SM-QG7 - Monitoring volatile organic compounds (VOCs)

1. Scope

This note outlines the procedures, standards and methods for monitoring volatile organic compounds (VOCs), both as total organic carbon (TOC) and specific VOCs. This note describes both continuous and discontinuous techniques.

2. Practical Guidance

2.1 Background

2.1.1 Definition of a VOC

A VOC as any organic compound which is emitted from non-natural processes and has a photochemical ozone creation potential (POCP). We interpret this as any organic compound released to the atmosphere from an operator’s plant or process, excluding releases of naturally produced VOCs from within the plant boundary and methane.

2.1.2 Impacts of VOCs

VOCs can have both direct and indirect impacts.

- The direct impacts typically include the impacts on human health that specific VOCs may cause; for example, benzene is a known carcinogen.
- Indirect impacts, whereby VOCs react with nitrogen oxides in the presence of sunlight to form photochemical oxidants.

2.2 Two main categories of sources of VOCs

The two main categories are:

- Point sources of controlled releases: These include industry stacks, chimneys and flues. These point sources usually have requirements for monitoring VOCs and typically have emission limit values (ELVs) as well.
- Fugitive emissions: These are leaks from devices such as flanges and valves. Operators may be required to monitor fugitive emissions and to minimise their releases.
2.3 Monitoring requirements and ELVs for VOCs

The monitoring requirements and ELVs for VOCs fall within two categories:

- **Specific VOCs:** The permit may require the operator to measure the emissions of specified VOCs or types of VOC.

- **Total organic carbon (TOC):** The permit may specify an ELV for TOC, rather than for individual VOCs.

The European Union BREF on the General Principles of Monitoring specifies the standards and methods which the Scottish Environment Protection Agency requires for monitoring specific VOCs and TOC. This states that a hierarchy of standards should be used with European (CEN) Standard Reference Methods (SRM) recommended as being the most suitable. The Waste Incineration Directive (WID) and Large Combustion Plant Directive (LCPD) state that CEN SRMs are mandatory where available and must be used for monitoring emissions. In the UK CEN SRMs are transposed as BS EN SRMs.

Current available SRMs are summarised in The Environment Agency Technical Guidance Note (TGN) M2.

Monitoring systems for continuous monitoring should be certified to an appropriate scheme (e.g. Environment Agency of England & Wales Monitoring Certification scheme (MCERTS) or German TUV/UBA certification scheme), if such systems are available. The following sections are a summary of the main techniques.

2.4 Techniques for monitoring VOCs

Techniques for monitoring VOCs may be continuous or discontinuous, extractive or in-situ. This section outlines the main methods, although there are other techniques available.

2.4.1 Continuous monitoring techniques for total VOCs, as Total Organic Carbon (TOC)

The techniques include flame ionisation detectors (FIDs), catalytic oxidation, and infra-red techniques (IR) such as infrared spectroscopy. The latter technique only realistically applies in cases where there are few VOCs and their proportions do not change; for example, IR techniques may be a suitable technique for monitoring one or two VOCs at a release point.

However, only FIDs are proven as the most accurate and precise method for monitoring TOC. Furthermore, at the time of writing, the only instruments to be certified for monitoring TOC are FIDs. Therefore if a permit requires the operator to monitor for TOC and there is an ELV for TOC, then only FIDs should be used.

Zero-checks and FIDs: Oxygen can produce a small positive response in FIDs. Therefore when performing zero checks, we recommend that users perform zero checks with nitrogen, rather than with
clean air. If clean air is used to set the zero reading on FIDs then the FID may report negative readings when the concentration of oxygen falls well below ambient concentrations.

2.4.2 Continuous techniques – specific VOCs

<table>
<thead>
<tr>
<th>Technique</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Differential Optical Absorption Spectroscopy (DOAS)</td>
<td>Measures certain specific VOCs such as benzene, toluene and xylene.</td>
</tr>
<tr>
<td>Non-dispersive infrared (NDIR)</td>
<td>Measures VOCs which have an infrared spectrum. Typically restricted to no more than a few VOCs at any one time, whilst moisture interference can be significant.</td>
</tr>
<tr>
<td>Fourier-transform infrared (FTIR)</td>
<td>Can measure many individual organic compounds simultaneously. Typically better performance than NDIR.</td>
</tr>
<tr>
<td>Continuously-cycling gas chromatography (GC)</td>
<td>Depending on the type of detector and GC column, this technique can measure a large number of VOCs at once. However, it is not a strictly continuous technique as the GC will take sequential samples and provide a series of regular, spot measurements, rather than a continuous measurement.</td>
</tr>
</tbody>
</table>

2.4.3 Sampling techniques – specific VOCs

In simple terms, VOCs are either extracted onto a solid medium such as charcoal or a synthetic absorbent material, or extracted into a liquid medium. In the case of most VOCs, the most widely used technique is to extract a sample and capture it within charcoal tubes. The applicable standard reference method for this technique is BS EN 13649.

2.4.4 BS EN 12619 and BS EN 13526, TOC measured using a reference method

Both these reference methods specify the use of FIDs. The FIDs used within these reference methods shall meet relevant performance standards (for example MCERTS) for the appropriate certification ranges.

2.4.5 BS EN 12619 and the control gas

BS EN 12619 specifies that users of the standard shall test the performance of the FID at specified intervals using a control gas. The overall concentration of the control gas shall be expressed as TOC, in mg.m⁻³. The supplier of the control gas should provide this information. Therefore when testing the
performance of the FID against the requirements of BS EN 12619, the reading of the FID shall be expressed as TOC, and this value shall be compared to the known value (as TOC) of the control gas.

3. Further information

3.1 Quick Guides

- SM-QG-01 Selecting continuous emission monitoring systems (CEMs)
- SM-QG-03 Application of EN 14181

3.2 Environment Agency Technical Guidance Notes

- TGN M2 – Monitoring of stack emissions to air

4. Feedback

Any comments or suggested improvements to this note should be e-mailed to Duncan Stewart at duncan.stewart@sepa.org.uk.

5. Acknowledgments

Content based on Environment Agency Monitoring Quick Guide 07, used with permission