Stack Emissions Monitoring
Method Implementation Document for EN 13725

BS EN13725:2003

Air Quality – Determination of odour concentration by dynamic olfactometry

Measurement of odour in stack gas emissions

Environment Agency
Version 2
April 2015

Record of amendments

Version number	Date	Amendment
2	Apr 2015	Replaced ISO 10780 with EN ISO 16911-1 and associated MID

Status of this document

This method implementation document may be subject to review and amendment following publication. The most recent version of this note is available from www.mcerts.net and on the Source Testing Association web site at:

www.S-T-A.org

Feedback

Any comments or suggested improvements to this MID should be e-mailed to Rupert Standring at rupert.standring@enviroment-agency.gov.uk.

Role of Method Implementation Documents

The Environment Agency recognises that European and International standards may need supplementing by Method Implementation Documents (MIDs) to ensure they are being implemented consistently.

We have established our Monitoring Certification Scheme: MCERTS to deliver quality environmental measurements. Organisations wishing to include a standard in their schedule of MCERTS accreditation shall follow the requirements of the standard and, where available, the associated MID.

It may not be necessary to produce a MID for every standard but where required they will be used to supplement standards called up by Technical Guidance Note M2. MIDs provide details on how the preferred standards shall be used for regulatory monitoring.

MIDs are produced in collaboration with organisations with an interest in stack emissions monitoring.

Copies of MIDs and further information on MCERTS including copies of performance standards and guidance can be obtained from our web-site at:

www.mcerts.net

Or from the STA web-site at:

www.S-T-A.org

Contents

Introduction

This Method implementation Document (MID) supplements BS EN 13725:2003 (referred to as EN 13725 in this MID). However, **it does not re-state the provisions of EN 13725** and organisations are reminded of the need to comply with the criteria detailed in EN 13725 in addition to those defined in this document.

1 Scope

This MID focuses on the collection of odour samples from stack gas emissions. The samples are subsequently analysed by delayed dilution olfactometry, in accordance with EN 13725.

The technique referred to as direct olfactometry in EN 13725 is not currently applied in the UK and is not discussed further within this document.

2 Normative references

The following referenced documents are essential for the interpretation and application of this MID:

- EN 13725, Air quality: Determination of odour concentration by dynamic olfactometry
- ISO 5492, Sensory analysis; vocabulary
- EN15259 - Stationary source emissions – Requirements for the measurement sections and sites and for the measurement objective, plan and report
- EN 16911-1 – Stationary source emissions – Manual and automatic determination of velocity and volume flow rate in ducts Part 1: manual reference method
- Method Implementation Document for EN 16911-1 - Application to manual stack emissions monitoring
- Technical Guidance Note (Monitoring) M1 – Sampling requirements for stack emission monitoring, Environment Agency
- MCERTS performance standard for manual stack emissions monitoring organisations, Environment Agency.

3 Terms, definitions, and symbols

No additional requirements to EN 13725

4 Principle of measurement (sampling)

No additional requirements to EN 13725

5 Performance quality requirements

5.1 General

The performance of the technique in terms of quality is influenced by a range of quantifiable sources of uncertainty. The component and overall uncertainty of the techniques used to collect and analyse odour samples shall be demonstrated and recorded.

The following quantifiable sources of uncertainty are associated with odour sampling:

- uncertainty of measurement of volume flow, pressure and temperature in accordance with EN 16911-1

Note: the uncertainty associated with flow affects the odour emission rate not the odour concentration.

- uncertainty of odour analysis according to EN 13725

- uncertainty associated with determining the dilution ratio during pre-dilution

The following sources of uncertainty are also associated with the technique, but are not directly quantifiable:

- The uncertainty associated with temporal variation in odour concentration within the stack, due to changes in process conditions.

  Note: this is likely to have a largest effect on the uncertainty.

- The uncertainty associated with the conservation of the sample whilst the sample is drawn from the sampled gas flow to the sample container (odour sampling bag).

- The uncertainty associated with the conservation of the sample during transportation and storage.

- The uncertainty associated with non-compliance with the sample location (e.g. positioning of sample plane or sample point in locations that are not representative of the stack gas).

It is important that the sample location allows representative sampling. Further information is provided in Environment Agency Technical Guidance Note M1.

It is very difficult to assess the effect of a non-compliant sample location, so by convention it shall not be included in the reported measurement uncertainty. However, it shall clearly state in the measurement report that the location was non-compliant (see the MCERTS performance standard for manual stack emissions monitoring organisations).

5.2 Accuracy – statistical model

No additional requirements to EN 13725.

5.3 Overall sensory quality requirements

No additional requirements to EN 13725.

5.4 Quality requirements for dilution apparatus

No additional requirements to EN 13725.

5.5 Quality requirements for dilution apparatus

No additional requirements to EN 13725.

6 Materials, gases and panel members

6.1 General properties of materials

No additional requirements to EN 13725.

6.2 Sampling equipment

6.2.1 General

No additional requirements to EN 13725.

6.2.2 Materials for sampling equipment

No additional requirements to EN 13725.

6.2.3 Conditioning of sampling equipment

No additional requirements to EN 13725.

6.2.4 Cleaning and re-use of equipment

Sample lines and dilution probes shall not be reused prior to cleaning and shall only be reused for collection of samples from a single source, where the odour is expected to remain at a stable concentration (i.e. the process is under the same stable operating conditions).

The cleaning procedure depends on the type of odorous contamination and sampling equipment used. EN 13725 provides an example of a cleaning procedure in section 6.2.4. The following are examples of other cleaning procedures that could be applied, especially for equipment that cannot be taken apart (e.g. swage lock valves):

- cleaning in an ultrasonic bath with 3% hydrogen peroxide solution
- flushing with 3% hydrogen peroxide solution
- heating to at least 100^{o}C for at least three hours

For equipment that can be taken apart, soaking with a cleaning product, followed by manual scrubbing may be used.

Detergents, bleach and dishwasher cleaning products that have an odour shall not be used.

Note: odourless non-foaming soap is a suitable cleaning product (e.g. Decon 90).

Following cleaning, the equipment parts shall be flushed with neutral gas during drying. The odour neutrality of the equipment shall confirmed by checking the air used after flushing for odour neutrality.

6.3 Sample container

6.3.1 Materials for sample container (bags)

EN 13725 lists materials that are suitable for sample containers. The following may also be used:

- electropolished stainless steel
- glass.

EN 13725 includes a note that states that polyvinylfluoride (PVF, Tedlar) may not be suitable because it has the potential to release solvents. These bags shall not be used unless the material has been tested for suitability.

Materials shall be tested for suitability by assessing if they are odourless and if they can hold a mixture of odorants with minimal changes for periods of storage (see 6.3.2).

6.3.2 Conditioning and testing of sample containers

It is recommended that sample containers are conditioned on-site immediately prior to use by flushing with a sample of the stack gas. This can be done by partially filling the container with sample and then evacuating the container manually or using a pump to ensure it is completely empty prior to sample collection.

If pre-dilution equipment is used, it is a requirement that the sample train is flushed with the diluted sample at the target dilution factor. The duration of flushing shall be determined on the basis of the length of the sampling train. The flushing shall be carried out with the diluted sample at the target dilution factor.

6.3.3 Cleaning and re-use of sample containers.

No additional requirements to EN 13725.

6.4 Gases

6.4.1 Neutral gas for pre-dilution

No additional requirements to EN 13725.

6.4.2 Reference material: odorant (n-butanol)

No additional requirements to EN 13725.

6.4.3 Reference material for calibration of dilution equipment

No additional requirements to EN 13725.

6.5 Dilution apparatus

Appropriate materials shall be used for those parts of the dilution apparatus that are in contact with the odour sample. The materials described in section 6.2.2 of EN 13725 are suitable.

6.6 Environment for observation by assessors

No additional requirements to EN 13725.

6.7 Panel

No additional requirements to EN 13725.

7 Sampling

7.1 General

<u>a) Design of sampling surveys and pre-site planning</u>

<u>i) Health and Safety</u>

Specific detailed consideration shall be given to ensuring safe access for the sample team to collect samples, the safety of staff involved in sample transportation, and the safety of the analysis panel.

Information on sampling facilities and health and safety are provided in the Environment Agency TGN M1 document ‘Sampling Requirements for Stack Emission Monitoring’, and the Source Testing Association (STA) booklet ‘Risk Assessment Guide: Industrial-emission monitoring’[1].

Note 1: There are many hazards associated with stack emissions monitoring. For example, falls from height, exposure to substances in stack gases and burns from hot surfaces or hot stack gases.

Olfactometry analysis involves presentation of odour samples to a panel of human assessors. The estimated concentrations of chemicals and substances contained within samples shall, where possible, be made clear on chain-of-custody forms provided by the analytical laboratory. Samples containing potentially hazardous (e.g. carcinogenic) components may not be analysed, if there is a risk to the safety of the laboratory operator or panellist.

<u>ii) Sample ports (for stack sampling)</u>

The sampling point requirements for stack sampling are defined in Environment Agency Technical Guidance Note M1 – Sampling requirements for stack emission monitoring.

iii) Site Specific Protocol (Measurement Plan)

Planning should be conducted in accordance with the MCERTS performance standard for manual stack emissions monitoring organisations.

This should also include detailed consideration of:

- The number and type of odour sources to be sampled
- Access requirements
- Physical and chemical characteristics of emissions
- Potential for process variability
- Number of samples to be collected, duration and frequency of sampling

iv) Sample volume

The volume of sample required for analysis is determined by the:

- Requirements of the analytical laboratory
- Objectives of the survey
- Maximum acceptable measurement uncertainty required

v) Sampling duration and sample numbers

The duration of sampling and number of samples collected should be defined on the basis of the:

- Survey objectives
- Maximum allowable measurement uncertainty
- Potential for variations in odour emissions, due to process factors.

The typical duration for collection of a single odour sample, using the lung principle is between 4 to 30 minutes. For stable processes, with stable odour emissions, triplicate samples are recommended. Typically sampling may produce an average triplicate sample over a 30 minute time period (i.e. 3 times 10 minutes). If fewer samples are collected, the justification for this shall be clearly explained in the test report.

Sample time shall be adapted (reduced or extended) depending upon the characteristics of the stack gas emissions being sampled. This may also have implications on the total number of odour samples collected. More samples and longer samples times are required for variable processes.

A stable process may have variable odour concentrations, which may affect sample number and duration.

For assessing compliance with permit conditions, the uncertainty of the measurement technique shall be taken into account when defining the number of replicate samples to be collected.

vi) Assessing the need for sample pre-dilution

The requirement for pre-dilution shall be determined prior to sampling, by consideration of the:

- Likely chemical components and concentrations of the sampled gas

Note 1: If pre-dilution is undertaken because of the likely chemical components and concentrations of the sampled gas, it can be carried out at the point of sampling or in the laboratory after sampling. However, for highly flammable or explosive gases it is recommend that dilution is carried out on site, rather than transporting to laboratory and doing it there.

- Moisture content, pressure and temperature of sampled gas

- Ambient temperature and pressure during collection, transport and storage.

The pre-dilution factor applied shall be sufficiently large to prevent condensation during collection, storage or transport of the samples.

Note 2: It is important to consider the dilution factor carefully because the uncertainty of the method increases as the dilution factor increases.

7.2 Choice of sampling method

7.2.1 Sampling for direct olfactometry

This technique is not currently applied in the UK and is not covered by this MID.

7.2.2 Sampling for delayed olfactometry

Delayed olfactometry is the analytical technique used in the UK.

Sample collection should be conducted using the lung principle or via a pre-dilution device. The direct pumping technique referenced in EN13725 shall not be conducted due to the risk of contamination of the sample.

7.3 Sampling procedures

7.3.1 Sample collection method (lung principle)

The following sample procedure shall be followed:

1. The volume flow rate, temperature and humidity of the air stream (for stack sources) shall be measured. Volume flow and temperature shall be measured in accordance with EN 16911-1.

2. The sample train shall be assembled to ensure there are no routes of leakage or ingress of dilution air.

3. The sample probe shall be positioned in the stack at a representative point.
4. The sample conditioning requirements of section 6.2.3 and 6.3.2 shall be followed.

5. The sampling vessel shall be evacuated and the odour sample collected in the sampling container (bag).

6. Once the sampling container has been filled to the desired level the container shall be removed from the sample train, sealed and packaged for transport to the analysis laboratory.

For stacks under negative pressure, the stack sample port shall be sealed prior to undertaking sampling, to prevent ingress of dilution air.

Sample lines shall be kept as short as possible (to minimise the possibility of absorption). Sample lines and probes shall be changed between odour sources or between samples, if the characteristics of the odour source are likely to change with time.

Condensation in the extraction tube and sample line, in the dilution equipment and in the sample bag shall be prevented. If condensation occurs, the sample shall be rejected.

If a sample is rejected because of condensation, the site specific protocol shall be modified in order to prevent it occurring again. This may require the use of dilution or increased dilution, if a dilution system was used in the first place.

If probes and sample lines are reused, they shall be cleaned and checked for odour-neutrality.

Filters shall be used if the particulate loading adversely affects the operation of the sample train.

7.3.2 Pre-dilution during sampling

Note: Pre-dilution refers to the mixing of a neutral odourless gas (i.e. nitrogen) at the time of sampling. Post-dilution refers to dilution carried out after sampling by the analytical laboratory.

7.3.2.1 General

Pre-dilution of the sample is applied for the following reasons:

- If there is a risk of condensation of the sample in the sample line and sample container during collection

- If there is a risk of condensation of the sample during storage and transport

- To reduce the concentration of toxic or flammable components prior to transport to the laboratory

- To reduce the concentration of the odour to within the range of the olfactometer used by the analytical laboratory.

7.3.2.2 Equipment and procedures for static pre-dilution during sampling

For sources under negative or positive pressure it is recommended that dynamic pre-dilution should be used.

Caution should be applied when using static dilution to reduce the temperature of the sample to below dew point, as it can be difficult to entirely eliminate the risk of condensation during mixing of the sample with neutral gas in a sample container.

7.3.2.3 Equipment and procedures for dynamic pre-dilution during sampling

Note 1: although referred to as dynamic dilution, the actual dilution rate is fixed during the test. Alternatively, it can be referred to as dilution at source.

Dynamic pre-dilution is preferably performed in a pre-dilution unit (e.g. injector), which can be situated in the gas flow to ensure that the pre-dilution gas and sample gas are under the same conditions in terms of temperature and pressure. If pre-dilution is performed outside the gas flow, the probe and sampling line shall be heated until pre-dilution is carried out to prevent condensation. In such circumstances, it may also be necessary to equalise the pressure between the probe and duct, depending upon the design of the dilution probe.

If the stack gas emissions are at ambient temperatures it is unlikely that condensation will occur. This means the pre-dilution unit does not have to be in the stack. This approach can be used when the size of the access port is too small for the head.

An estimated dilution ratio of the equipment shall be determined by means of the sample flow rate and dilution settings. It is also dependent on the temperature of the dilution equipment.

The accuracy of the dilution ratio shall be checked after collection of each sample. This is achieved either by calibration of the dilution probe using the procedure described in section 5.4 of EN 13725 or by measurement of the concentration of a defined indicator gas that is present within the undiluted and diluted odour sample (e.g. oxygen, carbon monoxide, carbon dioxide).

Olfactometry analysis involves presentation of odour samples to a panel of human assessors. The type and concentration of any tracer gas (e.g. carbon monoxide) shall be made clear on the chain-of-custody form provided by the analytical laboratory. Samples with high concentrations of potentially hazardous components may not be analysed where there is a risk to the safety of the laboratory operator or panellist.

Note 2: a potential error in the calibrated flow meters approach is the impact of stack gas pressure on the dilution factor. One proven way of determining the dilution factor is to measure stack gas oxygen and oxygen measured in the odour bag.

This indicator gas method of determining the pre-dilution factor can only be applied if the indicator concentration in the pre-diluted sample differs from that in the waste gas and the pre-dilution gas. A pre-dilution gas shall be used that does not contain the indicator gas (e.g. nitrogen).

The concentration of the selected indicator gas shall be determined during sampling of the waste gas and immediately after sample collection for each of the pre-diluted samples. If the indicator gas concentration in the waste gas is constant and no concentration variations are expected, a measurement prior to and following sample collection shall be sufficient for determination of the marker concentration in the waste gas. If the indicator gas concentration in the waste gas is not constant over time (e.g. combustion gas process), the indicator gas concentration shall be determined over the entire sampling period.

The pre-dilution factor Z is determined using the following equation:

$$Z_V = \frac{C_{\text{Ind, waste gas}} - C_{\text{Ind, predilution gas}}}{C_{\text{Ind, sample(pred.)}} - C_{\text{Ind, predilution gas}}} \qquad (1)$$

If the indicator gas is not contained in the pre-dilution gas, the following simplified equation applies:

$$Z_V = \frac{C_{\text{Ind, waste gas}}}{C_{\text{Ind, sample(pred.)}}} \qquad (2)$$

Key
ZV = Pre-dilution factor
C = Concentration
Ind = Indicator concentration
Sample (pred.) = Pre-diluted sample

The analyser employed to measure the indicator gas concentration shall be checked each day of the measurement with a zero gas and a span gas at an appropriate concentration as per standard gas reference methods. The zero and span drift criteria used in these methods shall be applied.

Note 3: If oxygen is used to determine the pre-dilution factor, the check can be carried out with ambient air (20.9% O_2) and nitrogen (0% O_2).

When using oxygen as a tracer gas, the procedure specified EN 14789[2] shall be followed (other reference methods are applicable if carbon monoxide or carbon dioxide are used as tracer gases).

The analyser used to measure the tracer gas shall be certified on the MCERTS scheme for either portable or transportable emission monitoring systems.

The analyser shall have an expanded uncertainty of ± 3% or less.

The limit of detection of the indicator gas analyser will impact on the dilution factor that can be achieved. Care should be taken to ensure that the sample is not over-diluted as this can lead to an over-estimation of odour concentration if the dilution reduces the concentration of the sample to below the limit of detection of the analytical technique.

All odour concentration data shall be expressed in accordance with the reference conditions described in EN 13725 (i.e. 20°C, 101.3 kPa on a wet basis).

Note 4: For ducts under high negative or positive pressure the use of pre-dilution equipment may not be possible or adversely impacted. This can be confirmed prior to undertaking sampling.

7.3.3 Transport and storage before measurement

All samples shall be clearly labelled with a unique sample identification code on collection. The samples shall be protected. Storage and transportation in a rigid container is recommended, as it prevents mechanical damage.

Consideration and control shall be applied to the following factors to preserve the integrity of the sample during transport:

- Prevention of condensation due to changes in the internal and external temperature of the sample container
- Leakage or air ingress due to pressure changes (e.g. when transported by air)
- Photochemical reactions (samples shall not be exposed to direct sunlight or strong daylight).

A full chain of custody shall be maintained for the odour sample bags from procurement from the supplier through use on site and arrival at the analysis laboratory. The chain of custody shall include details of how the transport and storage issues are controlled and mitigated.

EN13725 stipulates a maximum temperature during storage of 25°C. When working in hot conditions this temperature may be exceeded, provided the deviation from the standard is justified in the final monitoring report. As this is unavoidable when working in hot conditions, it is acceptable to claim MCERTS accreditation, in spite of this deviation.

7.4 Sampling strategy

No additional requirements to EN 13725.

8 Presentation of odorants to assessors

No additional requirements to EN 13725.

9 Data recording, calculation and reporting

9.1 Minimum data recording requirements

No additional requirements to EN 13725.

9.2 Calculation of odour concentration of a sample from a set of panel member responses

No additional requirements to EN 13725.

9.3 Calculation of odour flow from odour concentration and odour flow rate

No additional requirements to EN 13725.

9.4 Calculation of odour abatement efficiency

No additional requirements to EN 13725.

9.5 Presentation and minimum requirements for reporting and archiving results

No additional requirements to EN 13725.

9.5.1 The minimum data for reporting

If carrying out MCERTS accredited work, the monitoring report shall be submitted in the report format specified in the Manual stack emission monitoring performance standard for organisations.

9.5.2 The minimum data for archiving

No additional requirements to EN 13725.

Annex A (normative) Working conditions and working platform for sampling

Sample locations and facilities should meet the requirements of EN 15259 and Environment Agency Technical Guidance Note M1.

Annex B (informative) Physiological principles

No additional information to EN 13725.

Annex C (informative) Example of calculation of instrumental accuracy and instability

No additional information to EN 13725.

Annex D (informative) Example of calculation of odour measurements within one laboratory

No additional information to EN 13725.

Annex E (informative) Example of calculations for panel selection

No additional information to EN 13725.

Annex F (informative) Example of the calculation of the odour concentration from a set of panel member responses

No additional information to EN 13725.

Annex G (informative) Example of the calculation used to determine the number of odour concentration measurements required to achieve a defined precision

No additional information to EN 13725.

Annex H (informative) Example of the calculation used to determine the number of odour concentration measurements required to detect a difference between two means

No additional requirements to EN 13725.

Annex I (informative) Example of the calculation of the odour flow rate (standard conditions) for a wet emission

Unlike in stack emissions monitoring odour emissions are standardised at 20°C (293K), rather than 0°C (273k).

Annex J (informative) Sampling strategy

No additional information to EN 13725.

Bibliography

1. Source Testing Association (STA) booklet ‘Risk Assessment Guide: Industrial-emission monitoring’.

2. EN 14789:2005 Stationary Source Emissions – Determination of volume concentration of oxygen