

Technical Guidance Note M21
(Monitoring)

**Stationary source emissions — A procedure to use an Alternative
Method for measuring emissions of sulphur dioxide, using
instrumental techniques**

**Environment Agency
Version 1.1
January 2010**

Foreword

We have issued Technical Guidance Note (TGN) M21 within our series of TGNs, which provide monitoring support to our regulatory officers, as well as process operators, test laboratories, equipment suppliers, and those with interests in stack emissions monitoring.

This TGN describes a procedure to use an Alternative Method (AM) for measuring emissions of sulphur dioxide (SO₂) from industrial stacks and flues. The Environment Agency's policy for monitoring is that test laboratories and operators shall use CEN standards where available. The standard reference method (SRM) for measuring emissions of SO₂ is BS EN 14791. This SRM is a manual method which employs wet chemistry. However, test laboratories may use other methods instead of SRMs, which are known as Alternative Methods (AM), as long as the test laboratory can demonstrate that the AM produces results of an equivalent quality to the SRM. This Standard recognises that many test laboratories and operators wish to use an AM which uses instrumental methods for measuring SO₂, instead of using a manual SRM based on wet chemistry and subsequent laboratory analysis.

The scope of this TGN provides for the use of instrumental techniques within an AM. This TGN does not specify the exact type of technique, but does specify performance standards for the instrumental systems employed within the method. Such instrumental methods can be based on techniques such as non-dispersive infrared analysis (NDIR), electrochemical cells, UV-absorption analysis, and Fourier-Transform Infrared (FTIR) analysis. Test laboratories that wish to use FTIR also have to be accredited to an appropriate method for FTIR, such as ASTM 6348-3, since the use of FTIR requires a greater knowledge and understanding of spectroscopic analysis.

This AM has been validated at the National Physical Laboratory, during an exercise which assessed the method described in this AM, comparing it to the results from the SRM, BS EN 14791. The equivalence of this AM was assessed using the procedures described in BS EN 14793; the results of the exercise found that the AM is equivalent to the SRM.

Feedback

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

Record of Amendments

| Version number | Date | Section | Amendment |
|-----------------------|-------------|----------------|--|
| Version 1 | July 2008 | - | First publication |
| Version 1.1 | Jan 2010 | 3.2.4 | Amended procedure for confirming the correct operation of moisture removal systems |
| | | 6.4.3 | Amended leak check procedure |
| | | 8 | Deleted list of test report requirements |
| | | Annex A | Revised uncertainty calculation |

Contents

| | | |
|----------|---|-----------|
| 1 | Scope..... | 1 |
| 2 | Principle | 1 |
| 2.1 | General..... | 1 |
| 2.2 | Measuring principles – analytical techniques and sampling systems..... | 1 |
| 3 | Description of measuring equipment - Sampling and sample gas conditioning systems..... | 2 |
| 3.1 | General..... | 2 |
| 3.2 | Sampling line components..... | 2 |
| 4 | Monitoring systems | 4 |
| 4.1 | Monitoring systems and types of instrumental techniques to measure SO ₂ | 4 |
| 4.2 | Accreditation requirements and procedures..... | 4 |
| 4.3 | Pressure and temperature effects..... | 5 |
| 4.4 | Sampling pump for the analyser | 5 |
| 4.5 | Interferences due to infrared or ultraviolet absorbing gases | 5 |
| 5 | Determination of the characteristics of the method: analyser, sampling and conditioning line | 6 |
| 5.1 | General..... | 6 |
| 5.2 | Performance characteristics of the method and performance criteria | 7 |
| 5.3 | Establishing the uncertainty budget | 7 |
| 6 | Field operation..... | 9 |
| 6.1 | Sampling location | 9 |
| 6.2 | Sampling point..... | 9 |
| 6.3 | Choice of the measuring system | 9 |
| 6.4 | Setting of the analyser on site | 10 |
| 7 | Ongoing quality assurance | 12 |
| 7.1 | Introduction..... | 12 |
| 7.2 | Frequency of checks | 12 |
| 8 | Expression of results | 12 |
| 9 | Test report | 12 |
| | Annex A: Example of an uncertainty determination | 16 |
| A.1. | Required data for the uncertainty determination..... | 16 |
| A.2 | Estimation of the combined uncertainty | 18 |
| A.3 | Estimation of the overall uncertainty | 18 |
| | Bibliography | 20 |

1 Scope

This Technical Guidance Note (TGN) specifies a procedure to use an Alternative Method (AM) for measuring the concentration of sulphur dioxide (SO₂) emitted to the atmosphere from industrial stacks and flues. Test laboratories may use this AM instead of the Standard Reference Method (SRM) for SO₂, BS EN 14791¹. This TGN describes instrumental techniques, including the sampling system and sample gas conditioning system, together with an accompanying method, to determine SO₂ in stack and flue gases. The AM described in this TGN can be used for periodic monitoring, and for calibrating and verifying Continuous Emission Monitoring Systems (CEMs) permanently installed on a stack, for regulatory or other purposes. When used as a reference method, the test laboratory needs to show that the instrumental systems used within the method meet the MCERTS performance standards for CEMs at least, and that overall uncertainty of the method is less than the uncertainty budgets specified in applicable EC Directives.

This TGN has been developed for compliance assessment monitoring, as well as calibration and verification work, under applicable standards and EC Directives. These include BS EN 14181² for the quality assurance of CEMs, and regulatory monitoring required by EC Directives for waste incineration³, large combustion plant⁴, and integrated pollution prevention and control⁵.

The limit values of EU directives are expressed in mg.m⁻³, on dry basis and at the reference conditions of 273 K and 101.3 kPa.

2 Principle

2.1 General

This TGN describes the reference method for sampling, and determining SO₂ emissions by means of a method using an automatic analyser. This TGN does not prescribe a specific technique for the analyser; however, the TGN does prescribe performance specifications (see Table 1) for the analyser and associated sampling system. These performance specifications and the overall uncertainty of the method shall meet these performance criteria. This TGN also specifies requirements and recommendations for quality assurance and quality control for measurements in the field.

2.2 Measuring principles – analytical techniques and sampling systems

2.2.1 Complete systems

The monitoring systems that test laboratories use within reference monitoring for SO₂ shall be extractive and typically comprise the following parts:

- A sampling probe, usually equipped with a filter to remove particulate matter.
- A sampling line, which is typically heated to reduce the possibility of condensation of moisture.
- A gas conditioning system to remove water vapour (not required for heated systems).
- An analytical instrument.

There are a number of instrumental techniques available for the analyser, which can measure SO₂ in emissions. These include infrared (IR) absorption, ultraviolet (UV) absorption, UV fluorescence and electrochemical cells. These are examples, however, and test laboratories may use other instrumental techniques, if there is appropriate evidence to demonstrate that the instrumental system employing the technique meets the performance standards specified in Table 1, plus the requirements of the field tests. The concentration of SO₂ is measured in volume/volume units (if the analyser is calibrated using a volume/volume standard). The final results for reporting are expressed in milligrams per cubic metre (mg.m⁻³) and reported under standard conditions (refer to Section 8).

3 Description of measuring equipment - Sampling and sample gas conditioning systems

3.1 General

A representative volume of the emitted gas is extracted from the emission source for the required test period of time at a controlled flow rate. A filter removes the dust in the sampled volume before the sample is conditioned and passes to the analytical instrument.

Three different types of sampling and conditioning system can be used to avoid the water condensation in the measuring system. These are:

- Type A: removal of water vapour by condensation using a cooling system.
- Type B: removal of water vapour through elimination within a permeation drier
- Type C: All parts of the analyser which are in contact with the sampled gas are heated to keep the sample above the dew point. Typically such systems keep the heated components at around 180°C.

It is important that all parts of the sampling equipment upstream of the analyser are made of materials that do not react with or absorb SO₂. The temperature of its components coming into contact with the gas, shall be maintained at a sufficiently high temperature to avoid any condensation.

The conditions and layout of the sampling equipment contribute to the overall uncertainty of the measurement. In order to minimise this contribution to the overall measurement uncertainty, this Standard specifies performance criteria for the sampling equipment and conditions are given in sections 3.2 and 5.2.

3.2 Sampling line components

3.2.1 Sampling probe

In order to reach the representative measurement point(s) of the sampling plane, probes of different lengths and inner diameters may be used. The design and configuration of the probe used shall ensure the residence time of the sample gas within the probe is minimised in order to reduce the response time of the measuring system to a minimum.

The procedure described in 6.2 shall be used when the test laboratory suspects a lack of homogeneity in the flue gas.

The probe may be marked before sampling in order to demonstrate that the representative measurement points in the measurement plane have been reached.

The probe shall be made of suitable corrosion resistant material (e.g. stainless steel, borosilicate glass, ceramic or titanium could be used; PTFE is only suitable for sample gas temperatures lower than 200°C).

3.2.2 Filter

The filter shall be made of an inert material (e.g. ceramic or sinter metal filter with an appropriate pore size). It shall be heated above the water or acid dew point. The particle filter shall be changed or cleaned periodically depending on the dust loading at the sampling site.

Note: Overloading of the particle filter may increase the pressure drop in the sampling line.

3.2.3 Sampling line

The sampling line shall be heated between the probe and the conditioning system. The sampling system shall be maintained at a temperature of at least 180°C and shall be at least 20°C higher than the dew point of the sample.

3.2.4 Sample cooler (Type A)

A dew point temperature of 4°C shall not be exceeded at the outlet of the sample cooler.

The performance of the cooler shall be verified annually with a flue gas of moisture content greater than 10% v/v.

Two approaches may be used:

i) The sample cooler outlet dew point temperature can be determined from the water content of the gas after it has passed through the sample cooler.

Note: Refer to Annex A in BS EN 14790⁶ – Stationary source emissions – Determination of water vapour in ducts

ii) The temperature at the outlet of the sample cooler shall be measured. It shall not exceed 4°C.

Note: The concentrations, provided by this sampling configuration, are given on dry basis.

3.2.5 Permeation drier (Type B)

A dew point temperature of 4°C shall not be exceeded at the outlet of the permeation drier.

The performance of the drier shall be verified annually with a flue gas of moisture content greater than 10% v/v.

Two approaches may be used:

i) The sample drier outlet dew point temperature can be determined from the water content of the gas after it has passed through the sample cooler.

Note: Refer to Annex A in BS EN 14790⁶ – Stationary source emissions – Determination of water vapour in ducts

ii) The temperature at the outlet of the sample cooler shall be measured. It shall not exceed 4°C.

Note: The concentrations, provided by this sampling configuration, are given on dry basis.

3.2.6 Heated system (Type C)

The sampling system and optical bench shall be maintained at a temperature of at least 180°C in order to avoid condensation.

3.2.7 Sample pump

When a pump is not an integral part of the system, an external pump is necessary to draw the flue gas through the apparatus. It shall be capable of operating to the specified flow requirements which are compatible with the flow and pressure requirements for the analyzer as specified by the manufacturer of the analyser. The pump shall be resistant to corrosion, and compatible with the requirements of the analyser to which it is connected.

Note: The quantity of sample gas required can vary between 15 l/h and 500 l/h, depending upon the analyser and the expected response time.

3.2.8 Secondary filter

The secondary filter is used to separate fine dust, with a pore size of 1µm to 2µm. For example it may be made of glass-fibre, sintered ceramic, stainless steel or PTFE-fibre.

3.2.9 Flow controller and flow meter

This apparatus sets the required flow. A corrosion resistant material shall be used. The sample flow rate into the instrument shall be maintained within the analyser manufacturer's requirements. A controlled pressure drop across restrictors is usually employed to maintain flow rate control into the analyser.

Note: No additional flow controller or flow meter is necessary when they are part of the analyser itself.

4 Monitoring systems

4.1 Monitoring systems and types of instrumental techniques to measure SO₂

The analytical techniques used to measure SO₂ may include, but are not restricted to, the following techniques:

- Electrochemical cells.
- Gas-Filter Correlation Non-dispersive Infrared (GFC-NDIR)
- Ultra-violet Absorption (UVA)
- Ultraviolet Fluorescence (UF)
- Fourier-Transform Infrared (FTIR)

This TGN does not prescribe the technique which the test laboratory must use; instead, this TGN specifies requirements based on performance criteria (Table 1), regardless of the technique used to measure SO₂. Therefore the instrumental systems used within the method described in this TGN shall meet the MCERTS performance standards⁷ for the appropriate determinands and ranges for CEMs. If the instrument is MCERTS certified, additional ranges may be verified against the performance standard criteria by the provision of data for linearity, zero drift, span drift, interference, effects of ambient temperature and detection limit. Such data must be verifiable, and demonstrate that the monitoring system meets the MCERTS performance standards for the additional ranges.

Test laboratories may not use alternative sampling systems to those which were tested and certified, unless the test laboratory can provide evidence to demonstrate that the instrumental systems still meet the MCERTS performance specifications, when used with the alternative sampling systems.

If the instrumental systems are not MCERTS certified, then the test laboratory shall demonstrate that the systems meet the MCERTS performance standards through individual testing of each instrumental system. The performance tests shall be performed by a test laboratory which is accredited to the applicable MCERTS performance standards specified in the *MCERTS Performance Standards and Test Procedures for Continuous Emission Monitoring Systems, Version 3*⁷. Section 5 of this TGN describes further the performance requirements for instrumental systems, when this TGN is used as a reference method.

4.2 Accreditation requirements and procedures

The test laboratory shall have documented procedures which apply the requirements of BS EN ISO/IEC 17025⁸, the MCERTS performance standards for organisations⁹, and the requirements of this TGN. If the test laboratory intends to use a FTIR monitoring systems within the method described in this TGN, then the test laboratory shall also have documented procedures to apply the requirements of an FTIR

standard, and be accredited to either ASTM 6348-3¹⁰ or a standard which provides an equivalent quality of data when using FTIR for emissions monitoring.

4.3 Pressure and temperature effects

The output signal of the analyser is proportional to the density of SO₂ (number of SO₂ molecules) present in the measurement cell of the instrument and depends on the absolute pressure and temperature in the absorption cell. The effects of variations of inlet pressure, atmospheric pressure and temperature shall be taken into account by the instrument.

4.4 Sampling pump for the analyser

The sampling pump can be separate or part of the analyser. In any case, it shall be capable of operating within the specified flow requirements of the manufacturer of the analyser and pressure conditions required for the measurement cell.

4.5 Interferences due to infrared or ultraviolet absorbing gases

Note: This section applies to monitoring systems which uses techniques based on spectroscopic absorption.

4.5.1 General

As various gases absorb electromagnetic radiation, interference from these gases can occur when their infrared absorption bands coincide or overlap the SO₂ absorption bands in analysers which use spectroscopic principles to measure SO₂. The degree of interference varies among individual spectroscopic analysers.

4.5.2 Water vapour

The primary interferent is water vapour, especially in infrared analysers. However, water vapour interference should be minimised by using sampling and conditioning systems A or B and using narrow-band optical filters.

4.5.3 Carbon dioxide

Interference may be caused by carbon dioxide. The potential effects of interference caused by carbon dioxide shall be known and included within the estimation of the uncertainty of the method. The test laboratory shall also take into account the known or expected concentrations of carbon dioxide in the source emissions.

Note: Test reports, such as those for MCERTS certification, include data on the effects of interference caused by carbon dioxide.

4.5.4 Other interferents

Hydrocarbons and nitrous oxide (N₂O) may interfere. The potential effects of these interferents shall be known and included within the estimation of the uncertainty of the method. The test laboratory shall also take into account the known or expected concentrations of these interferents in the source emissions.

Note: Test reports, such as those for MCERTS certification, include data on the effects of interferents.

5 Determination of the characteristics of the method: analyser, sampling and conditioning line

5.1 General

When this TGN is used as a reference method, the test laboratory shall demonstrate that:

- the performance characteristics of the method at least meet the performance criteria in Table 1, and,
- the expanded uncertainty calculated by combining values of standard uncertainties associated to the performance characteristics given in Table 1 is less than 10 % at the daily emission limit value, on dry basis and before correction to the O₂ reference concentration.

The values of the selected performance characteristics shall be evaluated by means of a laboratory test and a field test, unless the instrumental system being used is MCERTS-certified for a certified range appropriate for the intended applications. The field trial must be on a process that either reflects the conditions where the instrument will be used, or on a controlled, laboratory test-rig which can simulate field conditions.

If the monitoring system is not appropriately MCERTS certified, then the test laboratory shall provide evidence to show that the monitoring system meets the requirements in the MCERTS performance standards for CEMS⁷, and specified in BS EN/TS 14793¹¹, for the intended application.

This shall be achieved by:

- carrying out laboratory tests according to the requirements of the MCERTS performance standards and test-procedures for CEMS, to demonstrate that the instruments meet the performance requirements specified in Table 1; and
- carrying out field tests under BS EN ISO/IEC 17025 accreditation to compare the instrument against the CEN reference method; or using an appropriate test rig, under BS EN ISO/IEC 17025 accreditation, to compare the instrument against the reference method;

Note 1: A test rig, such as that provided by the National Physical Laboratory, would be suitable.

As a minimum, the test rig or field tests shall meet the requirements of BS EN/TS 14793.

The accredited method shall specify the types of process on which the instrument may be used.

Note 2: An instrument manufacturer may wish to have their instrument tested to show that it is suitable for use within this AM.

Note 3: A list of approved AM instruments will be provided by us.

Once the technique has been proven in the field the stack emission monitoring organisation shall demonstrate that **each** instrument they use meets the performance criteria specified by this TGN in Table 1.

Additionally, the test laboratory using this AM shall check the performance characteristics with a periodicity given in Table 3 (Section 7.2), regardless of whether the monitoring system is MCERTS certified or not.

5.2 Performance characteristics of the method and performance criteria

The uncertainty of the measured values by the method is not only influenced by the performance characteristics of the analyser itself but also by:

- the sampling line and conditioning system
- the site specific conditions
- the calibration gases used.

Table 1 gives an overview of the relevant performance characteristics and performance criteria, which shall be determined during laboratory and field tests according to the relevant CEN procedures, and indicates values included in the calculation of the overall uncertainty.

5.3 Establishing the uncertainty budget

The test laboratory shall establish an uncertainty budget to determine if the analyser and its associated sampling system fulfils the requirements for a maximum allowable overall uncertainty.

The expanded uncertainty for this method used as a reference shall be lower than 10% at the daily emission limit value. This expanded uncertainty is calculated on dry basis and before correction to the O₂ reference concentration.

The principle of calculation of the expanded uncertainty is based on the law on propagation of uncertainty laid down in ENV 13005¹²:

- Determine the standard uncertainties for each value included in the calculation of the budget uncertainty by means of laboratory and field tests, and according to ENV 13005.
- Calculate the uncertainty budget by combining all the standard uncertainties according to ENV 13005, including the uncertainty of the calibration gas and taking variations range of influence quantities and interferences of the specific site conditions into account. If these conditions are unknown, default values defined in Table 2 shall be applied. When corrections for residual water content in the flue gas are applied, the uncertainty attached to this correction shall be added to the uncertainty budget.
- Values of standard uncertainty that are less than 5% of the maximum standard uncertainty can be neglected.

Note: Annex A provides an example of an uncertainty determination.

Table 1 — Relevant performance characteristics of the AM

| Performance characteristics | Lab. Test for the analyser | Field test | Performance criterion ^a | Performance characteristic to be included in calculation of overall uncertainty |
|---|----------------------------|------------|------------------------------------|---|
| Response time | ✓ | ✓ | ≤ 200 s | |
| Detection limit | ✓ | | ≤±2.0% | ✓ |
| Lack of fit | ✓ | | ≤±2.0% | ✓ |
| Zero drift | ✓ | | ≤±2.0%/24 hours | ✓ |
| Span drift | ✓ | | ≤±2.0% /24 hours | ✓ |
| Sensitivity to atmospheric pressure | ✓ | | ≤±3.0% / 2 kPa | ✓ |
| Influence of sample gas pressure at span point, for a pressure change Δp of 3 kPa | ✓ | | ≤±2.0% ^b | ✓ |
| Sensitivity to ambient temperature | ✓ | | ≤±3.0% / 10 K | ✓ |
| Sensitivity to electric voltage | ✓ | | ≤±2.0% /10V | ✓ |
| Interferents ^c | ✓ | | ≤±4.0% | ✓ |
| Losses and leakage in the sampling line and conditioning system | | ✓ | ≤±5.0% | ✓ |
| Standard deviation of repeatability in laboratory at zero | ✓ | | ≤±1.0% | ✓ ^d |
| Standard deviation of repeatability in laboratory at span level | ✓ | | ≤±2.0% | ✓ ^d |

a The performance criterion is expressed as a percentage of the MCERTS certification range.

b The tested volume flow range or pressure is defined as a percentage value of the upper limit of the certification range.

c Interferents that shall be tested are at least those given in EN 15267-3

The value of max (algebraic sum of uncertainties producing positive effects on the result, sum of uncertainties producing negative effects) shall be compared with the performance criterion.

d Only one of these values shall be included in the calculation : the first possibility is to choose the repeatability standard deviation got from laboratory tests corresponding to the closest concentration to the actual concentration in stack, or the higher (relative) standard deviation of repeatability independently of the concentration measured in stack.

Table 2 — Default variation-ranges of influence quantities and interferences to be applied for the determination of the uncertainty budget

| Performance characteristic | Default variations range on site |
|--------------------------------|---|
| Atmospheric pressure | $\leq \pm 2$ kPa |
| Sample volume flow variation | In accordance with the manufacturer's recommendations |
| Ambient temperature | $\leq \pm 15$ °C |
| Electric voltage at span level | 230 V \pm 20V |
| CH ₄ | 57 mg.m ⁻³ |
| CO ₂ | 15% by volume |
| N ₂ O | 40 mg.m ⁻³ |
| Moisture | 1% by volume |

6 Field operation

6.1 Sampling location

The sampling locations shall meet the requirements of BS EN 15259¹³ and provide representative samples. In addition, the sampling location shall be chosen with regard to safety of the personnel, accessibility and availability of electrical power.

6.2 Sampling point

The gas samples measured need to be representative of the average conditions inside the waste gas duct. In most cases, a single sampling point situated one third to half the duct diameter. For larger ducts, this point can be situated closer to the sampling port but not less than one meter from the centre of the duct, to avoid any disturbance of the flow or concentration due to influences from the sampling port.

However, when a non-homogeneity of the flue gas is suspected, the user shall refer to the procedures described in BS EN 15259.

6.3 Choice of the measuring system

To choose an appropriate analyser, sampling line and conditioning unit, the following characteristics of flue gases shall be known before the field monitoring exercise :

- temperature of exhaust gases;
- flue gas moisture content;
- dust loading;
- the expected concentration range of SO₂ and emission limit values;
- the expected concentration of potentially interfering substances, including at least the components listed in BS EN 15267-3¹⁴.

The full scale of the selected analyser shall not be less than peak emission and not less than twice the short-term average ELV. Regardless of the full-scale range of the analyser, the test laboratory shall be able to demonstrate that the performance and resolution of the analyser is not compromised by the use of higher ranges.

Note: The performance of the analyser is compromised when the selected range means that the monitoring system no longer meets the MCERTS performance standards for the intended application. A typical and appropriate operating would not ordinarily exceed 300% of the ELV.

To avoid long response times, the sample line should be as short as possible. If necessary a bypass pump should be used. A heated filter appropriate to the dust loading shall be used.

Before conducting field measurements, the laboratory shall verify that the analyser is functioning in accordance with the required performance criteria fixed in this Standard, and that the sampling line and conditioning unit are in a good operational condition.

6.4 Setting of the analyser on site

6.4.1 General

The complete measuring system, the sampling line including the conditioning unit and the analyser, shall be connected according to the manufacturer's instructions. The probe is placed at the representative point(s) in the duct (see 8.2).

The conditioning unit, sampling probe, filter, connection tube and analyser shall be stabilised at the required temperature.

After pre-heating, the flow passing through the sampling system and the analyser shall be adjusted to the chosen flow rate to be used during measurement. This flow shall be maintained at a constant level as far as practicable, and not vary by more than $\pm 10\%$.

When the test laboratory has set up the monitoring system, the test laboratory shall check the monitoring system to ensure that it is functioning properly. The results of these checks shall fulfil the requirements and limitations as set out by the manufacturer of the instrument, as well as the requirements (given by this Standard). The test laboratory shall record compliance with the requirements of this Standard and shall note any instances where it does not comply. Any deviations from this Standard shall be justified.

Any data recording, data processing and telemetry system used in conjunction with the measuring system shall be checked for proper functioning. If any components are changed, then these checks shall be repeated. All checks shall be documented. Time resolution of the data recording system used to calculate the mean values shall be below or equal to one minute.

6.4.2 Preliminary zero and span check, and adjustments

(i) Zero gas

The zero gas shall be a gas containing no significant amount of SO₂ (For example, purified nitrogen or air).

(ii) Span gases

The span gases used to adjust the instrument shall have a certified concentration of SO₂. The uncertainty on the analytical certificate of the span gas shall be less than or equal to $\pm 2\%$ for SO₂.

When the analyser is used for regulatory purposes, the span gas shall have a known concentration of approximately the half hourly ELV, or 50% to 90% of the selected range of the analyser.

(iii) Zero and span procedure for the analyser

At the beginning of the measuring period, zero and span gases are supplied to the analyser directly, without passing through the sampling system. Adjustments are made until the correct zero and span gas values are given by the data sampling system:

- adjust the zero value;
- adjust the span;
- finally, check again zero to see if there is no significant changes (zero deviation lower than twice the repeatability at zero). If there is any problem, repeat the procedure;
- when applying the zero and span gases, measure the T_{90} response time, and then wait at least three times the T_{90} value before taking the readings for zero and span.

(iv) Zero and span procedure for the entire sampling system

- Supply zero and span gases through the sampling system at sampling probe, as close as possible to the nozzle (in front of the filter if possible);

Note: It may be necessary to use a t-piece between the test-gas cylinders and the probe, in order to avoid over-pressurizing the analyser.

- when applying the zero and span gases, measure the T_{90} response time, and then wait at least three times the T_{90} value before taking the readings for zero and span;
- differences between the readings obtained during the zero and span check of the analyser, and during this check, shall be lower than 2% for zero, and less than 5% for span;
- the differences in T_{90} response times for the zero and span procedures, between the analyser and sampling system, shall be used to calculate the lag time due to the sampling system.

6.4.3 Checking the sampling system – leak test

The zero and span procedure given in Section 6.4.2 (iv) shall be used to demonstrate there is no significant leakage in the sample line. Differences in the readings obtained during the adjustment of the analyser and during the check shall be lower than 2%.

The following procedure may also be applied to check there is no significant leakage in the sampling line:

- assemble the complete sampling system. Close the probe tip and switch on the pump. After reaching minimum pressure, read or measure the flow rate with an appropriate measuring device. The leak flow rate shall not exceed 2% of the expected sample gas flow rate used during measurement.

6.4.4 Zero and span checks after measurement

At the end of the measuring period and at least once a day, zero and span checks shall be performed at the inlet of the sampling system by supplying test gases. The information shall be documented. In case of deviation between checks after measurement and preliminary adjustments, values of deviation shall be indicated in the report.

If the span or zero drifts are bigger than 2 % of the span value, the test laboratory shall have a procedure to correct for the drift.

The drift of zero and span shall be lower than 5 % of the span value; otherwise, the results shall be rejected.

7 Ongoing quality assurance

7.1 Introduction

Quality assurance and control is critically important in order to ensure that the uncertainty of the measured values for SO₂ are kept within the stated limits during extended automatic monitoring periods in the field. This means that maintenance, as well as zero and span adjustment procedures shall be followed, as they are essential for obtaining accurate and traceable quality data.

7.2 Frequency of checks

Table 3 shows the minimum required frequency of checks. The laboratory shall implement the relevant Standards for determination of performance characteristics.

Table 3 — Frequency of checks as reference method

| Checks | Frequency | Action criteria |
|--|--|--|
| Cleaning or changing of particulate filters ^a at the sampling inlet and at the monitor inlet | Every campaign if needed ^a | |
| Regular maintenance of the monitoring system | As required by manufacturer | As required |
| Lack of fit | At least every year and after repair of the instrument | As required and when the lack of fit exceeds ±2% of the certification range. |
| ^a The particle filter shall be changed periodically depending on the dust loading at the sampling site. During this filter change the filter housing shall be cleaned. Overloading of the particle filter may increase the pressure drop and decrease the flow. | | |

8 Expression of results

When required the readings from the analyser are converted to concentrations using the appropriate calibration graph. The results are expressed in milligrams per cubic metre, or parts per million by volume, on dry basis at 273 K and 101.3 kPa.

9 Test report

If carrying out MCERTS accredited work the monitoring report shall be submitted in the report format specified in the MCERTS performance standards for Manual stack emission monitoring for organisations available from www.mcerts.net. The report shall also include specific requirements specified by this TGN, as follows:

| Glossary of terms and definitions | |
|--|--|
| Adjustment (of a measuring system) | Operation of bringing a measuring system into a state of performance suitable for its use. |
| Ambient temperature | Temperature of the air around the measuring system. |
| Continuous emission monitoring system (CEM) | Automatic measuring system producing a continuous output signal upon continuous interaction with the sample gas characteristics. |
| Calibration | <p>Statistical relationship between values of the measurand indicated by the measuring system (CEM) and the corresponding values given by the standard reference method (SRM) or Alternative Method (AM) used during the same period of time and giving a representative measurement on the same sampling plane.</p> <p>Note 1: The result of calibration permits to establish the relationship between the values of the SRM/AM and the AMS (calibration function).</p> <p>Note 2: Calibration in this context refers to the process of calibrating with a SRM/AM. The term calibration is also often used to describe the process of adjusting a CEM by use of test gases – this is not calibration as defined in this standard.</p> |
| Drift | <p>Difference between two zero (zero drift) or span readings (span drift) at the beginning and at the end of a measuring period.</p> <p>Note: This refers to the difference between two zero or two span readings. The zero and the span values would be mean values over a period of time and not based on single readings.</p> |
| Emission limit value (ELV) | Emission limit value according to EU Directives on the basis of 30 minutes, 1 hour or 1 day. |
| Influence quantity | <p>Quantity that is not the measurand but that affects the result of the measurement.</p> <p>Note examples of influence quantities are variations in ambient temperature, atmospheric pressure, the presence of interfering gases in the flue gas matrix, and the pressure of the gas sample.</p> |
| Interference | A negative or positive effect upon the response of the measuring system, due to a component of the sample that is not the measurand. |
| Lack of fit | <p>Systematic deviation within the range of application between the measurement result obtained by applying the calibration function to the observed response of the measuring system measuring test gases and the corresponding accepted value of such test gases.</p> <p>Note 1 lack of fit may be a function of the measurement result.</p> <p>Note 2 the expression “lack of fit” is often replaced in everyday language by “linearity” or “deviation from linearity”.</p> |
| Measurand | Particular quantity subject to measurement. |
| Measuring system | Complete set of measuring instruments and other equipment assembled to carry out specified measurements. |
| Performance characteristic | One of the quantities (described, for example, by values, tolerances, and ranges) assigned to equipment in order to define its performance. |

| Glossary of terms and definitions | |
|---|--|
| Repeatability in the laboratory | <p>Closeness of the agreement between the results of successive measurements of the same measurand carried out under the same conditions of measurement.</p> <p>Note 1 repeatability conditions include: the same measurement procedure; the same laboratory; the same measuring instrument, used under the same conditions; the same location, and repetition over a short period of time.</p> <p>Note 2 repeatability may be expressed quantitatively in terms of the dispersion characteristics of the results in this standard the repeatability is expressed as a value with a level of confidence of 95%. [vim 3.6].</p> |
| Repeatability in the field | <p>Closeness of the agreement between the results of simultaneous measurements of the same measurand carried out with two sets of equipment under the same conditions of measurement.</p> <p>Note 1 these conditions include:</p> <ul style="list-style-type: none"> ▪ The same measurement procedure ▪ Two sets of equipment, the performance of which fulfils the requirements of the reference method, used under the same conditions ▪ The same location ▪ Implemented by the same laboratory ▪ Typically calculated on short periods of time in order to avoid the effect of changes of influence parameters (e.g. 30 min) <p>Note 2 repeatability may be expressed quantitatively in terms of the dispersion characteristics of the results.</p> <p>In this standard the repeatability under field conditions is expressed as a value with a level of confidence of 95 %.</p> |
| residence time in the measuring system | the time period for the sampled gas to be transported from the inlet of the probe to the inlet of the measurement cell. |
| Response time | <p>Time interval between the instant when a stimulus is subjected to a specified abrupt change and the instant when the response reaches and remains within specified limits around its final steady value</p> <p>Note by convention time taken for the output signal to pass from 0 % to 90 % of the final change.</p> |
| Sampling location | Specific area close to the sampling plane where the measurement devices are set up. |
| Sampling plane | Plane normal to the centreline of the duct at the sampling position. |
| Sampling point | Specific position on a sampling line at which a sample is extracted. |
| Span gas | <p>Test gas used to adjust and check a specific point on the response line of the measuring system.</p> <p>Note: this concentration is often chosen around 80% of the upper limit of the range or around the emission limit value.</p> |
| Standard reference method (SRM) | Measurement method recognised by experts and taken as a reference by convention, which gives, or is presumed to give, the accepted reference value of the concentration of the measurand (3.10) to be measured. |
| Uncertainty | Parameter associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand. |
| Standard uncertainty, u | Uncertainty of the result of a measurement expressed as a standard deviation, u |

| Glossary of terms and definitions | |
|---|--|
| Expanded uncertainty, U | Quantity defining a level of confidence about the result of a measurement that may be expected to encompass a specific fraction of the distribution of values that could reasonably be attributed to a measurand. $U = k \cdot u$ Note: In this Standard, the expanded uncertainty is calculated with a coverage factor of $k=2$, and with a level of confidence of 95 %. |
| Combined uncertainty, u_c | Standard uncertainty u_c attached to the measurement result calculated by combination of several standard uncertainties according to GUM. |
| Overall uncertainty, U_c | Expanded combined standard uncertainty attached to the measurement result calculated according to GUM. $U_c = k \cdot u_c$ |
| Uncertainty budget | Calculation table combining all the sources of uncertainty according to ENV 13005 in order to calculate the overall uncertainty of the method at a specified value. |

Annex A: Example of an uncertainty determination

A1. Required data for the uncertainty determination

The uncertainty determination requires the following data:

- Site conditions, for aspects such as variations in voltage and ambient temperature (Table A.1).
- Performance characteristics, as specified in Table 1 of this standard. The characteristics are shown in Table A.2.

Table A.1: Examples of site specific conditions

| Specific conditions | Value |
|--|---------------------------------------|
| Type of process | Incineration |
| Daily average emission limit value (ELV) | 50 mg.m ⁻³ |
| 95% confidence interval specified by legislation | 20% |
| MCERTS certification range of the monitoring system | 0 to 75 mg.m ⁻³ |
| Measurement range of the monitoring system | 0 to 300 mg.m ⁻³ |
| Measurement technique | Infrared analyser with a sample drier |
| Conditions on the field | |
| Atmospheric pressure variation | 99-100 kPa |
| Sample pressure variation | 100 ± 5 kPa |
| Fluctuations of temperature inside the enclosure compared to calibration temperature | 283 to 308 K |
| Temperature during adjustments to the analyser | 285 K |
| Voltage variation | 93.5V to 121V, 110V nominal voltage |

The part of the combined standard uncertainty influenced by the performance characteristics is determined by use of Equation (A1) and summation of the relevant uncertainty contributions u_i specified in Table A.2:

$$u_c = \sqrt{\sum_{i=1}^N u_i^2} \quad \dots(A1)$$

The total expanded uncertainty U is determined using Equation (A2):

$$U = 1.96 u_c \quad \dots(A2)$$

In the above calculation, most the values of u_i for a parameter i will be determined from test data, where the probability distribution of values is rectangular for most parameters and a normal distribution for a few parameters. The factor 1.96 may only be used if the number of measurements to determine the uncertainty and the number of degrees of freedom is sufficiently high (for example in the case of rectangular distribution).

The standard uncertainties for each performance characteristic (in the case of rectangular distributions) are then calculated according to EN ISO 14956¹⁵ with Equation (A3):

Note: BS EN ISO 14956 is an application of ENV 13005.

$$u(x_i) = \sqrt{\frac{(x_{i,\max} - x_{i,\text{adj}})^2 + (x_{i,\min} - x_{i,\text{adj}}) \times (x_{i,\max} - x_{i,\text{adj}}) + (x_{i,\min} - x_{i,\text{adj}})^2}{3}} \quad \dots(\text{A3})$$

Where:

$x_{i,\min}$ is the minimum value of the influence quantity X_i during the measuring period;

$x_{i,\max}$ is the maximum value of the influence quantity X_i during the measuring period;

$x_{i,\text{adj}}$ is the value of the influence quantity X_i during the adjustment of the analyser.

Equation A3 will typically be used for calculating the uncertainty of influence factors such as voltage and temperature variations.

Equation (A3) can be simplified in the following three cases:

If the value $x_{i,\text{adj}}$ is at the centre of the interval bounded by the maximum value $x_{i,\max}$ and the minimum value $x_{i,\min}$ of all values x_i , then the standard uncertainty of the values x_i is given by Equation (A4):

$$u(x_i) = \frac{(x_{i,\max} - x_{i,\min})}{\sqrt{12}} \quad \dots(\text{A4})$$

If the absolute values of the measured deviation above and below the central value are equal (see equation (A5)), then the standard uncertainty of the values x_i is given by Equation (A6):

$$|x_{i,\max} - x_{i,\text{adj}}| = |x_{i,\min} - x_{i,\text{adj}}| = \Delta x_i \quad \dots(\text{A5})$$

$$u(x_i) = \frac{\Delta x_i}{\sqrt{3}} \quad \dots(\text{A6})$$

If the value of $x_{i,\text{adj}}$ is the same as either $x_{i,\min}$ or $x_{i,\max}$, then the standard uncertainty of the values x_i is given by Equation (A7):

$$u(x_i) = \frac{(x_{i,\max} - x_{i,\min})}{\sqrt{3}} \quad \dots(\text{A7})$$

The uncertainty contributions of most the performance characteristics will be determined using equation A7.

Table A.2: Performance characteristics

| Performance characteristics | Performance criteria, as a percentage of the certification range | Results laboratory and field tests |
|---|--|------------------------------------|
| Response time | ≤180s | 120s |
| Detection limit | ≤±2% | ±0.7% |
| Lack of fit | ≤±2% | ±0.7% |
| Zero drift | ≤±2% / 24 hours | ±0.01% /24h |
| Span drift | ≤ ±2 % / 24 hours | ± 1% /24h |
| Sensitivity to sample volume flow | ≤±1% | ±0.2%, 10 l/h |
| Sensitivity to atmospheric pressure | ≤±3% | ±0.8% |
| Sensitivity of ambient temperature | ≤±3% / 10K | ±1% /10K |
| Sensitivity of electric voltage at span level | ≤±2% /10V | ±1% /10V |
| Interferents | ≤±4% | ≤±1.4% |
| Losses and leaks in the sampling line | ≤±5% | ±1.2% |
| Standard deviation of repeatability in laboratory at zero | ≤0±2% | ±0.15% |
| Standard deviation of repeatability in laboratory at span level | ≤2±% | ±0.8% |
| Uncertainty of calibration gas | ≤±2% | ±2% |

A.2 Estimation of the combined uncertainty

The combined uncertainty before correction to the O₂ reference concentration is given by equation A8:

$$u_c = \sqrt{u_{\text{fit}}^2 + u_{0,\text{dr}}^2 + u_{s,\text{dr}}^2 + u_1^2 + u_{\text{spress}}^2 + u_{\text{apress}}^2 + u_{\text{temp}}^2 + u_{\text{volt}}^2 + u_{0,\text{r}}^2 + u_{s,\text{r}}^2 + u_l^2 + u_{\text{cal}}^2} \quad \dots(\text{A8})$$

$$u_c = \sqrt{(0.30)^2 + (0.004)^2 + (0.43)^2 + (0.61)^2 + (0.09)^2 + (0.34)^2 + (0.96)^2 + (0.63)^2 + (0.11)^2 + (0.6)^2 + (0.52)^2 + (0.87)^2}$$

$$\underline{u_c = 1.87 \text{ mg.m}^{-3}}$$

A.3 Estimation of the overall uncertainty

Overall uncertainty before correction:

$$U_c = 1.96 u_c$$

$$U_c = \pm 3.7 \text{ mg.m}^{-3}$$

$$U_{\text{req}} = 20 \% \text{ at emission limit value; i.e } 20\% \text{ of } 50 \text{ mg.m}^{-3}, = 10 \text{ mg.m}^{-3}.$$

Consequently: $U_c < U_{\text{req}}$.

All values of the performance characteristics obtained in the laboratory and field tests are comply with the requirements. Conclusion: the measurement method fulfils the requirements.

Table A.3: Results of uncertainty calculation

| Performance characteristic | Standard uncertainty | Value of standard uncertainty, mg.m ⁻³ |
|---|----------------------|--|
| Lack of fit | u_{fit} | $\frac{(0.7/100) \times 75}{\sqrt{3}} = 0.30$ |
| Zero drift | $u_{0,\text{dr}}$ | $\frac{(0.01/100) \times 75}{\sqrt{3}} = 0.004$ |
| Span drift | $u_{s,\text{dr}}$ | $\frac{(1/100) \times 75}{\sqrt{3}} = 0.43$ |
| Sensitivity to interference | U_I | $\frac{(1.4/100) \times 75}{\sqrt{3}} = 0.61$ |
| Sensitivity to sample volume flow | u_{spress} | $\frac{(0.2/100) \times 75}{\sqrt{3}} = 0.09$ |
| Sensitivity to atmospheric pressure | u_{apress} | $\frac{(0.8/100) \times 75}{\sqrt{3}} = 0.34$ |
| Sensitivity of ambient temperature | u_{temp} | $\frac{(1/100)}{10} \times 75 \times \sqrt{\frac{(308 - 285)^2 + (308 - 285)(283 - 285) + (283 - 285)^2}{3}} = 0.96$ |
| Sensitivity of electric voltage | u_{volt} | $\frac{(1/100)}{10} \times 75 \times \sqrt{\frac{(121 - 110)^2 + (93.5 - 110)(121 - 110) + (93.5 - 110)^2}{3}} = 0.63$ |
| Repeatability in laboratory at zero | $u_{0,r}$ | $(0.15/100) \times 75 = 0.11$ |
| Repeatability in laboratory at span level | $u_{s,r}$ | $(0.8/100) \times 75 = 0.6$ |
| Losses and leak in the sampling line | u_l | $\frac{(1.2/100) \times 75}{\sqrt{3}} = 0.52$ |
| Uncertainty of calibration gas | u_{cal} | $\frac{(2/100) \times 75}{\sqrt{3}} = 0.87$ |

Bibliography

1. BS EN 14791: 2005 Stationary source emissions – Determination of the mass concentration of sulphur dioxide.
2. BS EN 14181:2004, Stationary source emissions – Quality assurance of automated measuring systems.
3. Directive 2000/76/EC of on the incineration of waste.
4. Directive 2001/80/EC on the limitation of emissions of certain pollutants into the air from large combustion plants.
5. Directive 2008/1/EC concerning integrated pollution prevention and control.
6. BS EN 14790 : 2005 Stationary source emissions – Determination of water vapour in ducts.
7. MCERTS Performance Standards and Test Procedures for Continuous Emission Monitoring Systems. For gaseous, particulate and flow-rate monitoring systems, Version 3.1, July 2008. Environment Agency, www.mcerts.net .
8. BS EN ISO/IEC 17025:2005, General requirements for the competence of testing and calibration laboratories.
9. MCERTS Manual stack emission monitoring performance standard for organisations, Environment Agency, May 2007. Available from www.mcerts.net.
10. ASTM D6348-3: 2003 Standard Test Method for Determination of Gaseous Compounds by Extractive Direct Interface Fourier Transform Infrared (FTIR) Spectroscopy.
11. BS EN/TS 14793:2005, Stationary source emissions. Intralaboratory validation procedure for an alternative method compared to a reference method.
12. BS ENV 13005: 1999 Guide to the expression of uncertainty in measurement.
13. BS EN 15259: 2007, Air quality. Measurement of stationary source emissions. Measurement strategy, measurement planning, reporting and design of measurement sites.
14. EN 15267-3:2007, Air quality — Certification of automated measuring systems — Part 3: Performance criteria and test procedures for automated measuring systems for monitoring emissions from stationary sources.
15. BS EN ISO 14956: 2002 Air Quality – Evaluation of the suitability of a measurement method by comparison with a stated measurement uncertainty.