon-hydrogen bonds.

If the stack gas is relatively hot and wet, or the VOCs are concentrated, then there is a high probability of condensation when the gas sample touches a surface cooler than that in the stack. A FID for stack monitoring should, therefore, have a means of preventing condensation of either moisture or VOCs in the sample line (i.e. be equipped with a heated-line, heated detector and a heated by-pass).

Where continuous or periodic sampling is carried out with an analyser close to the duct and the sampled gases are above ambient temperature, then the line (and its filter) carrying the sample to the analyser must be heated to prevent condensation and reduce adsorption losses. The lines within an analyser also need to be heated, while all gas chromatographs must have heated injection ports, ovens to heat the column and detectors in heated housings.

Many simple, unheated, portable FIDs have been designed for applications in health and safety screening, landfill gas monitoring, contaminated land measurements, and fugitive emissions monitoring. The simpler FIDs also usually have a wider spectrum

of response factors, so their accuracy and precision will never be as great as the highly engineered, complex, heated FIDs.

6.2 Catalytic oxidation

An instrument called a catalytic oxidiser is an alternative way of measuring total carbon, although the technique is not used as widely as FID. A sample of VOCs enters a combustion chamber which contains a catalyst, and within this, the carbon in the VOCs is oxidised to carbon dioxide (CO₂). The instrument then measures the concentration of CO₂ using an infra-red gas analyser.

This method has two disadvantages. First, the catalysts can be poisoned by some components of the gas stream and secondly, the conversion of carbon to CO₂ is not always completely efficient.

6.3 Photo Ionisation Detection (PID)

These work on a similar principle to FIDs, in that the sample gas is ionised. The difference is that the source of ionisation is an intense UV light and not a flame, so there is no need for support gases. They are not as suitable as FIDs for total carbon counting, especially from combustion processes. The other major differences between FIDs and PIDs are the response factors are much more variable than in FIDs and they have much weaker responses for the small saturated hydrocarbons.

They are not used as CEMs because of the problems caused by the high variability of response factors and difficulties with sample conditioning.

7. Techniques for monitoring individual VOCs

7.1 Sorbent tube followed by gas chromatography (GC) separation

Solid adsorbents are versatile media for collecting hundreds of types of VOCs. They work by collecting the VOC on the surface of the medium, which is usually contained within a tube. Prior to analysis, the sampled VOCs are removed by either thermal desorption or by solvent extraction.

There is no universal sampling sorbent, each tends to be suited for monitoring different categories of organic compound. For example, solid adsorbents such as charcoal are typically used for VOCs, while polymeric sorbents are used for semi-VOCs.

Organic polymeric sorbents include porous, polymeric resins such as 2,4-diphenyl-p-phenylene oxide (e.g. Tenax GC) and styrene di-vinylbenzene co-polymer resins (e.g. XAD). These materials are hydrophobic, so they usually collect minimal amounts of water during the sampling. This means they can be used to sample very large samples of air, which is important if the target analytes are present in very small concentrations. On the other hand, these resins are not well suited to collecting highly volatile compounds, or certain polar materials, such as alcohols and ketones.

Inorganic sorbents include magnesium aluminium silicate (e.g. Florosil), silica gel and molecular sieves. These are usually very polar adsorbents, so they are efficient for collecting high-polarity compounds. However, they are also efficient at collecting water, which tends to degrade the adsorbents, thus decreasing their efficiency.

Carbon sorbents have a polarity in between the inorganic and organic, polymeric adsorbent, so water is less of a problem. However, collection of water can still inhibit some sampling programmes. Carbon based sorbents have a much stronger adsorption than organic polymers, so they are very efficient for collecting a vast array of VOCs. However, VOCs, which adhere strongly to carbon sorbents are also difficult to desorb.

Apart from the versatility of the technique, its strength is that it effectively immobilises the sample on the adsorbent. However, there are caveats when using solid sorbents:

- the media often collect VOCs other than the target analytes, so the user must employ a means of separating the different VOCs once they have been removed from the medium;
- each medium has a saturation point, known as the *breakthrough concentration*. The user must therefore know when this occurs, which in turn means having some idea of the range of concentrations in the sampled gas. This can usually only be determined reliably by pre-surveys and some experimentation;
- there is no universal adsorbent for all VOCs;
- some VOCs cannot be entirely removed from the adsorbent medium once they have adsorbed onto it. The proportion of desorbed target analyte is known as the recovery rate, and the user must know this rate for the target VOCs and the media used to collect them;
- to apply this method correctly for compliance monitoring against an ELV, it is essential that the species of VOCs present in the stack gas is known beforehand. If they are not known, they may be determined by using this technique to carry out semi-quantitative screening. Once the species are known it is possible for the GC-FID analysis stage to be carried out quantitatively.

Another technique is to use a canister, which is coated with an inert surface, such as PTFE, to collect a volume of sample gas. This can be done by using a pump, utilising positive pressure in a stack or drawing the sample into a previously evacuated canister. Once taken, the samples can then be analysed using methods, such as GC-FID or GC-MS. The technique is suitable for emissions where the VOCs are highly concentrated and relatively free of particulates and water vapour. However, samples obtained by this technique may only be stable for a limited period and analysis is usually required within 24 hours.

Many VOCs may also be selectively trapped in liquid media. The VOC sample is passed through an impinger containing a solution, after which the target VOCs are analysed.

The above techniques require a sample to be extracted from a stack or duct and transported to a laboratory for subsequent analysis. For sources at ambient temperature this is relatively straightforward. If the stack contains water vapour and is at an elevated temperature, condensation in the sample container may cause problems. Condensation of water vapour can be dealt with by diluting the sample with dry air or nitrogen gas.

In terms of analysis, GC is a straightforward and accurate means of separating the components of even quite complex mixtures. The FID is a very useful detector

because of its cost, sensitivity, wide dynamic range, reliability, response to all carbon compounds, and linearity.

7.2 Non-dispersive infrared (NDIR) detection

All VOCs absorb electromagnetic radiation, while different compounds absorb energy at different frequencies. This means that VOCs have an electromagnetic finger-print which is known as a *spectrum*. This feature can be exploited for measurements by targeting a peak or peaks in a compound's spectrum.

The diatomic bonds in VOCs absorb infrared (IR) radiation and vibrate. This fact is exploited in the simplest and most widely used spectroscopic analysers. A source of radiation generates a beam which is then focused through a cell and a filter is placed in front of the beam in order to create a single wavelength beam of IR radiation. The wavelength is selected to coincide with an exclusive absorption peak in the spectrum of the target compound. The advantage of this technique is that most VOCs absorb strongly in the IR. However, if there is a mixture of VOCs, then the spectra can overlap. Therefore, the technique is suited best to single compounds or simple mixtures where there are no interferences.

For some applications, infra-red analysers are well suited to long term monitoring of VOCs. Acetylene, ethylene, ethane, propane, propylene, butene-1, butane, pentane and hexane can all be measured at concentrations below ppm.

7.3 Fourier transform infrared (FTIR)

FTIR uses the same basic principle as simple infra red (IR) analysers, but resolves interfering spectra by splitting the beam into two. One beam is then bounced off a fixed mirror while the other is bounced off a moving mirror. This causes the beams to be slightly out of phase. The beams are then directed by mirrors to collide, and the resulting new spectrum creates both constructive and destructive interference in such a way that software can carry out a Fourier transform calculation to identify distinct compounds.

All VOCs absorb IR radiation and most can be detected by FTIR. A typical application may include measurement of methane, ethane, ethene, propane, hexane and formaldehyde. However, analysis of a matrix containing more compounds is possible.

An assessment by a competent specialist of the feasibility of a speciated VOC measurement is required, particularly if there is a need to measure a low concentration of one VOC when another VOC is present at a high concentration. Many such applications are feasible but chemically similar compounds may have similar IR spectra and can be difficult to differentiate.

A technical procedure for using FTIR to carry out periodic stack emissions monitoring is provided in TGN M22³.

7.4 Differential optical absorption spectrometry (DOAS)

This technique was originally developed as an open-path monitor for atmospheric research. Most DOAS instruments use either UV or IR absorption to distinguish between different species. The technique can measure a selected handful of VOCs, such as benzene, toluene, ethylbenzene, xylene and formaldehyde.

7.5 Mass Spectroscopy

In electron impact mass Spectrometry (MS), organic molecules are bombarded with electrons and converted to energetic, positively charged ions, which can break up into smaller ions.

The charged ions are deflected by a series of either electric or magnetic fields to allow the selection of specific mass to charge species. Data is recorded in terms of either a full mass spectrum or by selected ion recording techniques.

Developments in this technique have resulted in on-line instruments, which can take direct readings from stacks. The benefits of the technique are that it has very rapid response times (typically in milliseconds) and a wide dynamic range, from ppb levels to 100% concentrations.

The technique can also monitor several compounds at once, although there is also the possibility of interference.

Mass spectrometry is very useful for identifying unknown compounds in a mixture but is less suited to long-term routine monitoring of emissions - largely on grounds of capital cost and maintenance.

8. Hierarchy of monitoring standards

A list of relevant standards for monitoring VOCs is given in the index of methods in TGN M2⁴. The standards in this index are selected from the following hierarchy:

- Comité Européen de Normalisation (www.cenorm.be)
- International Standardisation Organisation (www.iso.ch)
- National standards, such as US EPA (www.epa.gov/emc)

If the VOC cannot be monitored using standards covered by the above, then a method from the following may be specified in TGN M2:

- Method for the Determination of Hazardous Substances (<http://www.hse.gov.uk/pubns/mdhs/index.htm>) series published by the Health and Safety Executive (HSE)
- National Institute of Occupational Safety and Health (<http://www.cdc.gov/niosh/nmam/>)
- Occupational Safety and Health Administration (www.osha.gov/dts/sltc/methods/).

9. European periodic monitoring methods

BS EN 12619 - FID method for TOC

CEN developed BS EN 12619⁵ as a standard reference method (SRM) for monitoring the mass concentration of gaseous and vaporous organic substances (expressed as TOC) from waste incinerators and solvent using processes. For measurement at waste incinerators it was validated over a concentration range of 0 – 20 mg/m³ but can be used at a concentration range of up to 1000 mg/m³.

It specifies a set of minimum performance requirements for an instrument using a FID, together with procedures for its calibration and operation.

The system comprises a probe with a filter connected to a heated sample line, which is in turn connected to a heated FID.

BS PD CEN/TS 13649 - charcoal tube method for individual VOCs

BS PD CEN/TS 13649⁶ was developed for monitoring individual VOC emissions from solvent using processes. It specifies procedures for the sampling, preparation and analysis. The VOCs are expressed as concentrations of individual species, averaged over a sampling period.

This Technical Specification is suitable for use in the range from 0.5 mg/m³ up to 2000 mg/m³. The standard is based on the principles of sampling onto adsorption media followed by desorption and analysis by gas chromatography.

There are several analytical methods which have been developed for monitoring concentrations of VOCs in workplace atmospheres (MDHS, NIOSH, OSHA). These analytical methods can be adapted for use in stack emissions monitoring. However, it is important that the sampling part of the method follows the framework given in BS PD CEN/TS 13649.

10. CEMs

If a process operator's permit requires TOC to be measured continuously, the CEMs used must be MCERTS certified at the appropriate range. Information on our monitoring certification scheme is available from www.mcerts.net.

Annex 1: Guidance on approach to measuring highly harmful, class A and class B VOCs

Permits in the chemicals sector may categorise monitoring of VOCs based on three categories – highly harmful, class A and B.

A1.1 Highly harmful

If a VOC is categorised as highly harmful it should be listed in the Permit with its emission limit value (ELV), alongside the method that is used for its measurement. The monitoring method used must measure the individual VOC.

A1.2 Class A and B

Permits may also require an operator to measure class A and B VOCs.

Class A VOCs are medium harm VOCs, which should be listed in the Permit. These VOCs are usually but not always measured individually.

Class B VOCs are low harm VOCs, which are not usually listed in the Permit. These VOCs can be measured as a total mass of organic carbon.

There is no unique physical or chemical difference to distinguish class A VOCs from class B, which means there is no monitoring method available that can do this. To distinguish between class A and B VOCs, it is necessary to know the different species of VOCs that could be in the stack gas emissions, so that an appropriate monitoring approach can be applied.

Firstly, an operator should assess the possible class A VOCs that could be present in the stack gas emissions.

Class A VOCs are usually measured using the sampling framework provided by EN 13649, followed by analysis in an analytical laboratory. However, it is possible to measure class A VOCs using an instrumental analyser, such as FTIR, which can speciate each VOC.

Typically, class B VOCs make up the majority of the VOCs in a mixed VOC stack gas emission. As class B ELVs are expressed as mass concentration of TOC, they should be measured using an FID. The FID will not distinguish between highly harmful, class A or class B VOCs but will give the combined TOC mass concentration of all three. However, this is usually acceptable because the concentrations of highly harmful and class A VOCs should be significantly lower than for class B.

There are some exceptions to the above approach, for example:

- if there are a limited number of class B VOCs, it may be simpler to speciate them rather than use an FID.
- if there are a limited number of class B VOCs, which are known to have a poor response factor to an FID, it would be better to speciate them.

M16: Monitoring of volatile organic compounds in stack gas emissions

- if the mass concentration of class A VOCs is significant, when compared to the mass of class B, it is better, if possible, to speciate both the class A and B VOCs, so that the class B result does not contain class A VOCs.
- If there is only one class A species present, an FID could be used rather than using the sampling framework provided by EN 13649, followed by analysis in an analytical laboratory.

In summary, it is important that the monitoring requirements in an operator's permit are discussed with the organisation responsible for the monitoring, so that a suitable measurement plan can be developed.

References

1. 4. 2010/75/EU, Directive on industrial emissions (integrated pollution prevention and control).
2. The categorisation of Volatile Organic Compounds, HMIP, 1996. Available from the UK regulation section at <http://www.s-t-a.org/?page=regulation>
3. Guidance Note M22, Measuring stack gas emissions using FTIR instruments, Environment Agency (available from www.mcerts.net)
4. Technical Guidance Note M2, Monitoring stack emissions to air, Environment Agency (available from www.mcerts.net)
5. BS EN 12619 (2013) - Stationary source emissions - Determination of the mass concentration of total organic carbon at low concentrations in flue gases - continuous flame ionisation detector method.
6. BS CEN/TS 13649 (2014) – Stationary source emissions — Determination of the mass concentration of individual gaseous organic compounds — Sorptive sampling method followed by solvent extraction or thermal desorption.