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VGB STATISTICAL GUIDELINES FOR EMISSIONS COMPLIANCE EVALUATION

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VGB STATISTICAL GUIDELINES FOR EMISSIONS COMPLIANCE EVALUATION

prepared for
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SUMMARY

The Large Combustion Plant Best Available Techniques (BAT) Reference document, the LCP BREF, defines Associated Emission Levels (BAT-AELs), for daily and annual averaging periods, as concentration ranges. The Competent Authority sets Emission Limit Values (ELVs) from within these BAT-AEL ranges. The IED specifies that the 95% Confidence Interval of a single measurement (hourly average) shall not exceed a defined percentage of the Daily ELV. Towards the lower end of the BAT-AEL concentration range, *there are concerns that the measurement uncertainty could be higher than required* when monitoring pollutants continuously using Automated Measuring Systems (AMS).

The IED requires validation of daily averages by subtraction of the specified Confidence Interval from the reportable hourly average concentration, to allow for measurement uncertainty, although the detailed methodology varies between Member States. Compliance is then typically assessed based on these validated averages for Hourly, Daily and Monthly ELVs, noting that there may only be a few hours of operation within a day or a few days of operation within a month. However, for annual BAT-AELs *it needs to be confirmed that it is acceptable to validate an annual average emission concentration using the IED Confidence Interval*, as suggested by the JRC Reference Report on Monitoring.

If the Confidence Interval is subtracted for some averaging periods, and not others, this makes it more difficult for Operators to manage emissions, on a day-to-day basis, against a background of increasingly intermittent operation and reduced annual generation. This was not envisaged by Operators when the LCP BREF was developed and could affect both operations and investment decisions.

There are two main reasons for applying Confidence Intervals when reporting annual average emission concentrations. The first is the question of legal certainty and this is crucially important for compliance assessment since it needs to be clear to both the Competent Authority and the Operator when permit conditions are breached. The second is to account for the *systematic* uncertainty that is applicable to annual average concentrations relating to AMS calibration.

AMS are subject to the CEN standard EN 14181 which defines three Quality Assurance Levels - QAL1 (certification), QAL2 (calibration) and QAL3 (control) - along with an Annual Surveillance Test (AST calibration check). Various QA assessments are based on the Confidence Interval at the Daily ELV concentration, referred to as the Maximum Permissible Uncertainty (MPU).

In order to address the compliance concerns outlined above, an example measurement uncertainty budget has been developed to describe the *systematic* uncertainty that is applicable to NO_x emissions from Combined Cycle Gas Turbines (CCGT), with reference to EN 14181. *Standard* uncertainty components are identified and then combined, using the usual Root Sum of Squares approach, then multiplied by a coverage factor of 2 to obtain the *expanded* uncertainty at 95% confidence. The uncertainty budget has been developed using conservative assumptions and tolerances that are already defined in CEN standards or national guidance. However, the full range of LCP BREF pollutants has been considered in the overall analysis.

QAL1 requires certification (type approval) of the AMS with an *expanded* uncertainty ≤ ¾ MPU. For this top-level assessment, and for simplicity, it is assumed that the AMS: fully conforms with the certification requirements; *random* uncertainties are insignificant across an annual period, and *systematic* uncertainties are fully accounted for within the QAL2 calibration. This also presumes that a suitable AMS can be specified for a given application, noting that there may be no qualifying AMS available at the bottom end of the BAT-AEL concentration ranges. The certification process is costly and time-consuming making it difficult for new monitoring technologies to gain market entry.

QAL2 requires calibration of the AMS by an accredited test laboratory, using a Standard Reference Method (SRM) as defined in a suite of CEN standards for the LCP BREF pollutants. The calibration is a straight-line calibration relationship developed from at least 15 pairs of AMS-SRM measurements, obtained across at least three days of operation. The scatter in the data is characterised by the standard deviation of the differences, s_D, between the calibrated AMS and the SRM, and this must be below a specified threshold in order to pass the ‘Variability’ test. However, this does not take account of *systematic* uncertainty associated with the SRM measurement and s_D, alone, is insufficient to describe the overall uncertainty, as also indicated by EN 14181. Ideally, the SRM uncertainty would be negligibly small when compared with the AMS uncertainty. This is patently not the case, as recognised by the JRC Reference Report.

SRM uncertainty It is insufficient to base the SRM uncertainty solely on the repeatability declared by an individual test laboratory. Inter-laboratory reproducibility dominates the overall method uncertainty declared within each SRM standard, e.g., maximum 5% for NO_x as a *standard* uncertainty. However, the actual uncertainty may be lower than the maximum value and it is difficult to robustly partition this method uncertainty into *random* and *systematic* components. It is therefore assumed that the residual SRM *systematic* uncertainty is half of the maximum SRM uncertainty, e.g., 2.5% for NO_x.

It should also be noted that the SRM relative uncertainty increases as the concentration decreases. For many pollutants, the bottom end of the BAT-AEL concentration range may result in a higher SRM uncertainty than is normally considered to be acceptable. Re-validation of SRM CEN standards at lower concentrations is therefore also required. However, the validation results from a number of standards have been re-analysed within this study and these indicate that SRM performance at low concentrations is better than has been commonly assumed for selected components, especially NO_x. In the case of low concentrations of CO, Dust, HCl and HF, the EN 14181 calibration procedures are lacking and require improvement, although this additional uncertainty has not been considered here.

Limits of Detection (LOD) and Quantification (LOQ) of the SRM also need to be considered since many Competent Authorities require these to be substantially lower than the ELV.

Positional uncertainty The AMS must also be located at a representative sampling position within the emissions measurement plane. However, deviations in concentration at the AMS sampling location are assumed to be corrected by the QAL2 calibration. EN 15259 specifies an approach for assessing the homogeneity of flue gases and, if the concentration distribution is deemed to be homogeneous, an SRM sample can then be extracted from any point in the measurement plane. It is therefore important that the residual positional uncertainty of the SRM is taken into account within the uncertainty budget unless the SRM already takes a grid average sample.

The positional *standard* uncertainty, as defined by EN 15259, depends on the pollutant species considered, whether or not an abatement system is installed, and the sampling location. Essentially, the closer the sample point to the source of the inhomogeneity (the combustion system or the abatement system) then the higher the positional uncertainty. This has been evaluated for a number of different power plant types in order to assess typical values.

For CCGT with stack sampling, the positional *standard* uncertainty for NO_x is generally low (circa 2% on average) but this rises to circa 5% when sampling at the gas turbine exhaust and this is assumed to be a reasonable default uncertainty contribution. The positional *standard* uncertainty for CO can be 5% or more, even when sampling from the stack, since the distribution of CO within the combustion system is much less uniform than for NO_x. Higher positional uncertainties are encountered for other pollutants emitted from solid fuel fired power plant fitted with abatement equipment.

AST requires at least five hourly average SRM readings to be taken across at least one day of operation by an accredited test laboratory. The main aim is to check that the QAL2 calibration remains valid, and a tolerance is defined beyond which the SRM results are not allowed to deviate. This tolerance represents an additional *systematic* uncertainty since the QAL2 calibration is effectively allowed to shift, year-on-year, within this tolerance, before requiring a repeat QAL2 calibration after five years. The 'Validity' test requires that the absolute mean value of the differences, between the SRM and the original QAL2 calibration line, is less than ½ MPU or 10% of the Daily ELV for NO_x. This could be as high as 24% of the NO_x Daily ELV if the maximum allowed value of s_D were also to be taken into account. However, s_D is often small and has been neglected in this study. A tolerance of 10% of the Daily ELV then gives rise to a *standard* uncertainty of about 5%.

A modest in-year shift of the calibration relationship could be caused by a number of factors, including: i) a change in the spatial variation of concentration across the measurement plane; ii) degradation in AMS performance not identified by QAL3 checks; iii) different ambient conditions, plant operating conditions and flue gas composition between the QAL2 and the AST test periods in addition to iv) the use of a different test laboratory and/or Alternative Method.

QAL3 is intended to provide an audited check of ongoing AMS performance by conducting regular (typically weekly) zero and span checks of the AMS and comparing the measured drift against pre-defined Warning and Action limits. For example, EN 14181 allows the Action limit to be set at 10% of the Daily ELV for NO_x. Whilst it may be reasonable to make some allowance for this drift tolerance in an uncertainty assessment, the normal condition of the AMS, when under control, is to exhibit *random* deviations only so this is not considered further.

Oxygen correction - the uncertainty in the peripheral measurements, used to correct the raw concentrations to reference conditions, needs to be taken into account when assessing the uncertainty of the reportable data. For the purposes of the CCGT assessment, only the O_2 correction is considered and this can be especially significant for gas turbines. A *standard* uncertainty of 0.15 %O_2 is assumed, resulting in a *standard* uncertainty in the NO_x correction of about 2.5%. This is a conservatively low assumption since the span gas uncertainty alone is about 0.1 %O_2.

Overall uncertainty - combining the SRM and positional *standard* uncertainties at the Daily ELV (2.5% and 5% respectively) with the AST and oxygen correction uncertainties (5% and 2.5% respectively) gives an overall *standard* uncertainty of 7.9%. The resultant *expanded* uncertainty is then 15.8%, at 95% confidence, at the NO_x Daily ELV for the CCGT example. In relation to the hourly average, this allows for an additional *expanded* uncertainty of about 12% of the Daily ELV for AMS *random* fluctuations. In relation to the Annual ELV concentration, since this is lower than the Daily BAT-AEL concentration, the relative *systematic expanded* uncertainty would then be close to 20% at the Annual ELV concentration. The same approach can be extended to other pollutants using the information provided within this report.

This example uncertainty budget, employing relatively conservative assumptions relating to *systematic* uncertainty contributions, demonstrates that it is entirely appropriate to apply the IED Confidence Interval to all reportable emissions, including annual emissions, and this provides both the necessary legal certainty for compliance assessment and simplicity with regards to plant operation. When it is not possible to achieve the required uncertainty at low concentrations then the adoption of a fixed absolute uncertainty is recommended, for each pollutant, as already specified in The Netherlands and France.

More specifically, it is recommended that the Annual ELV is used instead of the Daily ELV for AMS assessment since this is more representative of the typical emission concentration. It is also recommended that SRM single point sampling should always be from the same point within the stack, during QAL2 and AST test campaigns, to minimise the influence of positional uncertainty.

It is clear that a number of challenges remain in relation to minimising and assessing measurement uncertainty: i) re-validation of SRM standards and the development of new test methods with lower LOD/LOQ; ii) improved SRM uncertainty assessment methodologies; iii) certification of new AMS with improved sensitivity and discrimination between pollutants; iv) improved AMS calibration procedures at low concentration, especially for reactive trace gases and Dust (requiring improvements within EN 14181).

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NOMENCLATURE

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a	Gradient of linear fit
AEL	Associated Emission Level
AM	Alternative Method
AMS	Automated Measuring System
AST	Annual Surveillance Test
b	Offset of linear fit
BAT	Best Available Technique
BREF	Best Available Techniques Reference Document
C	Concentration
CCGT	Combined Cycle Gas Turbine
Cd	Cadmium
CEMS	Continuous Emissions Monitoring System
CH_2O	Formaldehyde
CH_4	Methane
CI	Confidence Interval
CLD	Chemiluminescence detector
CO	Carbon monoxide
CO_2	Carbon dioxide
D	Diameter
|D|	Validity test - average absolute difference
DAHS	Data Acquisition and Handling System
D-ELV	Daily Emission Limit Value
DLN	Dry Low NO_x
EC	Electrochemical
EfW	Energy from Waste
ELV	Emission Limit Value
EN	EuroNorm
EU	European Union
$F_{N-1;N-1;0.95}$	Critical value of the F-factor
FID	Flame Ionisation Detector
FGD	Flue Gas Desulphurisation
FTIR	Fourier Transform Infra-Red
GT	Gas Turbine
GUM	Guide to the expression of uncertainty in measurement
H_2O	Water
HCl	Hydrochloric acid
HF	Hydrofluoric acid
HFO	Heavy Fuel Oil
Hg	Mercury
IED	Industrial Emissions Directive
IR	Infra-Red
ISO	International Organisation for Standardisation
JRC	Joint Research Centre
LCP	Large Combustion Plant
k_v	Variability test value based on a X^2-test with a β value of 50% for N tests
LOD	Limit of Detection
LOQ	Limit of Quantification
MCERTS	Monitoring Certification Scheme
MPU	Maximum Permissible Uncertainty
MPU_{AMS}	Maximum Permissible Uncertainty of AMS [= 0.75 * MPU]
n	Number of paired measurements

N	Number of tests or grid points
NG	Natural Gas
NH_3	Ammonia
N_2O	Nitrous oxide
NO_x	Nitrogen Oxides (NO + NO_2), expressed as NO_2 equivalent
O_2	Oxygen
p	Number of participating laboratories
PCDD	Polychlorinated dibenzodioxins
PCDF	Polychlorinated dibenzofurans
PT	Proficiency testing
QA	Quality Assurance
QAL	Quality Assurance Level
ROM	Reference Report On Monitoring
RSS	Root sum of squares
s	Standard deviation
SCR	Selective Catalytic Reduction
SNCR	Selective Non-Catalytic Reduction
SO_2	Sulphur dioxide
SO_3	Sulphur trioxide
SRM	Standard Reference Method
$t_{0.95;N-1}$	Value of the t distribution for N-1 degrees of freedom at 95% confidence
TDL	Tuneable Diode Laser
TGN	Technical Guidance Note
Tl	Thallium
TOC	Total Organic Carbon
TVOC	Total Volatile Organic Carbon
u	*Standard* uncertainty
U	*Expanded* uncertainty
UK	United Kingdom
UV	Ultra-Violet

SUBSCRIPTS

D	Differences in parallel measurements
grid	Grid sample points
L	Inter-Laboratory
min	Minimum
pos	Positional
r	Repeatability
R	Reproducibility
ref	Reference sample point

SYMBOLS

σ_0	Uncertainty requirement derived from legislative requirements

1 BACKGROUND

1.1 Industrial Emissions Directive

In European legislation, the Industrial Emissions Directive (IED) defines Emission Limit Values (ELVs) for Large Combustion Plant (LCP) and also specifies the related emissions monitoring requirements [1]. The IED specifies Monthly, Daily and Hourly (95th Annual Percentile) ELVs. The IED regulated species are: nitrogen oxides (NO_x), sulphur dioxide (SO_2) and Dust for solid and liquid fuel fired power stations. NO_x and carbon monoxide (CO) are regulated for Combined Cycle Gas Turbines (CCGT) and gas fired boilers. ELVs are defined in mg/m^3, in the dry flue gas, at 273.15K and 101.3 kPa and at a process specific reference dry oxygen concentration (3% for gas and oil fired boilers, 6% for solid fuel fired boilers and 15 $\%O_2$ by volume for gas turbines and reciprocating engines).

For LCP, ELVs apply during normal operation only, excluding start-up and shut-down and periods of malfunction or breakdown of abatement equipment subject to defined time limits. For gas turbines, ELVs apply when operating above 70% of ISO base load. Start-up and shut-down requirements for LCP are defined in a separate EU Implementing Decision [2].

For Waste Incineration and Co-Incineration plant, here referred to as Energy from Waste plant (EfW), the additional species that are regulated with ELVs are hydrogen chloride (HCl), hydrogen fluoride (HF), total organic carbon (TOC), polychlorinated dibenzodioxins (PCDD), polychlorinated dibenzofurans (PCDF) and trace metals, including mercury (Hg). The O_2 reference concentration are 11% by volume for Waste Incineration and 6% for Co-Incineration.

Continuous Emissions Monitoring Systems (CEMS), also known as Automated Measuring Systems (AMS), are mandatory for LCP (NO_x, SO_2, CO and Dust) subject to various monitoring derogations that are based on plant size, remaining operating hours, and fuel type. For EfWs, continuous monitoring is additionally required for HCl, HF and TOC, although the Competent Authority may instead approve periodic monitoring of acid gases if it can be demonstrated that the ELVs can never be exceeded. Periodic monitoring is required for PCDD, PCDF and trace metals.

The IED requires that the sampling and analysis of pollutants, as well as the Quality Assurance (QA) of AMS - and the reference measurement methods used to calibrate those systems - shall be carried out in accordance with CEN standards[1]. The importance of measuring emissions at a representative sampling location is recognised within the IED which also requires the Competent Authority to *determine the location of the sampling or measurement points*[2].

The Data Acquisition and Handling Systems (DAHS) used for emissions reporting are subject to EN 17255-1 [3]. A valid hourly average is calculated when there is more than 40 minutes of valid CEMS data within the hour. The raw concentration data are first corrected to the given reference conditions. The valid daily average is calculated from the hourly averages when there are at least 6 hours of valid CEMS data within the day. For longer averaging periods, typically 10% data availability is required, e.g., 72 hours for a monthly average.

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[1] If CEN standards are not available, ISO, national or other international standards which ensure the provision of data of an equivalent scientific quality shall apply.

[2] In practice, the Competent Authority approves the Operator’s sampling arrangements which may not be ideal on existing plant due to historic design constraints.

In order to allow for measurement uncertainty, the IED specifies that the 95% Confidence Interval of a single measured result (hourly average) shall not exceed defined percentages of the Daily ELV, as specified in Annex V (LCP) and Annex VI (EfW) and shown in Table 1.

The difficulty of achieving 10% measurement uncertainty for CO is widely recognised and a Confidence Interval of 20% is often allowed for in-service Quality Assurance (QA) assessments [4]. Conversely, a higher Confidence Interval of 40% is specified in the IED for the more difficult to measure reactive species, e.g., HCl and HF, and this is adopted by TÜV when certifying Hg and NH_3 AMS.

Table 1: Confidence Intervals for IED regulated species

Species	Confidence Interval
NO_x	20%
SO_2	20%
CO	10%
Dust	30%
HCl	40%
HF	40%
TOC	40%

Compliance assessment is then based on validated emissions data, i.e., following subtraction of the specified Confidence Interval from the hourly average values with daily averages calculated from the hourly validated data.

However, the detailed implementation of data validation and compliance assessment varies between Member States. Considering the example of a plant with a Daily NO_x ELV of 50 mg/m^3, some Member States define the Confidence Interval (CI) as a fixed absolute value, derived from the Daily ELV, e.g., the CI is 10 mg/m^3 [= 50 mg/m^3 * 20% / 100%]. Others define the CI as a percentage of the valid hourly average, e.g., for an hourly average NO_x reading of 36 mg/m^3, the CI is 7.2 mg/m^3 [= 36 mg/m^3 * 20% / 100%]. Others employ a measurement uncertainty determined from stack testing as discussed later.

1.2 Large Combustion Plant BREF Document

Under the IED, all combustion plant with an aggregated thermal input ≥ 50 MW_{th} must comply with the specified general permitting requirements and are required to implement Best Available Techniques (BAT) for controlling emissions to air, as specified in Best Available Techniques (BAT) Reference documents (BREFs). Monitoring requirements, specific to each regulated industrial activity/sector, are defined within each BREF along with the required monitoring standards. Further general guidance on the monitoring of emissions to both air and water is provided in the Reference Report on Monitoring (ROM), prepared by the Joint Research Centre of the European Commission [5].

The LCP BREF [6] defines more stringent Associated Emission Levels (BAT-AELs) as summarised within BAT Conclusions which are published separately [7]. BAT-AEL concentration ranges vary by plant type, thermal input, plant age and annual operating hours. The Competent Authorities in each Member State must derive new ELVs from these BAT-AEL ranges[3]. For existing plant, compliance is then required within four years of publication of the BAT Conclusions (by 17 August 2021 for existing plant).

The LCP BREF specifies BAT-AELs for both annual and daily averaging periods so there is a difference in approach between the IED and the LCP BREF which is addressed in national legislation, e.g., the IED averaging periods may be retained with the addition of an Annual ELV (UK), or the Monthly ELV may be adapted to give the same environmental benefit as achieved with the Annual ELV (The Netherlands). For gas turbines, BAT-AELs apply when the Dry Low NO_x (DLN) system is ‘effective’ rather than above 70% of ISO base load, as defined in the IED, and this is also subject to national interpretation.

The LCP BREF also defines more stringent monitoring requirements and addresses a wider range of pollutants from: solid fuel fired plant (CO, HCl, HF, Hg and trace metals); gas or oil fired reciprocating engines (CH_4 and CH_2O or TVOC, respectively); and Selective Catalytic Reduction (SCR) or Selective Non-Catalytic Reduction (SNCR) NO_x abatement processes (NH_3 and SO_3). Note that Total Volatile Organic Carbon (TVOC) is equivalent to TOC.

Either continuous monitoring, using AMS, or periodic monitoring, using reference methods, is required dependent upon the pollutant species and the plant technology, size, age and annual operating hours, as defined in BAT Conclusion Number 4 (BAT 4). The required monitoring frequency is given in Table 2, grouped by pollutant type and fuel category. However, in all cases*, the monitoring frequency does not apply where plant operation would be for the sole purpose of performing an emission measurement*, e.g., for plant with limited, intermittent operation.

Table 2: LCP BREF monitoring requirements

Group	Species	Applies to	Frequency	Unless	Then
I IED pollutants	NO_x	All fuels	Continuous	Plant < 100 MWth and < 1500 h/yr operation	Periodic (6m)
	CO	All fuels	Continuous	Plant < 100 MWth and < 1500 h/yr operation	Periodic (6m)
	SO_2	Coal, Biomass, HFO, Gas Oil	Continuous	Plant < 100 MWth and < 1500 h/yr operation	Periodic (6m)
				Oil fired without SO_2 abatement	Periodic (3m)
	Dust	Coal, Biomass, HFO, Gas Oil	Continuous	Plant < 100 MWth and < 1500 h/yr operation	Periodic (6m)
II Acid gases	HCl	Coal	Periodic (3m)	Emissions are 'sufficiently stable'	Periodic (12m)
				Plant < 100 MWth and < 1500 h/yr operation	Periodic (6m)
		Biomass	Continuous	Emissions are 'sufficiently stable'	Periodic (6m)
				Plant < 100 MWth and < 1500 h/yr operation	Periodic (6m)
				Plant < 100 MWth and < 500 h/yr operation	Periodic (12m)
	HF	Coal	Periodic (3m)	Emissions are 'sufficiently stable'	Periodic (12m)
				Plant < 100 MWth and < 1500 h/yr operation	Periodic (6m)
		Biomass	Periodic (12m)	-	-
III Metals	Hg	Coal (≥ 300 MW_{th})	Continuous	Emissions are 'sufficiently stable'	Periodic (6m)
		Biomass	Periodic (12m)	Emissions are 'sufficiently stable'	No monitoring
	Trace metals	Coal, Biomass, HFO, Gas Oil	Periodic (12m)	Emissions are deemed insignificant	Less frequent
IV Unburnts	TVOC	HFO, Gas Oil (engines)	Periodic (6m)	Emissions are 'sufficiently stable'	Periodic (12m)
	CH_2O	NG (engines)	Periodic (12m)	-	-
	CH_4	NG (engines)	Periodic (12m)	-	-
V Abatement	NH_3	All fuels with SCR/SNCR	Continuous	Plant < 100 MWth and < 1500 h/yr operation	Periodic (6m)
				Emissions are 'sufficiently stable' (SCR only)	Periodic (12m)
	SO_3	All fuels with SCR	Periodic (12m)	-	-

NG = Natural Gas; HFO = Heavy Fuel Oil

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[3] IED Article 15.4 allows a site-specific derogation from BREF AELs, subject to a cost-benefit assessment that takes into account local factors. However, this assessment must be recorded in the permit and the Commission informed. In this case, the specified permit ELV cannot then be higher than the ELV given in Annex V of the IED.

Table 2 includes the provisions for reciprocating engines but excludes gasification and co-incineration plant and process fuels used within the Iron & Steel and Chemicals industries.

Regarding Group I pollutants in Table 2, i.e., the existing IED pollutants (NO_x, SO_2, CO and Dust), there are no derogations from continuous monitoring for the largest plant. However, depending on national interpretation, there may be flexibility with regards to CO which is subject to 'indicative' BAT-AELs only. In any case, smaller LCP (< 100 MW_{th}) with limited operation (< 1500 hours/year) may instead monitor periodically (typically every six months).

Group II pollutants, i.e., the acid gases HCl and HF, can be subject to a reduced monitoring frequency if the emissions are deemed to be 'sufficiently stable' by the national Competent Authority. For example, large biomass fired plant may monitor HCl every six months, rather than continuously, or large coal fired plant may reduce the periodic HCl monitoring frequency from 3 to 12 months. Again, there is latitude to reduce the monitoring frequency for small plant with low annual operating hours which have a lower environmental impact.

Group III pollutants include mercury and other trace metals. In the case of mercury, the monitoring frequency can again be reduced if the emissions are deemed to be 'sufficiently stable' by the national Competent Authority. In the case of trace metals, a BAT-AEL is not specified but annual monitoring is required unless the emissions are deemed to be insignificant by the national Competent Authority *based on an assessment of the relevance of the pollutant releases*.

Group IV pollutants are unburnt fuel species, or partial combustion products, that survive the combustion process and these are monitored periodically in the emissions from reciprocating engines only.

Group V pollutants are monitored when SCR or SNCR processes are used for NO_x abatement. BAT-AELs are specified for ammonia (NH_3) with similar provisions as above for reductions in monitoring frequency. BAT-AELs are not specified for sulphur trioxide (SO_3) emissions but an annual periodic measurement is nevertheless required, noting that a reference test method is not defined in BAT 4 for this species.

Peripheral measurements are required in order to correct the raw measured emission concentrations to standard reporting conditions. As a minimum, for dry gas concentration measurements, the oxygen content of the flue gas sample must be measured. For 'wet' gas concentration measurements, the water vapour content must also be measured for correction to the dry reporting condition. For in-situ or extractive Dust measurements, the flue gas temperature and pressure are additionally required. In order to report mass emissions of pollutants, the flue gas flow rate is also needed. Flow monitoring is not formally required under the IED but this is mandated by the LCP BREF as a process parameter (BAT 3).

Confidence Intervals for Hg and NH_3 are not yet standardised, although a value of 40% is typically assumed, as stated on TÜV certificates. Confidence Intervals and 'ELVs' are not yet standardised for oxygen (O_2) and water vapour (H_2O) although these are typically assumed to be 10% for O_2 and 30% for H_2O [4]. Surrogate Daily 'ELVs' are required when assessing AMS for O_2 and H_2O measurement and these are typically taken to be 21 %O_2 and 30 %H_2O [4].

However, BAT-AELs are applicable to annual averaging periods as well as, in some cases, daily averaging periods, raising a number of compliance issues.

1.3 European Emissions Monitoring Standards

The IED and the LCP BREF require the implementation of CEN standards for monitoring emissions to air, especially EN 14181 [8] which is supplemented by EN 13284-2 for Dust [9], EN 14884 for mercury [10] and EN ISO 16911-2 for flue gas flow rate [11]. CEMS are referred to as Automated Measuring Systems (AMS) within EN 14181 which specifies three Quality Assurance Levels relating to AMS certification (QAL1), on-site calibration using an accredited test laboratory (QAL2) and on-going control of the AMS (QAL3), which requires regular zero and span drift checks. The on-site QAL2 calibration is checked annually by an accredited test laboratory by means of an Annual Surveillance Test (AST).

Quality Assurance (QA) requirements are based on the Daily ELV. As the Daily ELV is lowered, under the LCP BREF, the QA requirements become more difficult to pass. The AMS performance tests are based upon the Maximum Permissible Uncertainty (MPU) which is equal to the IED Confidence Interval at the Daily ELV, e.g., for a Daily NO_x ELV of 50 mg/m^3, MPU = 10 mg/m^3 [= 50 mg/m^3 * 20% / 100%].

QAL1 requires an assessment of the suitability of the AMS. New analysers should be type tested, at a suitable certification range, under an appropriate certification scheme, e.g., TÜV or MCERTS, to the requirements of EN 15267-3 [12]. The certification range must be less than 2.5 * Daily ELV for LCP and less than 1.5 * Daily ELV for EfW plant. The monitoring equipment must also be located so that a representative reading can be obtained, as demonstrated by duct concentration surveys performed according to EN 15259 [13].

QAL2 requires calibration of the monitors against test methods - Standard Reference Methods (SRM) - as defined in a further suite of European standards and as applied by a test laboratory accredited to EN ISO 17025 [14]. The prescribed linear calibration relationship between the AMS and the SRM test data is established by taking at least 15 pairs of measurements obtained across at least 3 days of normal plant operation although, for Dust, a reduced number of tests may be carried out as long as the total test duration is ≥ 7.5 hours across three days and, for flue gas flow rate, the minimum time period is five hours across at least one day. Any scatter in the data comparison is assumed to be caused by the AMS[4] and this scatter (Variability) must be below a threshold, based on the Daily ELV, in order to pass the Variability test.

QAL3 is intended to provide an audited check of ongoing AMS performance by conducting regular zero and span checks, usually using reference gases, then comparing the measured drift against pre-defined warning and action limits using a control chart approach. The control chart limits may be based on the Daily ELV.

Annual Surveillance Tests are intended to validate the calibration established under QAL2 by, again, employing an accredited test laboratory to take a reduced number of parallel measurements during a single day of plant operation. The Variability test tolerance, applicable to the data scatter, is widened for the AST and an additional test compares the mean deviation of the new data from the original calibration line. This Validity test pass criterion is also based on the Daily ELV, as are the various functional tests that must be performed prior to either a QAL2 or an AST, e.g., linearity testing using reference gases.

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[4] EN 14181 § 6.7 refers to the need for the AMS to pass the variability test. § 6.6 states that the variability test shall be performed on the calibrated values of the AMS and § 6.2 explicitly states that the uncertainties in the peripheral parameters are attributed to the AMS. However, § 6.7 recognises that *the variability obtained includes uncertainty components associated with the repeatabilities of both the AMS and the SRM, but not the overall uncertainty of the SRM (therefore an imprecise implementation of the SRM can result in an apparent poorer variability of the AMS and could result in its false rejection during the variability test)*.

1.4 Measurement Uncertainty

The assessment of measurement uncertainty is a complex subject area. The JRC Reference Report on monitoring [5] provides a considerable body of background information and highlights that there are two fundamentally different approaches: i) a direct approach that evaluates all of the uncertainty contributions in one step, and ii) an indirect approach that considers each potential uncertainty contribution in detail prior to combining these to obtain the overall uncertainty. This is fully explained in the 'Guide to the expression of uncertainty in measurement' or GUM [15].

The building block for an indirect uncertainty assessment is the relative *standard* uncertainty which, for a given measured parameter, is equal to the standard deviation of the result divided by the mean value. Provided that each uncertainty component has an equal influence on the overall uncertainty, then *standard* uncertainties are combined by taking the square root of the sum of squares (RSS) of the individual components, according to the *law of propagation of uncertainty*. However, if there is not a linear relationship between the uncertainty of the parameter of interest and the component uncertainty, then the component uncertainty must first be multiplied by a sensitivity coefficient that accounts for the influence of that parameter on the calculated result.

The overall relative *expanded* uncertainty, at 95% confidence, is then obtained by multiplying the combined *standard* uncertainty by a coverage factor of 2, assuming a normal distribution for the dispersion of errors. For example, if the relative *standard* uncertainty is ± 3% for each of three *standard* uncertainty contributions that contribute proportionately to the final result, then the *expanded* uncertainty is: $2 * \sqrt{(3^2 + 3^2 + 3^2)}$, that is, ± 10.4% at 95% confidence.

When considering a tolerance or a bias, this must first be converted to a *standard* uncertainty, for use in the above analysis, by dividing by a suitable coverage factor. When the type of statistical distribution is unknown, a rectangular probability distribution can be assumed with a coverage factor of 1.732 ($\sqrt{3}$). The rectangular distribution simply implies that there is an equal probability of the actual value lying anywhere within the assumed tolerance or bias.

There are two types of uncertainty contribution that need to be considered: *random* and *systematic*. The relative importance of each type depends on the averaging period under consideration.

Random uncertainty components describe short term fluctuations about a mean value that can be either negative or positive. An example would be the performance of an AMS across an hourly period in which numerous factors that could affect the result are varying, such as ambient conditions, the AMS supply voltage and the pollutant concentration. Over a long period of time, these *random* fluctuations tend to be self-cancelling. For a defined number of measurements, N, the *random* uncertainty decreases by $\sqrt{N}$.

For an hourly *random* fluctuation, the uncertainty therefore reduces by about a factor of 5 ($\sqrt{24}$) across a day. However, it could be argued that influencing factors, such as ambient conditions, and the plant load conditions, vary more across the daily time-scale rather than within a single hour. For a daily *random* fluctuation, this also reduces by about a factor of 5 ($\sqrt{30}$) across a month. With regards to AMS performance, this is complicated by the fact that there may be intermittent plant operation with only a few operating hours per day or a few days per month.

Systematic uncertainty components describe underlying differences between the mean value and the 'true' value and these can be regarded as bias terms. An example would be the *systematic* uncertainty relating to sampling from a single point within a sampling plane where there is a spatial variation in concentration across that plane. *Systematic* uncertainties are inherent within the system of interest and do not reduce across a period of time. In fact, these elements may increase with time. Using the same example, the spatial variation across a sampling plane may change over a period of time due to changes in abatement system performance, for example.

2 INTRODUCTION

The LCP BREF defines BAT-AELs for annual averaging periods. The basis of compliance with Annual ELVs, if specified, needs to be clarified. The LCP BREF makes it clear that the annual average is determined from hourly averages[5]. The simplest approach is to continue to use validated hourly averages for determining the annual average emission concentration, having subtracted the applicable IED Confidence Interval, in line with the approach for reporting other averaging periods. This makes compliance assessment straight-forward for Operators and provides the necessary legal certainty.

However, it is often assumed that the uncertainty of the hourly average is considerably higher than for the annual average, which calls into question the appropriateness of applying the IED Confidence Intervals. This issue is relevant to all processes and fuel types, and is explored within this report, by reference to both *random* and *systematic* uncertainty components, prior to making industry recommendations. The example of NO_x emissions from Combined Cycle Gas Turbine (CCGT) plant is used throughout this report, but other species are also considered in some detail.

The other key question relates to the lower end of the BAT-AEL concentration range; there are concerns that the measurement uncertainty could be higher than required when monitoring pollutants continuously using Automated Measuring Systems (AMS).

3 CONFIDENCE INTERVALS FOR ANNUAL AVERAGING PERIODS

3.1 Main Issues

There are two main reasons for applying Confidence Intervals when reporting annual average emission concentrations. The first is the question of legal certainty which is crucially important for compliance assessment. The second is to account for the *systematic* uncertainty that is applicable to annual average concentrations. Both of these issues are considered individually below.

However, it is also important that a consistent and harmonised approach is adopted so that all Operators are regulated in the same way and that compliance management is straight-forward. If the Confidence Interval is subtracted from some averages and not others, this makes it more difficult to manage emissions on a day-to-day basis against a background of increasingly intermittent operation and reduced annual generation. This was not envisaged by Operators when the LCP BREF was developed and could affect operations and investment decisions.

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[5] BAT Conclusions, General Considerations

3.2 Legal Certainty

For regulatory purposes, it needs to be clear to both the Competent Authority and the Operator when permit conditions are breached. If there is an insufficient allowance for measurement uncertainty, this could give rise to legal challenges associated with both the general principles of compliance assessment and also the specific circumstances surrounding an individual breach.

The LCP BREF does not make recommendations concerning the application of Confidence Intervals or the assessment of measurement uncertainty, noting that the BAT-AEL concentrations are quoted without subtraction of the Confidence interval[6]. This aspect is devolved to the Competent Authorities in each Member State. However, information on the expected hourly average measurement uncertainty was collected during development of the LCP BREF and reported in Annex IV of the BREF[7] where this is related to the annual average concentrations.

Given that detailed instructions were not provided in the BREF questionnaire, and individual Operators are unlikely to be qualified to perform a full uncertainty assessment, it is perhaps unsurprising that the quoted uncertainties, related to the annual averages, lie within the IED Confidence Intervals of 20% for NO_x and SO_2 and 30% for Dust. Whilst the vast majority of returns indicated uncertainties below 15% for NO_x and SO_2, and 20% for Dust, the reported absolute uncertainties confirm that the assessments are fundamentally flawed. For instance, 25% of the plant reported Dust *expanded* uncertainties of ≤ 0.1 mg/m^3 which is both physically unrealistic and unachievable.

The scope of the JRC Reference Report on monitoring [5] specifically excludes '*assessing compliance with emission limit values*'[8]. However, the ROM does contain general information on measurement uncertainty and notes that, for compliance assessment, '*the expanded uncertainty may be taken into account for each measurement result or for the average before comparing the value(s) with the ELV given in a permit*'[9]. In this context, a summary of the IED Confidence Intervals is then presented. Employing the validated hourly average as the basis for reporting annual averages is not precluded: '*Based on these validated averages, other averages such as daily, monthly or yearly averages can be calculated and used for further assessment*'[10].

The JRC Reference Report also recognises the truism that the relative measurement uncertainty, expressed as a percentage of the measured value, increases with decreasing emission levels[9]. At very low concentrations, the relative uncertainty is very high and either cannot be assessed, when concentrations are below the Limit of Detection (LOD), or the uncertainty is considered to be unacceptably high, when below the Limit of Quantification (LOQ). Although the JRC Reference Report recommends that these factors are taken into account when evaluating monitoring data[11], this is evidently not the case in relation to the LCP BREF data analysis. It is also noted that the measurement uncertainties of peripheral

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[6] LCP BREF Section 1.3.9 Plant-specific data collection for the LCP sector. This section also notes that, when the validation process was not specified, valid data were back-calculated using default uncertainties corresponding to 2% for CO emissions, 3% for NO_X and SO_2 emissions, and 4% for Dust emissions. This implies a negative bias on AEL concentrations.

[7] LCP BREF Section 13.4

[8] JRC Reference Report Section 2 Scope

[9] JRC Reference Report, Section 3.4.4.3 Measurement uncertainty

[10] JRC Reference Report, Section 4.3.2.6 Data treatment

[11] JRC Reference Report, Section 3.4.4 Data treatment

measurements, required to convert raw concentrations to reference conditions, contribute to the measurement uncertainty of the individual pollutants[12].

In summary, there is no legal imperative, based on either the LCP BREF, or the JRC Reference Report on monitoring, that would preclude applying the IED Confidence Intervals when assessing compliance against Annual ELVs. In fact, the JRC Reference Report notes that annual averages can simply be produced from validated hourly averages[10].

3.3 Measurement Uncertainty

For annual averages, only *systematic* uncertainty contributions are important since it can be assumed that all truly *random* uncertainty components will dwindle into insignificance across an annual averaging period. However, for hourly averages, *random* uncertainties are significant and need to be included in the uncertainty budget.

A high-level assessment of *random* and *systematic* uncertainties, related to the QA process defined in EN 14181 [8], is given in the following sections. In particular, the *systematic* uncertainty associated with the QAL2 calibration of the AMS is explored in detail.

4 QAL1 (CERTIFICATION)

4.1 General Considerations

This section provides an overview of the main contributions to the uncertainty budget arising from the underlying AMS performance characteristics that are assessed during AMS certification/type-approval (QAL1).

QAL1 requires an assessment of the suitability of the AMS. Therefore, all new AMS must be certified (type-approved), with a suitable certification range, under a certification scheme that is acceptable to the Competent Authority, e.g., TÜV in Germany or MCERTS in the UK. AMS performance tests are defined in EN 15267-3 [12]. Not all EN 15267-3 performance characteristics contribute directly to the uncertainty budget, e.g., the AMS response time.

QAL1 certification (under EN 15267-3) requires the evaluation of two, nominally identical, AMS in the laboratory and in the field. In the laboratory, influencing parameters, such as AMS supply voltage, sample pressure and ambient conditions are varied across pre-determined ranges to determine their impact on AMS performance. The ranges are set to represent realistic deviations which the AMS may experience on-site. In the field, the two AMS are compared to each other over an extended period of time (at least three months) in order to determine the reproducibility of the measurements, i.e., the differences between the two tested AMS. The zero and span drift are also evaluated over this period. A QAL2 is also performed at the beginning and at the end of this endurance test so that the AMS are compared with an independent Standard Reference Method (SRM). EN 15276-3 defines performance criteria for both the laboratory and field testing from which uncertainty contributions can be defined.

EN 15267-3 requires that the total AMS *expanded* measurement uncertainty is ≤ 75% of MPU which is specified at the Daily ELV. This QAL1 uncertainty target is now referred to as MPU_{AMS} throughout this report. Using NO_x as an example, the Confidence Interval is 20% and MPU is therefore 0.20 * Daily ELV. For NO_x, MPU_{AMS} is therefore 0.15 * Daily ELV, i.e., the *expanded* uncertainty of the AMS must ≤ 15% of the Daily ELV. The absolute measurement uncertainty is

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[12] JRC Reference Report, Section 4.3.2.5.2 Specific considerations for continuous measurements

quoted on the certificate in concentration units. EN 15267-3 also requires that the certification range is ≤ 2.5 * Daily ELV for LCP and ≤ 1.5 * Daily ELV for EfW. In general terms, the lower the certification range, the better the AMS performance, although multiple certification ranges are often specified to demonstrate acceptable performance over a wider concentration range.

The AMS *expanded* uncertainty from the QAL1 certificate can be used to indicate the lowest Daily ELV with which the AMS could be used (in compliance with ≤ 75% of MPU). In some cases, the certification range requirement is closely aligned with the absolute uncertainty requirement, resulting in the same Daily ELV. In other cases, the certification range appears to be conservative and the absolute uncertainty indicates that the AMS may be suitable for compliance with a lower Daily ELV. This may be because the manufacturer chose to certify at a higher range than necessary in order to align with historic regulatory limits. Or in the case of CO_2, for example, for which there are no IED compliance requirements, a higher certification range may have been selected to cover a wide range of process applications. In other cases, the AMS may have struggled to pass a single performance characteristic at lower concentrations, requiring a higher certification range than indicated by the overall performance.

By considering the relevant performance criteria (following the approach given in EN 15267-3 Annex D) it is possible to better understand the *random* and *systematic* uncertainties that are associated with an AMS that achieves QAL1 certification, for the range of species regulated under the LCP BREF. Those characteristics that potentially depend on a fluctuating influencing quantity, such as ambient temperature or AMS supply voltage, are considered here to be *random*. Those characteristics that cause a measurement offset or bias, such as cross-interference from other species in the flue gas, are considered here to be *systematic*.

4.2 Maximum AMS Uncertainty

EN 15267-3 performance characteristics and acceptance criteria are summarised in Table 3 for an AMS based on extractive gas sampling, and these criteria can be used to produce a worst-case estimate of the intrinsic AMS uncertainty. It is important to note that certain performance criteria are defined as standard deviations of repeated measurements and others are defined as tolerances. AMS repeatability and reproducibility are given as the standard deviations of repeated measurements and these already represent *standard* uncertainties. The remaining performance characteristics are defined as maximum allowable deviations, e.g., the maximum deviation caused by cross-interference from other species within the flue gas matrix must be ≤ 4%. These criteria must first be adjusted to become a *standard* uncertainty estimate when producing an uncertainty budget.

Regarding these performance criteria, since deviations can be either positive or negative, the stated tolerances represent the half-interval of a rectangular probability distribution; the *standard* uncertainty contribution is then obtained by dividing each tolerance by a suitable coverage factor, usually 1.732 [= √3] based on a rectangular probability distribution (Section 1.4). Determination of the component uncertainties that are quoted on the QAL1 certificates are fully described in Annex D of EN 15267-3, based on EN ISO 14956 [16].

Not all of the performance characteristics defined in the main text of the standard are included in the uncertainty determination described in Annex D of the standard. For example, the influence of ambient temperature is measured at both the zero and span points but only the span result is included within the uncertainty budget since the drift tends to affect both zero and span readings in the same way.

The performance criteria in Table 3 are given as percentages of the upper limit of the certification range for all gases (except O_2) and for particulate matter (Dust). For Dust, the span repeatability criterion is instead defined as 5% of the Daily ELV in EN 15267-3; for comparison purposes, this has been converted to 2% of the certification range (the lowest possible value assuming that the certification range = 2.5 * Daily ELV). The performance criteria for O_2 are given as absolute values (%O_2) following the convention in EN 15267-3.

Each performance characteristic is categorised as being either a *systematic* or a *random* uncertainty in Table 3 and the coverage factor that is required to calculate the *standard* uncertainty contribution is also listed. Of course, the decision to describe a particular characteristic as either *random* or *systematic* is not always straight-forward. For example, the field zero and span drift are described as being *random* uncertainties in Table 3, assuming that the AMS remains under control according to QAL3. However, they could equally well be described as *systematic* uncertainties if the drift is considered to be monotonic (in one direction).

Table 3: EN 15267-3 performance criteria

No.	**Performance characteristic**	**Performance criterion (%)**			**Type of contribution**	**Coverage factor**
i		**Gases**	**Dust**	**O_2**		
1	Lack of fit	2.0	3.0	0.20	*Systematic*	1.732
2	Zero drift from field test	3.0	3.0	0.20	*Random*	1.732
3	Span drift from field test	3.0	3.0	0.20	*Random*	1.732
4	Influence of ambient temperature at span	5.0	5.0	0.50	*Random*	1.732
5	Influence of sample gas pressure	2.0	-	0.20	*Random*	1.732
6	Influence of sample gas flow	2.0	-	0.20	*Random*	1.732
7	Influence of supply voltage	2.0	2.0	0.20	*Random*	1.732
8	Cross-sensitivity (interference)	4.0	-	0.40	*Systematic*	1.732
9	Repeatability standard deviation at span	2.0	2.0	0.20	*Random*	1.000
10	Reproducibility standard deviation at span	3.3	3.3	0.20	*Systematic*	1.000
11	Reference material uncertainty	1.6	1.6	0.21	*Systematic*	1.960
	Random uncertainty components	4.3	4.0	0.39		
	Systematic uncertainty components	4.3	3.8	0.34		
	Combined *standard* uncertainty	**6.0**	**5.5**	**0.52**		
	Combined *expanded* uncertainty	**11.9**	**10.8**	**1.01**		

The criterion/tolerance associated with each performance characteristic is divided by the given coverage factor in order to obtain a *standard* uncertainty. As already noted, AMS repeatability and reproducibility are assigned a coverage factor of 1 since they already represent standard uncertainties. The combined uncertainties, at the bottom of the table, are calculated using a Root Sum of Squares (RSS) approach from these component contributions (i = 1 to 11) in the usual way (Section 1.4).

When performing an uncertainty calculation using measured AMS performance data, either the repeatability or reproducibility standard deviation is incorporated into the uncertainty budget, whichever is higher. Since the reproducibility criterion is higher than that for repeatability, the reproducibility criterion only is used in this uncertainty budget.

The *expanded* uncertainty of the reference material, e.g., span gas, that is used to make internal adjustments to the AMS, is assumed to be 2% of the span concentration, noting that it cannot be higher than 3% according to EN 15267-3. Assuming that the span concentration is 80% of the certification range (a maximum of 2 * Daily ELV) then the reference material *expanded* uncertainty becomes 1.6% [= 2% * 2.0 / 2.5] when referenced to the certification range. Although a coverage factor of √3 is specified in the Annex D example for SO_2, a coverage factor of 1.96 is assumed here since the uncertainty quoted by the gas manufacturer is usually stated to be at 95% confidence and is based on an assumed normal distribution. The relative *expanded* uncertainty for the O_2 reference material is assumed to be 1% at a reference concentration of 21 %O_2, equating to the absolute value of 0.21 %O_2 quoted in Table 3.

Not all of the performance characteristics listed in Table 3 for extractive gas analysers are applicable to in-situ cross-duct gas analysers but an additional performance criterion of 2% then applies to the *excursion of the measurement beam of in-situ AMS* (performance characteristic number 12 in Annex D). More surprisingly, this characteristic is not mentioned in relation to Dust AMS which are often in-situ cross-duct devices. Sample pressure is described as being more applicable to in-situ, rather than extractive, AMS but it is included in Table 3 since it is also listed in the Annex D example for an extractive SO_2 AMS.

Regarding the combined uncertainties at the bottom of Table 3. For gases, excepting O_2, the *random* and *systematic standard* uncertainty components are of similar magnitude and they are each about 4% of certification range. These components combine to give an overall *standard* uncertainty of about 6% (RSS approach) which gives an overall *expanded* uncertainty of about 12% of certification range when multiplied by a coverage factor of 2 (more accurately, 1.96).

The results are similar for Dust although it must be remembered that the QAL1 mostly assesses the measurement of an optical property of the particulate matter, such as scattered light intensity. The gravimetric calibration, in mg/m^3, is provided by the QAL2.

An additional uncertainty, associated with the NO_2 converter efficiency, is applicable to NO_x AMS (performance characteristic number 13 in Annex D). The converter efficiency must be ≥ 95% and this introduces a potential low bias into the NO_x measurement which is more difficult to incorporate into the uncertainty budget. The simplest approach is to assume that the converter efficiency is 97.5% ± 2.5% such that the additional *standard* uncertainty contribution is 1.44% [=2.5%/√3]. This increases the maximum *expanded* uncertainty of the NO_x measurement from 11.9% to 12.8% using the RSS approach. Additional uncertainties, applicable to TOC AMS, relating to oxygen synergy and the response factors for specific organic chemical groupings, are not considered further in this report.

The *expanded* uncertainties quoted in Table 3 are based on the certification range of the AMS. In theory, this range can be 2.5 * Daily ELV for combustion plant which would result in an increase of the maximum *expanded* uncertainty from 12% of the certified range to 30% of the Daily ELV. However, in practice, the AMS performance is generally better than the maximum tolerance and EN 15267-3 requires that the total AMS measurement uncertainty is ≤ 75% of MPU which is specified at the Daily ELV. From a practical point of view, the assessment in Table 3 can therefore be regarded as being the uncertainty at the Daily ELV, based on test tolerances. Whilst individual tolerances may be failed by specific AMS, certification is granted if the MPU_{AMS} is satisfied. It can therefore be assumed that MPU_{AMS} [= 0.75 * CI * D-ELV] represents the maximum *expanded* uncertainty for each species with similar contributions from both *random* and *systematic* influences.

The additional margin of 25% of MPU allows for "*the uncertainty contribution from the individual installation of the AMS … to pass the QAL2 and QAL3 of EN 14181 successfully"*. This includes the additional uncertainty associated with correction of the raw emission concentrations to reference conditions.

The results for O_2 in Table 3 appear to be reasonable at first sight but the impact of the O_2 uncertainty is process dependent because of the non-linearity of the correction of NO_x etc. from the measured O_2 concentration to the O_2 reference condition, as shown in Figure 1. For a gas fired boiler, an *expanded* uncertainty of 1 %O_2 gives rise to an additional *expanded* uncertainty of about 5% when correcting the NO_x to 3 %O_2. For a gas turbine, the same O_2 uncertainty of 1 %O_2 gives rise to an additional *expanded* uncertainty of about 20% when correcting the NO_x to 15 %O_2 which could cause the AMS to be non-compliant. This highlights the importance of having a good O_2 measurement for gas turbines.

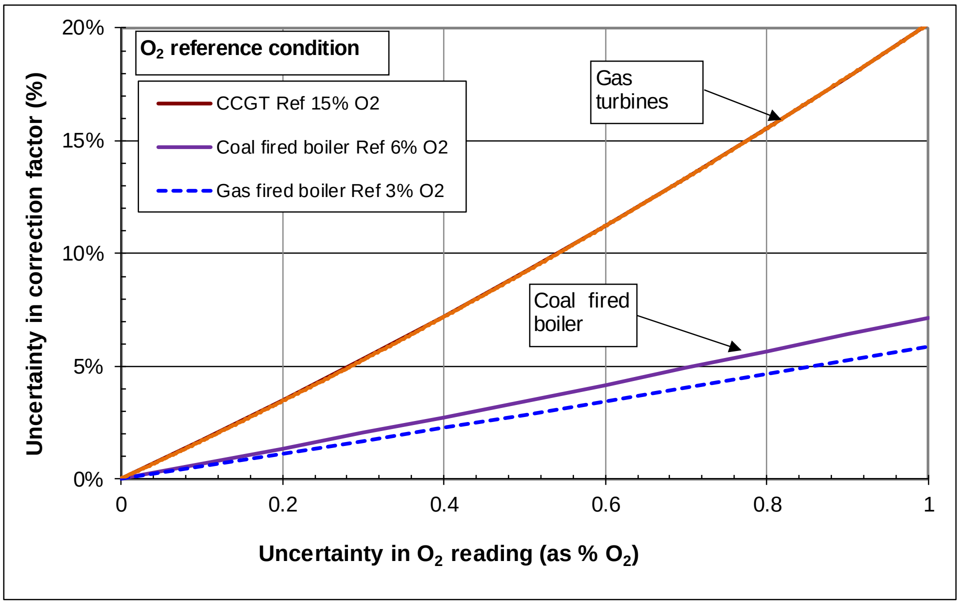

Figure 1: Influence of O_2 uncertainty on the O_2 correction

Conversely, for pollutants that are measured on a wet basis, the influence of the water vapour correction is linear and not so dependent on the process H_2O concentration, as shown in Figure 2. In this case, an uncertainty of 1 %H_2O gives rise to an uncertainty of approximately 1.1 to 1.5% in the water vapour correction, depending on the fuel type.

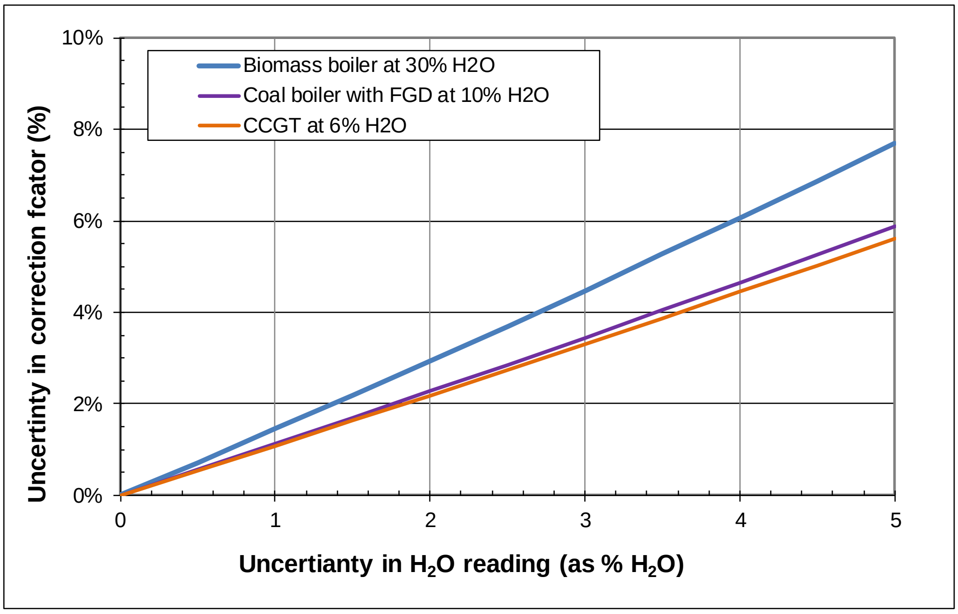

Figure 2: Influence of H_2O uncertainty on the H_2O correction

4.3 AMS Performance and Selection

In order to indicate how many certified AMS can meet the LCP BREF monitoring requirements, the overall absolute AMS uncertainties, taken from the AMS certificates, can be compared with the required MPU_{AMS} at the top and bottom of the BAT-AEL concentration ranges for the largest plant of each type[13]. This is illustrated in Figure 3, for NO_x, in which each data point represents the *expanded* uncertainty quoted on the AMS certificate. When the AMS measures NO separately, rather than total NO_x, the QAL1 uncertainties are first converted from $mgNO/m^3$ to $mgNO_2/m^3$.

The BAT-AEL concentration ranges, for different plant types, produce ranges of required MPU_{AMS} that are plotted as vertical lines in Figure 3. The ranges of AMS uncertainties are plotted as horizontal bars in Figure 3 for AMS of different technology types. This information is provided for all LCP BREF species in Appendix A for AMS certified before June 2018.

It can be seen that specific NO_x AMS, with UV or chemiluminescence detectors (CLD), are suitable for measuring across the full CCGT BAT-AEL concentration range. Other types of NO_x AMS are more suitable for monitoring at coal and biomass fired plant. However, this is simply an indication of AMS capability since, in individual cases, the AMS may not comply with the certification range requirements and, ultimately, re-certification at lower ranges may be required.

A similar analysis is shown for oxygen in Figure 4. In this case the Confidence Interval is assumed to be 10% but, as noted earlier, an ‘ELV’ is not specified in legislation and 21 $\%O_2$ is often specified. The impact of changing the ‘ELV’ on the MPU_{AMS} requirement is obvious in Figure 4. A high ‘ELV’ allows certification of AMS with a high uncertainty and some of the currently certified AMS are not suitable for measuring O_2 at gas turbine plant. An even higher ‘ELV’ of 25 $\%O_2$ is often used for certification purposes since this is the typical certification range. This means that an expanded uncertainty of 1.875 $\%O_2$ could be allowed [$MPU_{AMS} = 0.75 * 0.10 * 25\%$] and this is an unacceptably high threshold.

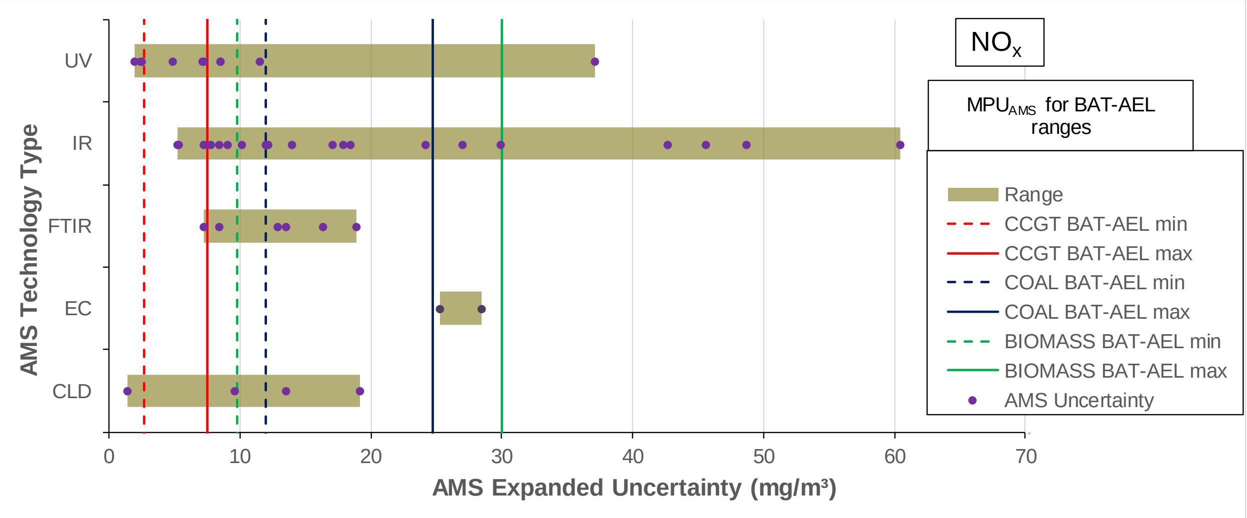

Figure 3: NO_x AMS performance by technology type

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[13] The BAT-AEL ranges considered here apply to CCGT plant ≥ 600 MW_{th}, coal plant ≥ 1000 MW_{th} and biomass plant ≥ 300 MW_{th}.

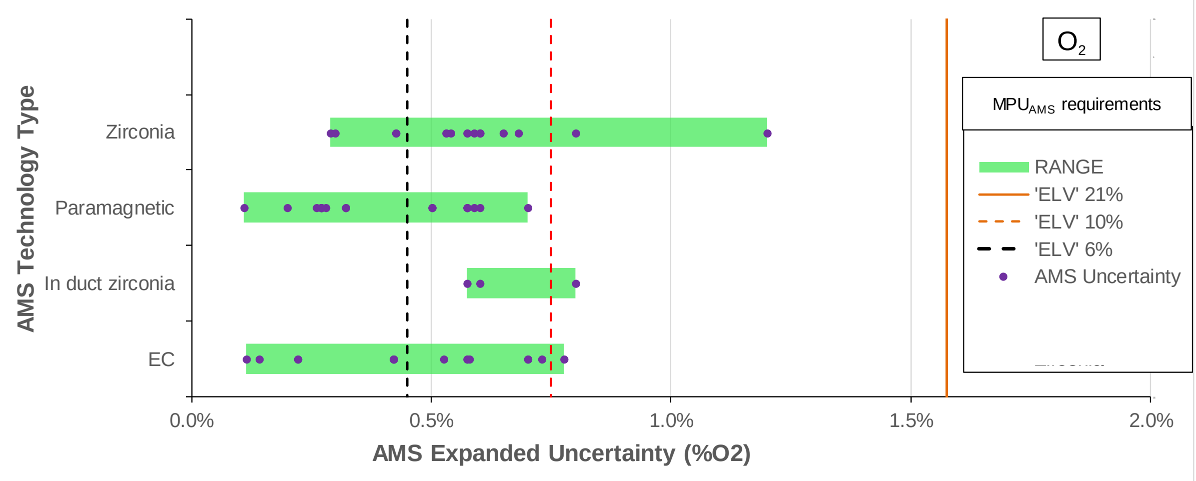

Figure 4: O_2 AMS performance by technology type

Indicative numbers of AMS, certified pre-June 2018, capable of meeting the MPU_{AMS} requirements, are provided in Table 4, for the full suite of LCP BREF pollutants, and the main points are summarised below (with further details given in Appendix A):

- Current CO AMS cannot comply with the bottom of the annual 'indicative' BAT-AEL range for CCGT plant and only one AMS can meet the requirements at the top of the BAT-AEL range[14]. However, since CO BAT-AELs are *indicative*, higher ELVs may be agreed with the Competent Authority in practice.
- Current SO_2 AMS cannot comply with the bottom of the BAT-AEL ranges for large biomass plant.
- Current HCl or TOC AMS cannot comply with the bottom of the BAT-AEL ranges for large coal or biomass plant.
- There are only two commercially available Hg AMS that can meet the BAT-AEL requirements.

Table 4: Number of AMS which meet MPU_{AMS} in the BAT-AEL ranges

Species	MPU_{AMS} (% D-ELV)	*Random* or *Systematic* U_{AMS} (% D-ELV)	Number of AMS which meet MPU_{AMS} at the minimum and maximum of the BAT-AEL ranges					
			CCGT		COAL		BIOMASS	
			Min	Max	Min	Max	Min	Max
NO_x	15%	10%	4	11	21	33	18	37
SO_2	15%	10%	N/A	N/A	3	37	0	39
Dust	22.5%	15%	N/A	N/A	12	22	6	22
CO*	7.5%	5%	0 (0)	1 (20)	0 (0)	28 (33)	1 (20)	24 (33)
Hg	30%	15%	N/A	N/A	2	2	2	2
HCl	30%	15%	N/A	N/A	0	12	0	15
NH_3	30%	15%	6	12	6	12	6	13
TOC	30%	15%	N/A	N/A	0	7	0	7
HF	30%	15%	N/A	N/A	5	8	5	5

*Results for a Confidence Interval of 20% are shown in parentheses

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[14] Some Competent Authorities allow a CI of 20% to be used for CO AMS assessment, i.e., MPU_{AMS} = 15% of Daily ELV. Even with this relaxation there are no AMS capable of meeting the MPU_{AMS} at the bottom of the CCGT BAT-AEL range, but 20 AMS could then meet the requirement at the top end of the CCGT BAT-AEL range.

4.4 QAL1 Discussion

When choosing AMS for Large Combustion Plant, the requirement for the certification range to be ≤ 2.5 * D-ELV generally gives a conservative selection since the actual AMS expanded uncertainty can be much lower than required. However, as ELVs are lowered under the LCP BREF, it is recommended, for existing AMS, that the AMS *expanded* uncertainty declared on the QAL1 certificate is always checked for compliance with $MPU_{AMS} \leq 0.75 * CI * D\text{-}ELV$. According to EN 14181, the Competent Authority may approve continued use of the AMS provided that the remaining QA requirements are passed (QAL2/AST and QAL3).

In some cases, the actual AMS uncertainty is close to this requirement and, in fact, specific criteria may have failed to pass when considering the applicable D-ELV proposed on the certificate. This may limit the scope of application of the AMS and the Operator should therefore always take care to check the detailed notes on the certificate.

In specific cases, there may not be suitable new AMS available based on the certification ranges and/or the AMS uncertainty. Certification of new AMS with improved sensitivity and discrimination between pollutants is required. However, the certification process is costly and time-consuming making it difficult for new monitoring technologies to gain market entry.

In situations when only an Annual ELV is specified, i.e., when there is no Daily ELV, the Annual ELV should be used for QA assessment. It also makes sense to use the Annual ELV for assessment when the Annual ELV is much lower than the Daily ELV since it follows that most daily averages will be lower than the Annual ELV in order to achieve annual compliance and the AMS must be suitable for measuring the lower concentrations.

For the purposes of generic uncertainty assessment, the worst-case AMS *expanded* uncertainty can be used [$MPU_{AMS} = 0.75 * CI * D\text{-}ELV$] as also shown in Table 4 as a percentage of the D-ELV. Based on inspection of the EN 15267-3 performance criteria, it can be assumed that the uncertainty is equally partitioned between *random* and *systematic* uncertainty contributions although this obviously varies somewhat between AMS. Using the same assumptions, the RSS approach can be used to back calculate the worst-case *random* and *systematic expanded* uncertainty contributions and these are approximately each equal to 0.5 * CI * D-ELV, also shown in Table 4 as a percentage of the D-ELV.

These estimates are useful when assessing the *random expanded* uncertainty of short-term emission averages. The above estimate of 0.5 * CI * D-ELV can be used for Hourly ELV assessment which would apply in the case of Annual 95th percentiles since the individual hourly averages are ranked in order of concentration value. Since the DAHS standard specifies that a minimum of six hours data is needed to calculate a daily average then the hourly *random* uncertainty can be divided by 2.5 [$\approx \sqrt{6}$] to give a worst-case *random expanded* uncertainty estimate of 0.2 * CI * D-ELV for Daily-ELV assessment. The *random* AMS uncertainty can be neglected in relation to long term averages.

In general terms, it can be assumed that the QAL1 *systematic* uncertainties are fully corrected by the QAL2 calibration. This is not strictly true since the plant emissions may change over time, and with plant load, such that the concentrations of the measured pollutant, and the background cross-interferents in the flue gas, may be different to those encountered during the original QAL2 calibration. This can lead to systematic deviations from the QAL2 calibration line. However, this aspect is addressed when considering the Annual Surveillance Test (AST) and, as a first approximation, the QAL1 *systematic* uncertainties are now neglected.

5 QAL2 (CALIBRATION)

5.1 General Considerations

QAL2 calibration is briefly described in Section 1.3. The AMS is calibrated using stack test data obtained using a Standard Reference Method (SRM) as applied by an accredited test laboratory. Prior to a QAL2 calibration, or an AST, various functional tests, such as linearity and response time of the AMS, must also be performed in order to demonstrate that the AMS performance remains acceptable when compared with the original QAL1 certification, noting that the functional test acceptance criteria are more relaxed than the QAL1 functional test criteria discussed previously (Section 4).

The straight-line calibration relationship is obtained by taking at least 15 pairs of measurements, from the AMS and the SRM, obtained across at least three days of operation. The aim is to obtain a wide range of concentrations during normal plant operation but this is not always possible due to operational and commercial constraints. The linear calibration relationship between the AMS and the SRM is described by: $y_i = a + bx_i$, where y_i is the calibrated raw AMS concentration, which then aligns with the SRM, and x_i is the ‘as measured’ raw AMS concentration. Perfect absolute agreement between the AMS and the SRM is indicated by a gradient of 1.0 and an offset of 0.0. However, the absolute agreement may be poor and there is no requirement to identify and correct the root cause of any absolute differences between the AMS and the SRM (which is assumed to be unbiased).

Assessment of the quality of the calibration is instead based upon the deviations between the individual data points and the calibration line which must be below a specified threshold in order to pass the QAL2 ‘Variability’ test:

$$s_D \leq \sigma_o * k_v$$

where s_D is the standard deviation of the differences between the SRM and the calibrated AMS test results, with AMS and SRM concentrations now corrected to reference conditions, and σ_o is the uncertainty requirement which is 50% of the Confidence Interval at the Daily ELV, i.e., MPU / 2. For example, σ_o is 10% of D-ELV for NO_x and SO_2 and 15% of D-ELV for Dust.

The statistical parameter, k_v, depends on the number of tests, N, as defined in Annex I of EN 14181. For 15 QAL2 tests, k_v is close to unity ($k_v = 0.9761$) and s_D must therefore be approximately ≤ 10% of the D-ELV for NO_x and SO_2. It can be seen that the Variability test becomes more difficult to pass as the D-ELV is lowered. Whilst the acceptance criterion is generous, EN 14181 recognises that an ‘imprecise’ implementation of the SRM can nevertheless lead to a failure of this test.

Regarding peripheral measurements, such as O_2, that are needed to correct the raw AMS calibrated result to reference conditions, EN 14181 recommends that a QAL2 is performed but this is not mandatory. The standard is unclear with regards to the application of the O_2 QAL2 factors when reporting emissions and when performing the Variability test for the main pollutants. In fact, an O_2 QAL2 should always be performed and the O_2 QAL2 factors should always be applied prior to performing both the data correction and the Variability test for the regulated pollutants. Not doing so would introduce an additional uncertainty that is not evaluated in this study.

Since the AMS is calibrated using the SRM, then the AMS is forced to align with the SRM for the subsequent five-year period. The quality of the SRM measurements is therefore of paramount importance since the SRM uncertainty will be transferred onto the AMS for that period of operation.

5.2 Maximum SRM Uncertainty

5.2.1 Required SRM Performance

The required performance characteristics of the European Standard Reference Methods are provided in a suite of SRM standards that are listed in Appendix B. Ideally, since the SRM is used to calibrate the AMS, the SRM uncertainty should be substantially lower than both the AMS and the IED uncertainty requirement [MPU = CI * D-ELV / 100%]. However, this is patently not the case. Relative maximum permissible SRM uncertainties (MPU_{SRM}) are defined in most of the SRM standards as a percentage of the D-ELV, as also summarised in the ROM [Table 3.3 in [5]] and reproduced in Table 5 below. These requirements apply to the raw concentration values prior to O_2 correction but on a dry gas basis.

The ROM does not specify an MPU_{SRM} value for HF but this is specified as 30% in the later publication of the HF SRM Technical Specification. The ROM does not specify an MPU_{SRM} value for Hg so this is assumed to be the same as for HCl and HF.

The ROM also gives the MPU_{SRM} for O_2 as 6 % (relative) or 0.3 %O_2 (absolute). The MPU_{SRM} value for H_2O is specified to be 20% (relative) and both the O_2 and H_2O requirements are given as a percentage of the measured value since there is no D-ELV specified for the peripherals.

Table 5: SRM *expanded* uncertainty requirements

Species	CI (% D-ELV)	MPU_{SRM} (% D-ELV)
NO_x	20%	10%
SO_2	20%	20%
CO	10%	6%
Dust	30%	20%
HCl	40%	30%
HF	40%	30%
Hg	40%	30%

The range in (MPU_{SRM} / CI) is from 0.5 (NO_x) to 1.0 (SO_2). The SO_2 requirement is an anomaly since there is no allowance for any additional uncertainty relating to the O_2 correction, for example. Although the MPU_{SRM} requirements are, to some extent, based on validation data, it would be helpful if the maximum MPU_{SRM} requirement could be harmonised to be the same as for the AMS, i.e., MPU_{SRM} = 0.75 * CI * D-ELV, whilst recognising that much lower uncertainties are preferred.

5.2.2 Historic SRM Performance

The original performance characteristics in the SRM standards are based on validation field trials and the subsequent statistical data analysis which is described in detail in ISO 5725. The method 'repeatability' is described by the standard deviation of repeated measurements conducted by a single test laboratory (s_r). The method 'reproducibility' is defined by the standard deviation of repeated measurements conducted by multiple test laboratories (s_R) and the overall method *expanded* uncertainty (U_R) is based on the reproducibility, i.e., $U_R \approx 2\ s_R$. The method uncertainty therefore describes the full dispersion of results that can be obtained by different test laboratories.

ISO 5725 makes it clear that the repeatability is dominated by *random* uncertainty components and the reproducibility is dominated by *systematic* uncertainty components, i.e., systematic differences between different test laboratories. The *systematic*, inter-laboratory standard deviation (s_L) is therefore obtained by subtracting the intra-laboratory repeatability s_r from the reproducibility s_R using the RSS approach: $s_L = \sqrt{}(s_R^2 - s_r^2)$.

With regards to QAL2 calibration, since at least 15 data points are obtained across at least three days of normal operation, any *random* uncertainty associated with the SRM will be reduced by a factor of 4 [$\approx \sqrt{}15$]. The residual *random* uncertainty is therefore given approximately by s_r / 4. However, any *systematic* uncertainty, given as a *standard* uncertainty by s_L, is transferred directly to the AMS via the QAL2 calibration.

The *expanded* uncertainty of the SRM, for each of the key LCP BREF pollutants, is reviewed in Appendix B where it is noted that the overall method *expanded* uncertainty, U_R, is dominated by the inter-laboratory *systematic* uncertainties. It would therefore reasonable to use the overall SRM *expanded* uncertainty, U_R, to be an estimate of the *systematic expanded* uncertainty of an hourly average value.

In Appendix B, the results of the original validation field trials are plotted as the relative *expanded* uncertainty U_R (%), as a function of concentration C (mg/m^3). The relative uncertainty increases substantially as the concentration falls, as expected, such that it is not possible to meet the specified relative uncertainty requirements at very low concentrations.

For the gaseous IED pollutants (NO_x, SO_2 and CO), detailed field validations were undertaken and linear functions were derived for the absolute uncertainty U_R (mg/m^3) as a function of concentration: $U_R = a + bC$. In the case of SO_2, the combined result for both of the specified analytical methods is considered here with further details given in Appendix B. A similar approach has been used to derive linear functions for Dust, HCl and Hg, based on much more limited validation data. In the case of HF, there is no method validation data, although s_R is specified in relation to the analysis of impinger solutions by the analytical laboratory. Estimates based on plant mass balance data are therefore used for HF in Appendix B.

With regards to the BAT-AEL concentration ranges, the ability of the SRMs to meet the MPU_{SRM} requirements is shown in Table 6 for each species. It is clear that, based on the stated historic field trial performance, the SRMs cannot meet the requirements at the minimum concentrations from the BAT-AEL ranges for Large Combustion Plant. At the maximum concentrations from the BAT-AEL ranges, the requirements can be comfortably achieved for NO_x, SO_2 and HCl and the final column in Table 6 shows the minimum D-ELVs that could be specified in these cases whilst still meeting MPU_{SRM} (from a monitoring perspective).

For CO and for HF, MPU_{SRM} cannot be achieved at the maximum BAT-AEL concentrations but the result is within the specified Confidence Interval. The final column in Table 6 shows that the minimum D-ELV is higher than the BAT-AEL range in order to meet MPU_{SRM}. However, current CO method performance is better than indicated by the standard as discussed in Appendix B.

For Hg, MPU_{SRM} cannot be achieved at the maximum BAT-AEL concentration and the uncertainty is higher than the specified Confidence Interval. The D-ELV would need to be increased to about 8 µg/m^3 in order to meet MPU$_{SRM}$. However, current method performance is better than indicated by the standard as discussed in Appendix B.

For Dust, the method uncertainty based upon limited validation data is so high that MPU$_{SRM}$ can never be achieved. However, the validation tests were limited to 30 minute sampling duration and it was noted that the results were dependent upon the flue gas conditions. When the gas temperature is above the dew point of the flue gas, the LOD is approximately 0.3 mg/m^3. When the gas temperature is at or below the dew point, the LOD increases to approximately 2.0 mg/m^3.

Table 6: SRM capability in relation to BAT-AEL ranges

			BAT-AEL		Linear U at BAT-AEL		Min D-ELV (mg/m^3)
Species	**CI (% D-ELV)**	**MPU$_{SRM}$ (% D-ELV)**	**Min (mg/m^3)**	**Max (mg/m^3)**	**Min MPU$_{SRM}$ (% D-ELV)**	**Max MPU$_{SRM}$ (% D-ELV)**	
NO$_x$	20%	10%	15	165	33%	6%	71
SO$_2$	20%	20%	25	165	26%	17%	55
CO	10%	6%	5	100	147%	10%	232
Dust	30%	20%	3	11	*69%*	*60%*	-
HCl	40%	30%	1	4	*67%*	21%	2.5
HF	40%	30%	1	3	*64%*	*32%*	3.4
Hg	40%	30%	0.001	0.004	*191%*	*53%*	*0.0081*

However, in Appendix B, it is shown that the linear relationships developed in the standards are inappropriate when describing the relative uncertainty at low concentrations. A power law fit better describes the relationship between relative uncertainty and concentration: $U_R = bC^{-a}$. This is well understood within the analytical chemistry field in which such relationships are used to quality assure analytical test laboratory performance [17]. For the gaseous IED LCP pollutants (NO$_x$, SO$_2$ and CO), a power law fit to the extensive validation data produces lower uncertainties as shown in Table 7.

Table 7: Revised SRM capability assessment for IED pollutants

			BAT-AEL		Power Law U at BAT-AEL		
Species	**CI (% D-ELV)**	**MPU$_{SRM}$ (% D-ELV)**	**Min (mg/m^3)**	**Max (mg/m^3)**	**Min MPU$_{SRM}$ (% D-ELV)**	**Max MPU$_{SRM}$ (% D-ELV)**	**Min D-ELV (mg/m^3)**
NO$_x$	20%	10%	15	165	13%	5%	33
SO$_2$	20%	20%	25	165	24%	16%	53
CO	10%	6%	5	100	84%	9%	167
Dust	30%	20%	3	11	*33%*	*9%*	5

As always, CO is problematic since the IED Confidence Interval is too constraining. However, the minimum D-ELVs, at which MPU$_{SRM}$ is achieved, are reduced substantially in all cases. The SRM performance for both NO$_x$ and SO$_2$ at the minimum BAT-AEL is still somewhat higher than required but the minimum D-ELVs are about 30 mg/m^3 for NO$_x$ and about 50 mg/m^3 for SO$_2$.

The Dust SRM performance is more problematic. The Dust SRM standard specifies an *expanded* uncertainty target of 20% at 5 mg/m^3, based on extended sampling, and this has been used to define the SRM performance in Table 7. Of course, the minimum D-ELV is then 5 mg/m^3, even though this may be too low for the uncertainty target to be met in specific process applications.

This analysis partly contradicts the results from an INERIS study which concluded that the minimum Daily ELVs, from a monitoring perspective, should be 75 mg/m^3 for NO_x, 150 mg/m^3 for SO_2, 120 mg/m^3 for CO and 50 mg/m^3 for Dust with regards to EfW plant [18]. That study was based on the results from multiple test laboratories taking part in an annual proficiency testing (PT) scheme. The INERIS study correctly highlights the importance of considering *systematic* uncertainty contributions and also highlights that the relative uncertainty increases with decreasing concentration.

It is possible that the higher uncertainties reported by INERIS are, in part, due to the greater number of test laboratories participating in the PT scheme. However, the study was criticised by the regulatory community on the grounds that i) there was insufficient focus on calibration at the lowest concentration ranges and ii) there was insufficient investigation of the failure to meet the specified uncertainty requirements. Under normal circumstances, participants failing a PT test would be expected to make improvements in order to pass on re-testing.

Although the overall SRM uncertainty is dominated by systematic uncertainty components, as discussed above, it is now conservatively assumed that 50% of the maximum method uncertainty is a reasonable estimate when considering the SRM contribution to the overall uncertainty budget. This allows for better current performance of the method in the field.

However, it needs to be recognised that it may not be possible to achieve the required uncertainties at low concentrations and the use of fixed absolute uncertainties may then be a suitable approach as already allowed in The Netherlands (see Appendix B) and France.

5.3 Positional Uncertainty

Obtaining a representative sample of flue gas is critically important for both the AMS and the Standard Reference Method (SRM) that is used to calibrate the AMS. Deviation at the AMS sampling location is assumed to be corrected by the QAL2 calibration provided that the SRM sampling location is fully representative.

EN 15259 [13] specifies an approach for assessing the homogeneity of flue gases across a measurement plane. The standard deviation of the spatially varying concentration measured across, typically 20, traverse points in a large duct, s_{grid}, is compared with the standard deviation of the time-dependent concentration measured simultaneously at a fixed reference point, s_{ref}. The quantity s_{grid} nominally describes the spatial variation across the measurement plane but also incorporates the temporal variations that are measured at the fixed reference point, s_{ref} which, in turn, is influenced by time-dependent process fluctuations. If the concentration distribution is deemed to be homogeneous, an SRM sample can be extracted from any point within the measurement plane. It is therefore important that the residual positional uncertainty of the SRM is taken into account within the uncertainty budget in situations when the SRM employs single point sampling.

Because the EN 15259 acceptance criterion is based on the relationship between spatial and temporal deviations, rather than specifying an absolute spatial deviation, a false FAIL is possible when both the spatial and temporal (process) variations are very low. This is often the case at Combined Cycle Gas Turbine (CGGT) plant, requiring additional guidance to address this issue. In England, the Environment Agency considers the location to be homogeneous when $s_{grid} < 5\%$ of the Daily ELV and $s_{grid} < 0.3\ \%O_2$ [19].

The magnitude of the positional *standard* uncertainty defined by EN 15259 [$s_{pos} = \sqrt{(s_{grid}^2 - s_{ref}^2)}$] depends on the pollutant species considered, whether or not an abatement system is installed and the sampling location. Essentially, the closer the sample point to the source of the inhomogeneity (the combustion system or the abatement system) then the higher the positional uncertainty. EN 15259 results have therefore been evaluated for a number of different plant types in order to assess typical values of the positional uncertainty. It should be noted that s_{pos} cannot be evaluated when $s_{ref} > s_{grid}$. In this situation, it is possible to correct the spatial variation for temporal and oxygen variations, giving a direct estimate of the positional uncertainty, $s_{grid,t}$, as described in Appendix C.

For CCGT with stack sampling, the positional *standard* uncertainty for NO_x is generally low (circa 2%) but this rises to circa 5% when sampling at the gas turbine exhaust (upstream of the Heat Recovery Steam Generator). This is illustrated in Figure 5 in which both s_{pos} and $s_{grid,t}$ are plotted for 15 CCGT units. However, the positional *standard* uncertainty for CO can be 5% or more, even when sampling at the stack, since the distribution of CO within the combustion system is much less uniform than for NO_x.

For coal fired power plant with Flue Gas Desulphurisation (FGD), the positional *standard* uncertainty for SO_2 is generally higher than for NO_x since the sample point is closer to the source of the inhomogeneity (the FGD unit). In this case, the positional uncertainty is circa 5% on average but it can be much higher, even when EN 15259 indicates that the sample plane is ‘homogeneous’. This is illustrated in Figure 6 in which both s_{pos} and $s_{grid,t}$ are plotted for 13 coal fired units.

For the purposes of this assessment, an SRM positional *standard* uncertainty of 5% of the Daily ELV is therefore assumed, in line with UK Environment Agency guidance for CCGT [19]. This does not consider the positional uncertainty allowed for the oxygen measurement ($0.3\ \%O_2$), which could give rise to a further 5% uncertainty contribution when reporting NO_x emissions from a CCGT. This contribution has been neglected within this assessment since the oxygen variation is generally low for a CCGT and the NO_x and O_2 spatial distributions are likely to be inter-dependent.

It should be noted that residual SRM positional uncertainty, which introduces a *systematic* uncertainty into the AMS calibration, can be higher for other plant types, as described in Appendix C, but this can be assumed to be negligible when the SRM is implemented as a grid measurement.

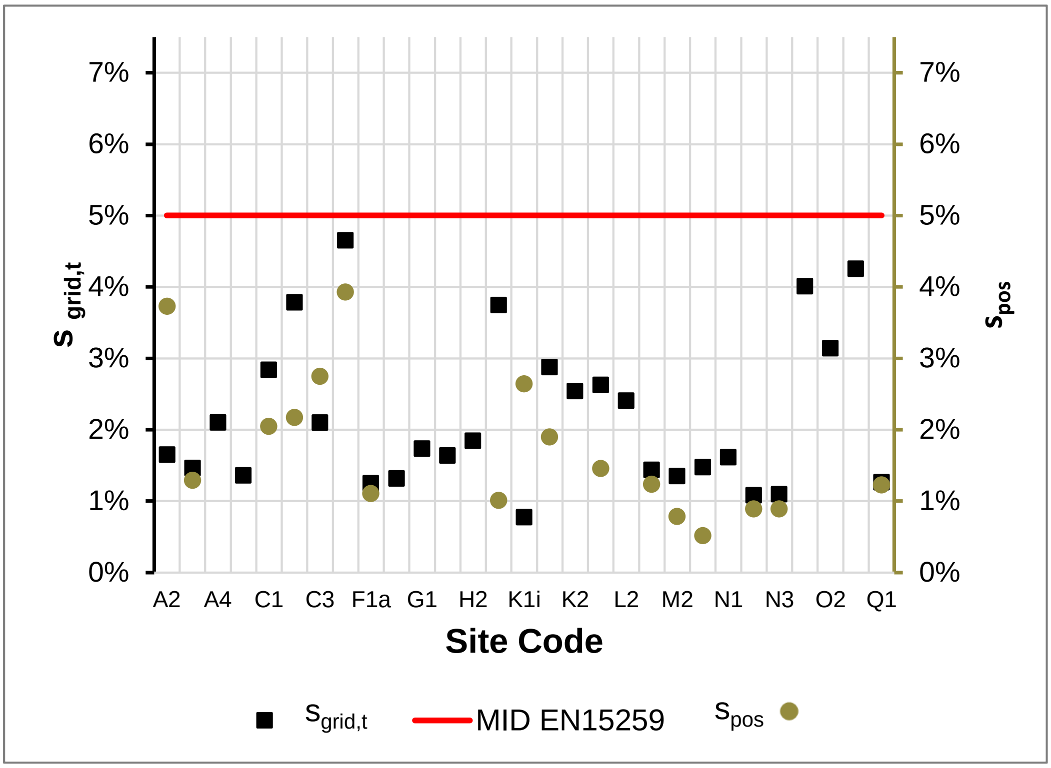

Figure 5: Positional NO_x uncertainty assessment for CCGT plant

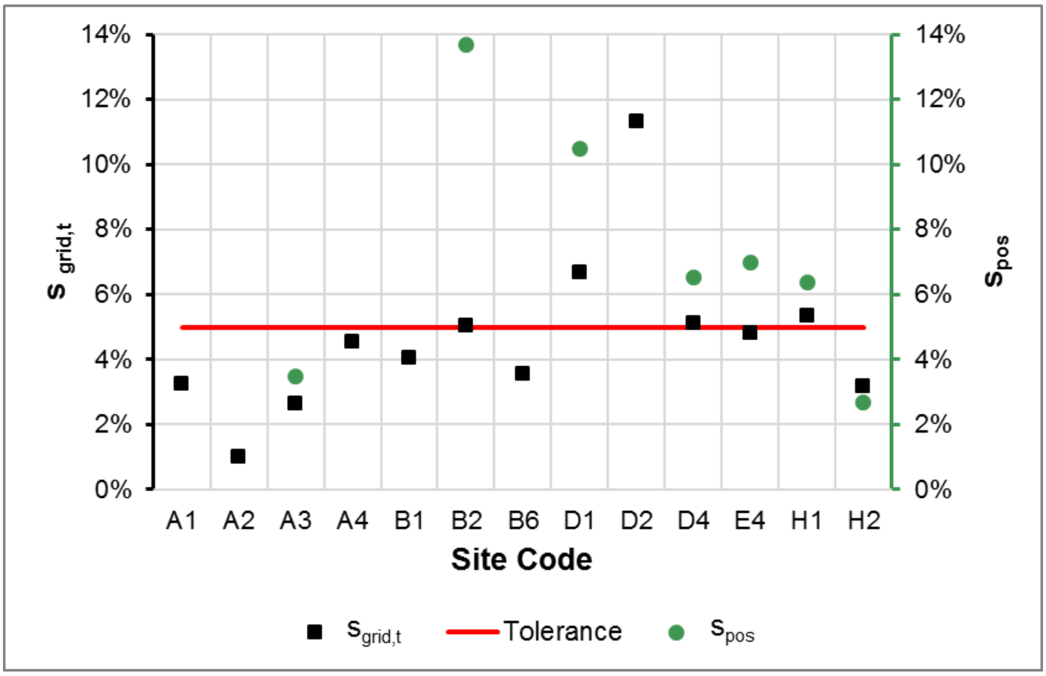

Figure 6: Positional SO_2 uncertainty assessment for coal fired plant with FGD

5.4 QAL2 Discussion

Many of the original SRM field trial validations were conducted at higher emitted concentrations than allowed under current regulations, e.g., mercury as measured under EN 13211. Whilst aspects of SRM implementation have improved over the years, the standards have not been formally revised and revalidated which should be undertaken for all pollutants, in due course, so that the full method uncertainty can be re-evaluated at low concentrations.

In the case of wet chemical SRMs, the real-world performance of the methods has improved in relation to both the field implementation and the third-party analysis in an analytical laboratory. Taking the example of mercury, the influence of sample contamination can be reduced by using full-size impingers and higher sample flow rates rather than using mini-impingers combined with side-stream sampling from an iso-kinetic sampling train. Analysis can be improved by switching from atomic absorption to atomic fluorescence techniques.

However, since the overall method uncertainty is generally much higher than the analytical uncertainty it is not obvious how much improvement will be obtained from longer sampling durations which can be used to increase the quantity of collected mercury and the mercury concentration in the impinger solution. Factors relating to sample train preparation, contamination and rinsing-recovery from the sample probe and lines are very important. However, even assuming that uncertainty is simply proportional to sampling duration, the dilution of the impinger contents with flue gas moisture needs to be taken into account. Figure 7 shows that the expected improvement with sampling duration (increasing Hg collection) - represented by the zero flue gas moisture curve (blue) - is reduced by the collection of sample condensate (reducing Hg concentration in solution) - as plotted for flue gas containing 10% and 30% moisture. Of course, the sampling duration is also limited by the quantity of condensate that can be collected in the fixed volume impingers. This aspect is common to all wet chemical methods.

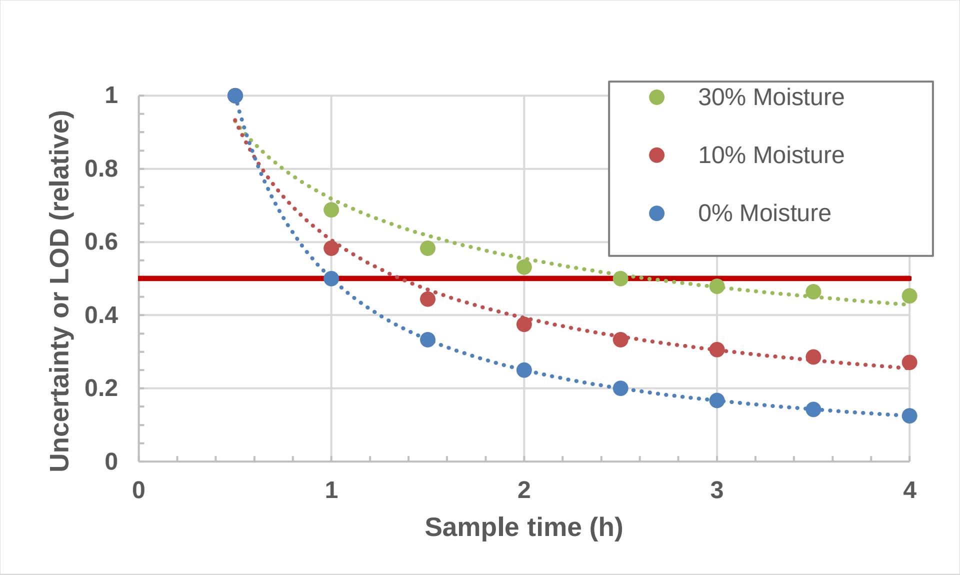

Figure 7: Influence of sampling duration on wet chemical method uncertainty

However, there has been a progressive shift from a direct assessment approach, based on the declared method uncertainty derived from field trial validation data given in each standard, to an indirect ‘bottom-up’ approach in which the test laboratory produces an uncertainty budget for each measurement based upon individual component uncertainties, e.g., the uncertainty of the sample flow metering, temperature measurement, reference materials used for calibration, etcetera.

Many SRM standards now include an example uncertainty budget to inform the indirect assessment approach. However, it is not clear that all of the relevant uncertainty contributions are included in the analysis and, in the case of wet chemical SRMs, the analytical testing is regarded as a ‘black-box’. The determination of LOD and LOQ, for example, can be inconsistent between analytical laboratories and also the treatment of field blanks and reagent blanks, as noted in a Finnish Inter-Laboratory Comparison of heavy metals and mercury sampling and analysis [20].

The indirect assessment approach generally produces very low uncertainty estimates that are close to the repeatability that can be obtained by an individual test laboratory. These estimates are generally much lower than the systematic uncertainty contributions that become apparent when performing inter-laboratory comparisons, either within full method evaluation studies or more limited proficiency testing schemes in which a number of test laboratories sample from a well characterised flue gas which may be synthetic or generated from a combustion rig, for example. Proficiency testing schemes for emissions measurements are the subject of standardisation activities under CEN Working Group 45.

The current situation with regards to the assessment of SRM uncertainty is therefore unsatisfactory since i) systematic uncertainty derived from historic field trial validation studies by direct assessment can be higher than current SRM performance levels and ii) systematic uncertainty is not well represented within test laboratory uncertainty budgets produced by indirect assessment giving too low an estimate of the method uncertainty. The indirect approach is also informative, rather than normative, in monitoring standards, and there is a lack of guidance on the analytical aspects associated with wet chemical methods.

The indirect assessment approach could be improved by introducing an allowance for otherwise uncharacterised *systematic* uncertainties. This could be based on proficiency testing, when this is representative of the real-world flue gas matrix and sampling environment. Or by including *systematic* uncertainty estimates from on-stack validation studies. Ring-testing of wet chemical samples by a number of analytical laboratories can also be useful in order to better understand analytical uncertainties. For example, a recent exercise in which a blind comparison of sulphate measurements, conducted by five accredited laboratories, brought into question the monitoring communities’ ability to routinely meet the uncertainty requirements associated with IED SO_2 emission limits and concluded that further work is needed to validate the SO_2 SRM at lower emission levels associated with the LCP BREF [21].

It also needs to be recognised that the QAL2 calibration procedures within EN 14181 are not fit-for-purpose when considering low concentrations of acid gases and Dust. Procedure C was introduced in 2014 to give more flexibility when the minimum SRM concentration, at reference conditions, is less than 15% of the D-ELV and the data range (SRM maximum – SRM minimum) is less than MPU. In this situation, zero and span concentrations can be added to the calibration data set. However, the calibration is still based on data that is below the Limit of Quantification of the SRM which can lead to poor quality calibrations. The gradient of the calibration line then depends on how the data set is constructed and the quality of the SRM data.

There are situations when the use of Procedure D from EN ISO 16911-2 would improve the calibration, i.e., forcing the calibration line to pass through zero. In certain cases, it would be more appropriate to rely solely upon calibration using reference materials, e.g., based on the results from the linearity functional test. These procedural aspects can increase the uncertainty of the measurement but are not considered further here.

In the case of dust, the variability of the SRM at low concentrations (≤ 5 mg/m^3) is too high to consistently pass the QAL2 Variability test and the only practical solution is to allow the use of a higher absolute uncertainty at lower concentrations, e.g., based on an ELV of 10 mg/m^3. In the longer term, an alternative test method, with better performance characteristics, is required.

6 AST (CALIBRATION CHECK)

The Annual Surveillance Test (AST) requires at least five hourly average SRM readings to be taken across at least one day of operation by an accredited test laboratory. The main aim is to check that the QAL2 calibration remains valid, for the full five year period, and a tolerance is defined beyond which the SRM results are not allowed to deviate. This tolerance represents an additional *systematic* uncertainty since the QAL2 calibration is allowed to shift, year-on-year, within this tolerance, before a repeat QAL2 is required. This absolute agreement between the original QAL2 and the AST test points is assessed by means of a Validity test. Failure of the AST Validity test results in a repeat QAL2. The tolerance applicable to the data scatter, assessed by the Variability test, is increased for the AST.

The Validity test criterion defined in EN 14181 is:

$$|D| \quad \leq \quad [\, t_{0,95;N-1} * \; s_D/\sqrt{N} \,] \quad + \quad \sigma_o$$

Where |D| is the absolute mean value of the differences between the SRM results and the calibrated AMS values. The Student t-factor, $t_{0,95;N-1}$, depends on the number of tests, N, as defined in Annex I of EN 14181 ($t_{0,95;N-1}$ = 2.132 for five AST tests). s_D is the standard deviation of the differences between the SRM test results and the calibrated AMS results at reference conditions. σ_o is the uncertainty requirement which is 50% of the Confidence Interval at the D-ELV, i.e., 10% of the D-ELV for NO_x and SO_2 and 15% of the D-ELV for Dust.

The maximum value of s_D is given by the AST Variability test criterion:

$$s_D \leq 1.5 * \sigma_o * k_v$$

The statistical parameter k_v depends on the number of tests, N, as defined in Annex I of EN 14181 (k_v = 0.9161 for five AST tests). It can be seen that s_D can vary between 0 and 1.374 * σ_o. Since s_D is generally small, a zero value of s_D has now been conservatively assumed within the Validity test. This offsets the additional *random* SRM uncertainty components introduced by having five test points rather than 15 as required for the QAL2.

The Validity test then becomes:

$$|D| \quad \leq \quad \sigma_o$$

or

$$|D| \quad \leq \quad [(\text{Confidence Interval})\,/2] * \text{Daily ELV}$$

For NO_x and SO_2, the lowest tolerance applicable to the QAL2 calibration shift is then 10% of the D-ELV. This tolerance could be divided by √3 in order to obtain a *standard* uncertainty contribution since the cause and nature of a potential calibration shift are unknown. However, for simplicity, a normal distribution is now assumed, with a coverage factor of 2, giving a *standard* uncertainty contribution of 5% of the Daily ELV.

Figure 8 shows the year-on-year mean AST deviations for a number of CCGT plant and these results indicate that a tolerance of 10% of the D-ELV is broadly appropriate, assuming that the D-ELV is 50 mg/m^3 and the tolerance is 5 mg/m^3. The QAL2 results are indicated as red circles. Whilst some of the results indicate almost *random* behaviour, others indicate *systematic* offsets that persist for several years, e.g., Plant 14-F1.

All of the results were obtained by a single accredited test laboratory which should eliminate any *systematic* differences associated with SRM implementation. However, there is no guarantee that the same test point is used on every occasion so there is a potential contribution from positional uncertainty; it should be a requirement for the AST to use the same sample point as the QAL2.

A modest in-year change in the calibration relationship could be caused by a number of factors, including: i) a change in the spatial variation of concentration across the measurement plane; ii) degradation in AMS performance not identified by QAL3 checks; iii) different plant operating conditions and flue gas compositions between the QAL2 and the AST test periods; iv) the use of a different test laboratory and or reference method.

For all of these reasons, it is appropriate to assign the AST a *standard* uncertainty component of 5% of the D-ELV.

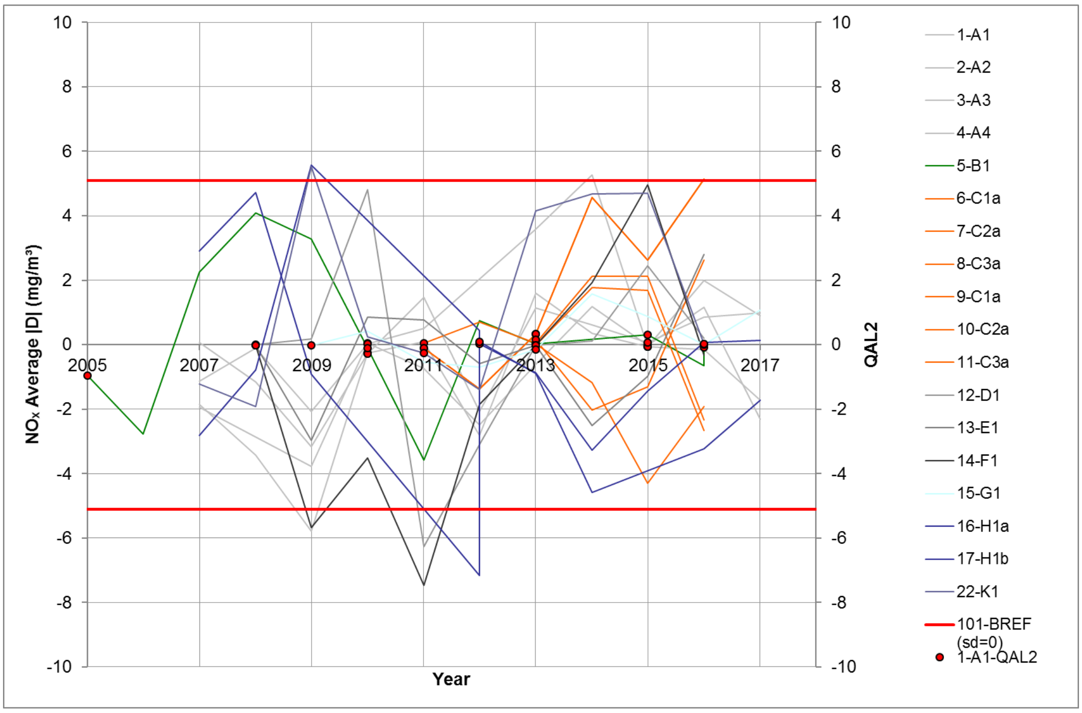

Figure 8: AST mean deviation for CCGT units

7 QAL3 (CONTROL)

QAL3 is intended to provide an audited check of ongoing AMS performance by conducting regular (typically weekly) zero and span checks and comparing the measured drift against pre-defined Warning and Alarm (Action) limits. EN 14181 allows the Action limit to be set at 50% of the Maximum Permissible Uncertainty, i.e., 10% of the Daily ELV for NO_x and SO_2. That is, in the worst case, the AMS is allowed to drift until the Action limit is reached.

Whilst it may be reasonable to make some allowance for this drift tolerance in an uncertainty assessment, relating to periods of monotonic drift, as illustrated in Figure 9, the normal condition of the AMS, when under control, is to exhibit random deviations only so this is not considered further here.

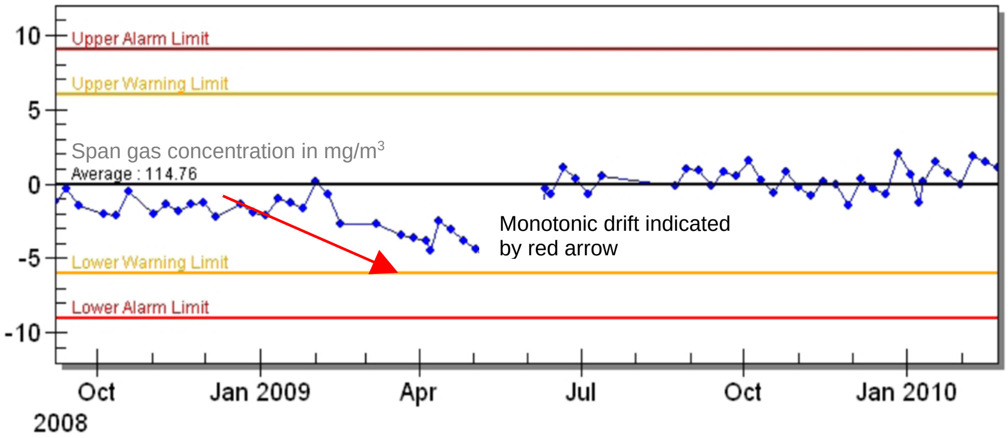

Figure 9: QAL3 Span drift for CCGT NO_x

8 OTHER UNCERTAINTY CONTRIBUTIONS

8.1 Peripheral Measurements

The uncertainty in the peripheral measurements, used to correct the raw concentrations to reference conditions, needs to be taken into account when assessing the uncertainty of the reportable data, as noted earlier.

For the purposes of this assessment, only the oxygen correction is considered further and this is assumed to be significant only for CCGT. The oxygen correction is non-linear and is much more significant at the CCGT reporting condition of 15 $\%O_2$ than the utility boiler reporting condition of 6 $\%O_2$ for solid fuels.

For QA purposes, TGN M20 defines an ‘ELV’ of 21% by volume and a Confidence Interval of 10% in line with QAL1 assessments conducted by TÜV. Since this results in rather wide QA tolerances, the power industry prefers a lower ‘ELV’ of 6 $\%O_2$ for utility boilers and 10 $\%O_2$ for CCGT [22]. Using these modified criteria, it follows that the AST would give rise to a *systematic standard* uncertainty of 0.25 $\%O_2$[15]. The SRM has a relative *expanded* uncertainty of 6% of reading, giving 3% as a *standard* uncertainty. At 15 $\%O_2$, this gives an absolute *standard* uncertainty of about 0.22 $\%O_2$, assuming that the residual SRM uncertainty is half the method

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[15] CI = 10%, ELV = 10 $\%O_2$; $|D| \leq CI/2 * \text{Daily ELV}$; $|D| \leq 0.05 * 10\ \%O_2$; $|D| \leq 0.5\ \%O_2$; *standard* uncertainty = $|D|/2 = 0.25\ \%O_2$

uncertainty, as before. The peripherals contribution to the positional uncertainty is assumed to be zero for CCGT, as noted earlier.

An arbitrary *standard* uncertainty of 0.15 %O_2 is therefore conservatively assumed, resulting in an uncertainty in the NO_x correction of 2.5%. (Note that a calibration gas containing 21 %O_2 with an *expanded* uncertainty of 1% would have a *standard* uncertainty of about 0.1 %O_2.)

8.2 Other Factors

There is a requirement in EN 14181 to check, on a weekly basis, that the reportable hourly averages are within the Valid Calibration Range established during QAL2 testing. It is recognised that the uncertainty of measurements that lie outside of this Valid Calibration Range is likely to be higher than those within the range. Since this uncertainty is related to an unknown number of hourly averages it is not considered further here.

Uncertainties related to the Data Acquisition and Handling System (DAHS), such as drift in the calibration of analogue outputs or inputs, are not considered further here.

For Large Combustion Plant comprised of multiple units, the stack flow weighted average of the unit AMS data needs to be determined in order to report the plant emission. Any additional uncertainty relating to the stack flow weighting is not considered further here.

9 OVERALL UNCERTAINTY BUDGET

The following specimen uncertainty budget is based on the example of CCGT NO_x that has been used throughout this report and this is summarised in Table 8 with reference to the Daily ELV (D-ELV).

The QAL1 uncertainty contribution is conservatively assumed to be zero, presuming that a suitable type-approved AMS can be specified for the application (Section 4). *Rando*m AMS uncertainty is assumed to be negligible over the longer term emissions reporting periods. *Systematic* AMS uncertainty is assumed to be addressed by the QAL2 calibration.

The uncertainty associated with the QAL2 calibration is made up of several components (Section 5).

Firstly, the uncertainty of the Standard Reference Method (SRM) that is used to calibrate the AMS, assuming that the maximum allowed SRM uncertainty can be achieved across the D-ELV concentration range. The *random* uncertainty, which is related to the method repeatability applicable to a single test laboratory, is reduced substantially across ≥ 15 QAL2 test points. However, the *systematic* uncertainty, which can be estimated from the reproducibility across multiple test laboratories, dominates the overall method uncertainty. SRM uncertainty is reviewed in Section 5.2 where it is concluded that 50% of the maximum SRM uncertainty is a suitable estimate for a number of SRMs based on historic validation data. For NO_x, the maximum SRM *expanded* uncertainty is 10%, giving a *standard* uncertainty of 5% and a contribution of 2.5 %D-ELV for the uncertainty budget.

Secondly, the positional uncertainty, defined in EN 15259, that is associated with single-point SRM sampling within a nominally homogeneous sampling plane. This is taken to be a worst-case of 5 %D-ELV for a CCGT which relates to sampling from the GT exhaust rather than the stack (Section 5.3).

Thirdly, the year-on-year QAL2 calibration drift which is assessed by the AST Validity test (Section 6). The smallest allowed annual deviation of AST test points from the QAL2 calibration line is used to define a *systematic* uncertainty contribution associated with calibration drift across the five-year QAL2 period. This is conservatively taken to be σ_o / 2 which equates to 5 %D-ELV for NO_x.

Fourthly, the uncertainty associated with correcting the raw pollutant concentration to reference conditions (Section 8.1). This is dominated by the oxygen correction for a CCGT since the process O_2 concentration is high and the extractive sample is usually dry. For other processes, the water vapour measurement must also be assessed and, for Dust, the stack temperature and pressure must also be considered. For NO_x correction at a CCGT, a conservative estimate of the correction factor uncertainty is 2.5 %D-ELV.

The combined QAL2/AST uncertainty is obtained using the Root Sum of Squares (RSS) approach, in the usual way, to give 7.9 %D-ELV for the CCGT NO_x example.

The QAL3 uncertainty contribution is conservatively assumed to be zero, presuming that the AMS remains under control at all times. In reality, there may be periods of monotonic drift within the control chart limits.

Since QAL1 (underlying AMS performance) and QAL3 (AMS stability) are assumed to not contribute to this uncertainty budget, the QAL2/AST *standard* uncertainty of 7.9 %D-ELV is then multiplied by a coverage factor of 2 to obtain the *expanded* uncertainty of 15.8 %D-ELV shown in Table 8. In relation to the hourly average, this allows for an additional *expanded* uncertainty of about 12 %D-ELV for AMS *random* fluctuations which should be sufficient to cover the AMS *random* uncertainty components (Section 4).

However, it should be noted that the Annual BAT-AEL for a large CCGT, for example, is typically 40 mg/m^3 compared with a Daily BAT-AEL of 50 mg/m^3. The *expanded* uncertainty, as a proportion of the Annual BAT-AEL, is therefore increased to about 20%. This is an important point since, by definition, the emission concentration must be at, or below, the Annual ELV for most of the time in order to achieve compliance.

This example uncertainty budget, employing relatively conservative assumptions relating to *systematic* uncertainty contributions, demonstrates that it is entirely appropriate to apply the IED Confidence Interval to annual emission concentrations and this will provide the necessary legal certainty for compliance assessment.

By contrast, the practice of basing the compliance assessment on the standard deviation of differences (s_D) between the SRM and the calibrated AMS QAL2 readings is fundamentally flawed. s_D represents a combined repeatability of the AMS and the SRM and since the AMS repeatability is often lower than the SRM repeatability, this is not even a good estimate of the SRM repeatability which should be determined from paired measurements conducted by a single test laboratory. Neither does this approach recognise the *systematic* uncertainty associated with the SRM and the other *systematic* uncertainty contributions reviewed within this study. This is recognised within EN 14181 which states that *the variability obtained s_D includes uncertainty components associated with the repeatabilities of both the AMS and the SRM, but not the overall uncertainty of the SRM*.

It should also be noted that EN ISO 16911-2, a daughter standard of EN 14181, recognises the importance of SRM *systematic* uncertainty contributions in stack flow determination, especially in relation to annual emission totals determined for emissions trading purposes [11]. The flow

SRM uncertainty assessment is therefore focussed on *systematic* uncertainty, as described in EN ISO 16911-1 [23].

Table 8: CCGT NO_x example uncertainty assessment

Uncertainty Source	**%D-ELV u**	**Comment**
QAL1	**0.0%**	Assume that *systematic* uncertainty is removed by QAL2 calibration
QAL2/AST	**7.9%**	
SRM method	2.5%	SRM uncertainty / 2
SRM location	5.0%	MID EN 15259
AST drift	5.0%	σ_0 / 2
Oxygen correction	2.5%	Equivalent to 0.15 $\%O_2$
QAL3	**0.0%**	Assume that the AMS is under control at all times
Total *standard*	**7.9%**	Combined *standard* uncertainty
Total *expanded*	**U** **15.8%**	Combined *expanded* uncertainty

Regarding uncertainty budgets for other species and processes. The SRM positional uncertainty can be higher for CO although there is very little duct survey data available since CO emissions are often below the detection limit during the normal operation of combustion plant. However, at low load conditions and during episodes of poor combustion, the CO emissions can be appreciable and, due to the nature of CO formation processes, the CO can be the most inhomogeneous component within the duct or stack. This is particularly unfortunate since the Confidence Interval for CO is only 10%.

The SRM positional uncertainty can be much higher for SO_2, and other acid gas, emissions downstream of FGD units at solid fuel fired power plant, as discussed in Section 5.3 and Appendix C, when the SRM measurement employs single point, rather than full grid, sampling. The SRM maximum allowable *expanded* method uncertainty for SO_2 is 20%, rather than 10% for NO_x, which would also double the SRM method contribution, presuming that the SRM can achieve 20% *expanded* uncertainty at low concentrations.

In that respect, this study has not focussed on the SRM Limits of Detection and Quantification (LOD and LOQ). The ROM states that *Any measurement method applied should have an appropriate LOD/LOQ in relation to the emission level to be measured. In many cases, the LOD is required to be less than 10 % of the ELV in order to guarantee that the LOQ is clearly below the ELV. Some Member States have set stricter performance requirements, e.g. in France the LOQ should be less than 10 % of the ELV*.

Improved SRM performance at the lower concentrations envisaged by the LCP BREF needs to be demonstrated by means of CEN revalidation trials, having first improved the methods where possible. In the case of Dust, there is a case for the development of a new SRM standard, perhaps based on dilution sampling coupled with ambient particulate measurement technologies. In the case of mercury, a superior reference method has been standardised, based on the use of sorbent traps [24], but this is awaiting validation in Europe. The delays in

CEN funding for these important standardisation activities are causing major difficulties in resolving key technical aspects relating to LCP BREF implementation.

It is important to consider how the full SRM uncertainty can be assessed at lower concentrations. One possible approach would be to allow inter-laboratory proficiency testing data, in lieu of re-validation data, to be combined with the test laboratory uncertainty assessment. In the case of wet chemical SRMs, the uncertainty associated with the analytical laboratory testing also needs to be much better characterised and incorporated into the uncertainty budget.

In the mean-time, below a defined concentration, the use of absolute uncertainty thresholds can be considered in place of Confidence Intervals for validating reportable AMS concentrations, as allowed in The Netherlands (see Appendix B) and France.

10 CONCLUSIONS

Random uncertainty components are self-cancelling across an annual averaging period and, in this assessment, the QAL1 AMS *random* uncertainty is assumed to be zero and the AMS *systematic* uncertainty is assumed to be corrected by the QAL2 calibration, presuming that a suitable type-approved AMS can be specified for the application. However, suitable AMS are not always available at the bottom end of the BAT-AEL concentration ranges.

The QAL2 calibration is the largest uncertainty source and this mostly relates to the transfer of SRM uncertainty to the AMS. The *random* SRM uncertainty is reduced substantially across ≥ 15 QAL2 test points. However, the *systematic* uncertainty, which is related to the reproducibility across multiple test laboratories, dominates the overall method uncertainty. This can only be properly assessed by inter-laboratory comparisons via formal validation studies supplemented by proficiency testing schemes. When the SRM samples from a single point, the residual positional uncertainty within the measurement plane can also be significant.

Whilst some of the SRMs cannot achieve the required performance at low BAT-AEL concentrations, a re-evaluation of historic SRM validation data indicates that the performance of key SRMs is generally better than stated within the SRM standards. Nevertheless, there is a general need to revalidate SRM standards at lower concentration ranges.

Potential year-on-year drift of the QAL2 calibration can be accounted for using the AST Validity test tolerance and, finally, the uncertainty of the oxygen concentration, that is used to correct the pollutant concentration to reference conditions, must also be taken into account. Also, other peripheral measurements depending on the process and the pollutant of interest.

An example uncertainty budget has been developed using conservative assumptions and tolerances that are already defined in CEN standards or national guidance. An overall *standard* uncertainty of 7.9% would then be applicable to the case of NO_x emissions from a CCGT. The resultant *expanded* uncertainty is then 15.8%, at 95% confidence, at the Daily ELV. In relation to the hourly average, this allows for an additional *expanded* uncertainty of about 12% of the Daily ELV for AMS *random* fluctuations which is consistent with the QAL1 performance criteria. In relation to the Annual BAT-AEL concentration, since this is lower than the Daily BAT-AEL concentration, the relative *systematic expanded* uncertainty would then be close to 20%. It is anticipated that similar uncertainty estimates will be appropriate for other species, such as SO_2, although the balance between the individual uncertainty contributions will vary.

This example uncertainty budget, employing relatively conservative assumptions relating to *systematic* uncertainty contributions, demonstrates that it is entirely appropriate to apply the IED Confidence Interval to annual emission concentrations and this provides the necessary legal certainty for compliance assessment and simplicity with regards to plant operation. When it is not possible to achieve the required uncertainty at low concentrations then the adoption of a fixed absolute uncertainty is recommended, for each pollutant, as already specified in The Netherlands and France.

More specifically, it is recommended that the Annual ELV is used instead of the Daily ELV for monitoring assessment since this is more representative of the typical emission concentration. It is also recommended that SRM single point sampling should always be from the same point within the stack, during QAL2 and AST test campaigns, to minimise the influence of positional uncertainty.

It is clear that a number of challenges remain in relation to minimising and assessing measurement uncertainty: i) re-validation of SRM standards and the development of new test methods with lower LOD/LOQ; ii) improved SRM uncertainty assessment methodologies; iii) certification of new AMS with improved sensitivity and discrimination between pollutants; iv) improved AMS calibration procedures at low concentration, especially for reactive trace gases and Dust (requiring improvements within EN 14181).

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APPENDIX A

QAL1 (AMS CERTIFICATION)

A.1 AMS PERFORMANCE IN RELATION TO BAT-AEL RANGES

The uncertainty declared on MCERTS certificates is often defined as a percentage of a notional Daily ELV that is proposed by the AMS manufacturer. These notional ELVs differ between AMS certificates making comparisons difficult. In these cases, relative uncertainties have therefore been converted to absolute uncertainties in mg/m^3, for most pollutants, or $\mu g/m^3$ for Hg, or absolute volume percent for O_2 and H_2O. TÜV certificates quote the absolute AMS *expanded* uncertainty directly.

The *expanded* uncertainty of each certified AMS has been plotted, by species, using the template given in Figure A-1. These uncertainties are compared with the required MPU_{AMS} derived from the BAT-AEL ranges applicable to large LCP of different types. The resultant graphs for the individual species are given in Figures A-2 to A-12, as listed in Table A-1.

Table A-1: Index of graphs by species

Species	Figure
Template	Figure A-1
NO_x	Figure A-2
SO_2	Figure A-3
Dust	Figure A-4
CO*	Figure A-5
Hg	Figure A-8
HCl	Figure A-9
NH_3	Figure A-10
TOC	Figure A-11
HF	Figure A-12

*CO values are based on indicative Annual BAT-AELs

The IED gives the Confidence Intervals (CI) for NO_x, SO_2, CO and Dust for LCP, and for HCl, HF and TOC for incinerators. Where the CI is not specified in the IED the following values are used to calculate the MPU_{AMS}: 40% for Hg and NH_3 as currently specified by TÜV.

An annotated example of the graphs is shown in Figure A-1. The vertical lines represent the maximum (solid) and minimum (dashed) MPU_{AMS} calculated from the Daily BAT-AEL ranges for CCGT (red), coal (black) and biomass (green) plant.

The CO BAT-AELs are ‘indicative’ Annual BAT-AELs and the QA approach when there is no Daily BAT-AEL is unclear. The BREF MPU_{AMS} lines on the CO graph (Figure A-5) are therefore based on the annual indicative BAT-AELs, noting that higher ELVs may be agreed with the Competent Authority in practice.

Table A-2 shows the total number of AMS which can comply with the MPU_{AMS} at the top and bottom of the BAT-AEL ranges by species, for CCGT, coal and biomass plant . It should be noted that this is the least conservative approach that will indicate the highest number of suitable AMS since the certification range may still not be deemed to be suitable for the process application. The key conclusions are:

- No commercially available AMS can meet the CO MPU_{AMS} at the bottom of the BAT-AEL range for CCGT/coal plant (one AMS can meet the lowest CO BAT-AEL for biomass). Only one analyser can meet the requirement at the top of the CCGT BAT-AEL range.
- Some Competent Authorities allow a CI of 20% to be used for CO AMS assessment[16] (i.e., MPU_{AMS} = 15% of Daily ELV). Despite this, still no AMS are capable of meeting the MPU_{AMS} at the bottom of the BAT-AEL range, but 20 AMS could then meet the requirement at the top end of the range for CCGT plant.
- No commercially available AMS for HCl or TOC is capable of meeting MPU_{AMS} at the minimum coal or biomass BAT-AELs.
- There are only three commercially available AMS for Hg, of which only one meets the MPU_{AMS} requirements at any BAT-AEL.
- Four AMS meet minimum CCGT NO_x requirements, but three of these are variants of the ABB Limas (Limas 11, 21 and 23).

Table A-2: Number of AMS which meet MPU_{AMS} associated with the BAT-AELs

Species	Figure	Number of AMS which meet MPU_{AMS} at the minimum and maximum of the BAT-AEL range					
		CCGT		COAL		BIOMASS	
		Min	Max	Min	Max	Min	Max
NO_x	Figure A-2	4*	11	21	33	18	37
SO_2	Figure A-3	N/A	N/A	3	37	0	39
Dust	Figure A-4	N/A	N/A	12	22	6	22
CO+	Figure A-5	0 (0)^	1 (20)^	0 (0)^	28 (33)^	1 (20)^	24 (33)^
Hg	Figure A-8	N/A	N/A	2	2	2	2
HCl	Figure A-9	N/A	N/A	0	12	0	15
NH_3	Figure A-10	6	12	6	12	6	13
TOC	Figure A-11	N/A	N/A	0	7	0	7
HF	Figure A-12	N/A	N/A	5	8	5	5

Notes
* 3 are variants of ABB Limas
\+ Annual indicative values
^ Number of AMS which meet MPU_{AMS} if CI of 20% is used is indicated in brackets

Peripheral measurements of H_2O and O_2 are required for correction of other species to dry conditions and a reference O_2 concentration of 6% for coal/biomass plant and 15% for CCGT plant. The uncertainty of H_2O and O_2 measurements therefore affect the corrected measurements of other species as discussed in the main text. No ELVs or CIs are specified in the IED or LCP BREF for H_2O and O_2.

For QA purposes, an O_2 surrogate ELV of 21 %O_2 and CI of 10% are often used by the Competent Authorities although the certification bodies instead use the certification range as the ELV and this is typically 25 %O_2, although the same CI of 10% is used. For H_2O, a surrogate ELV of 30% and a CI of 30% are often used by the Competent Authorities but the certification bodies instead use the certification range as the 'ELV' and a CI of 10%. Due to this variability in assumed tolerances, the MPU_{AMS} calculated from the more stringent surrogate ELVs recommended by the UK energy industry[17] are also plotted in Figure A-6 and Figure A-7.

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[16] The IED CI for CO AMS of 10% is still the value used for data validation when reporting emissions data to the Competent Authority.

[17] The UK energy industry recommends an H_2O QA surrogate ELV of 6% and for O_2 a QA surrogate ELV of 10% for CCGT and 6% for coal/biomass

Table A-3 shows the number of peripheral AMS which meet the MPU_{AMS} from the typical guidelines provided by Competent Authorities. Table A-3 also shows the number of AMS which meet MPU_{AMS} from the more stringent UK energy industry guidelines. For many AMS, the sample is dried prior to measurement and therefore H_2O correction is not required. Table A-3 shows that there are 22 AMS which meet the most stringent O_2 MPU_{AMS} (for coal/biomass plant). Consequently, selection of a suitable AMS should not present technical difficulties.

Table A-3: Number of AMS which meet MPU_{AMS} from the BREF AEL

Species	**Figure**	**Number of AMS which meet MPU_{AMS}**		
		UK Industry guidance		Competent Authority recommended
		CCGT	Coal/biomass	
H_2O	Figure A-6	2		19
O_2	Figure A-7	50	22	54

A.2 FIGURES

On each graph, AMS uncertainty is grouped by measurement technique (acronyms used are shown in Table A-4).

Table A-4: Acronyms used for AMS measurement techniques

Acronym	**AMS method**
CLD	ChemiLuminescence Detector
EC	ElectroChemical
FID	Flame Ionisation Detector
FTIR	Fourier Transform Infrared
IR	Infra-Red
TDL	Tunable Diode Laser
UV	Ultra-Violet

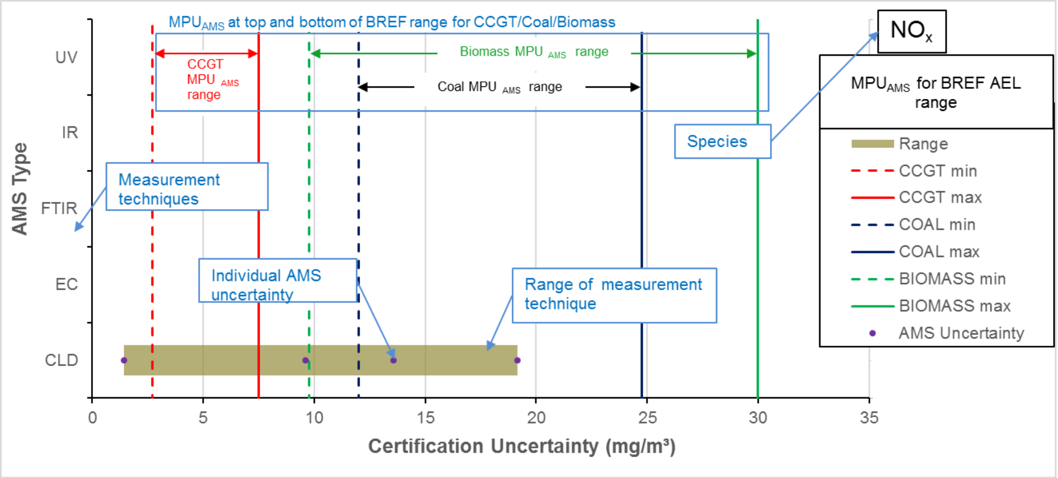


Figure A-1: Layout of graphs

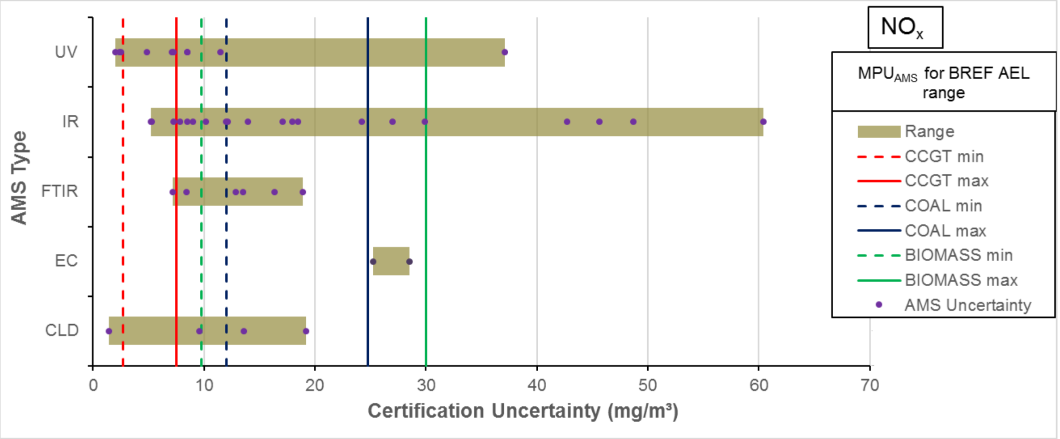


Figure A-2: NO_x absolute uncertainty from certification

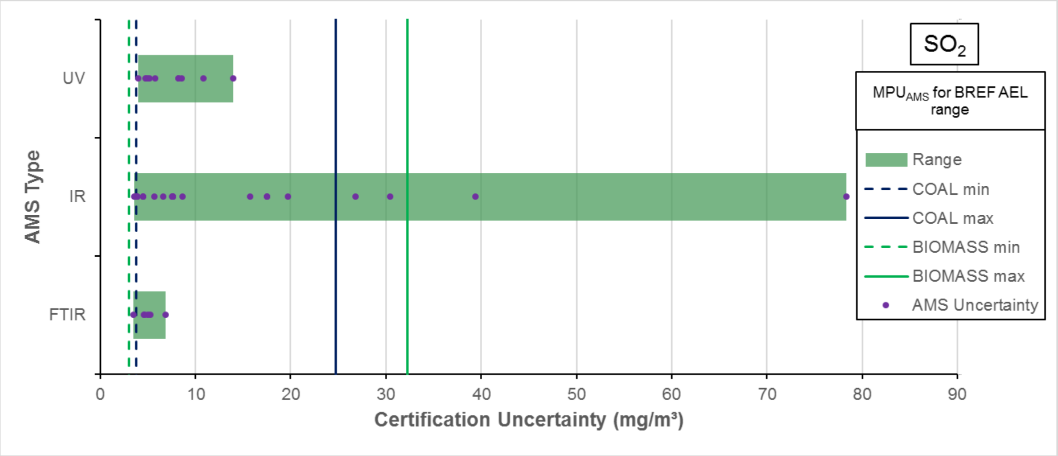


Figure A-3: SO_2 absolute uncertainty from certification

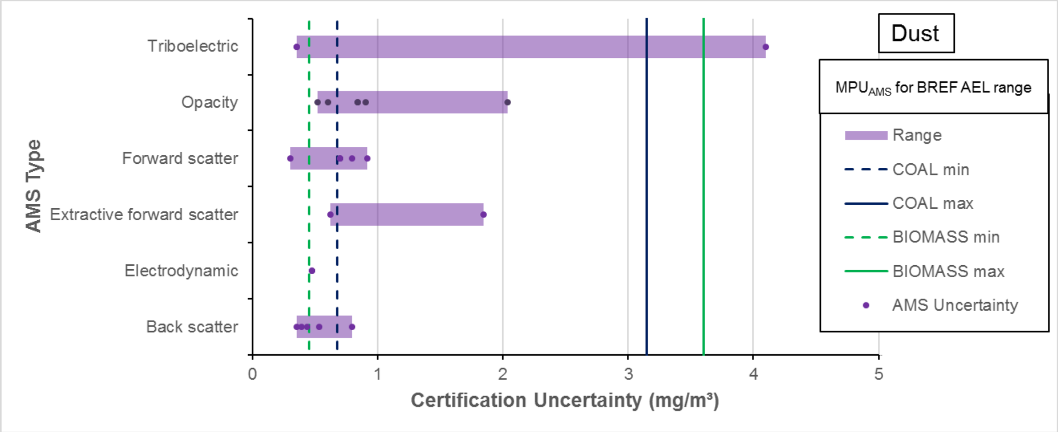


Figure A-4: Dust absolute uncertainty from certification

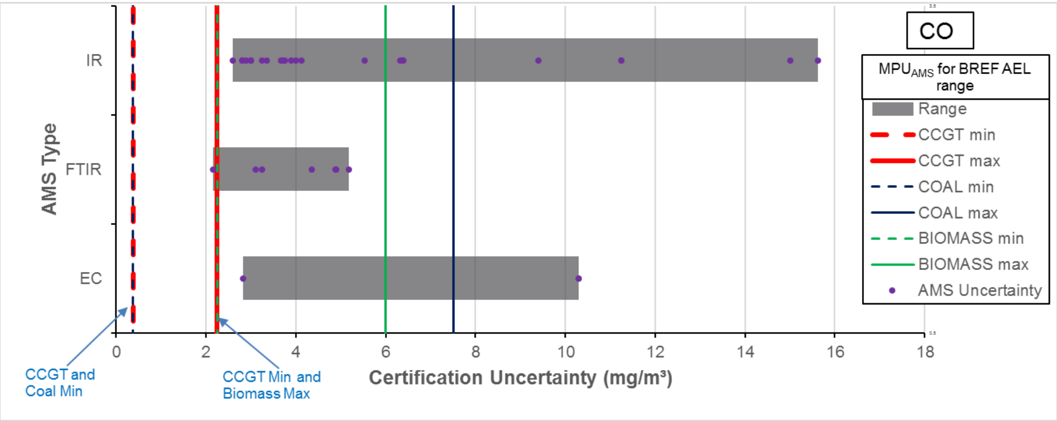


Figure A-5: CO absolute uncertainty from certification

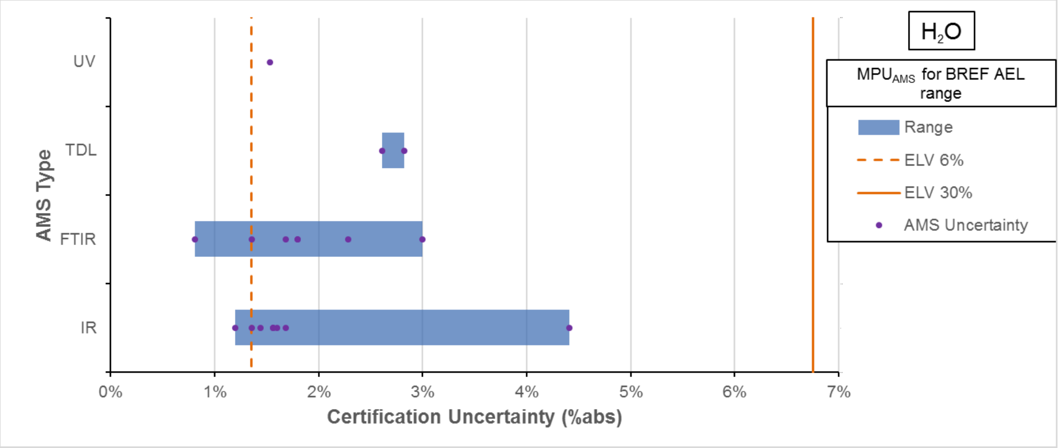


Figure A-6: H_2O absolute uncertainty from certification

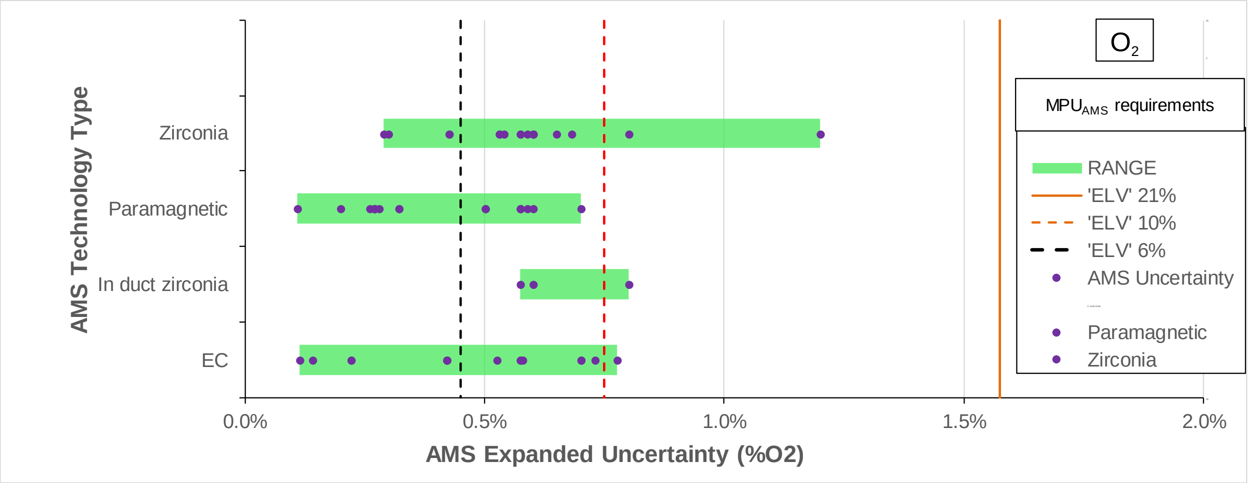


Figure A-7: O_2 absolute uncertainty from certification

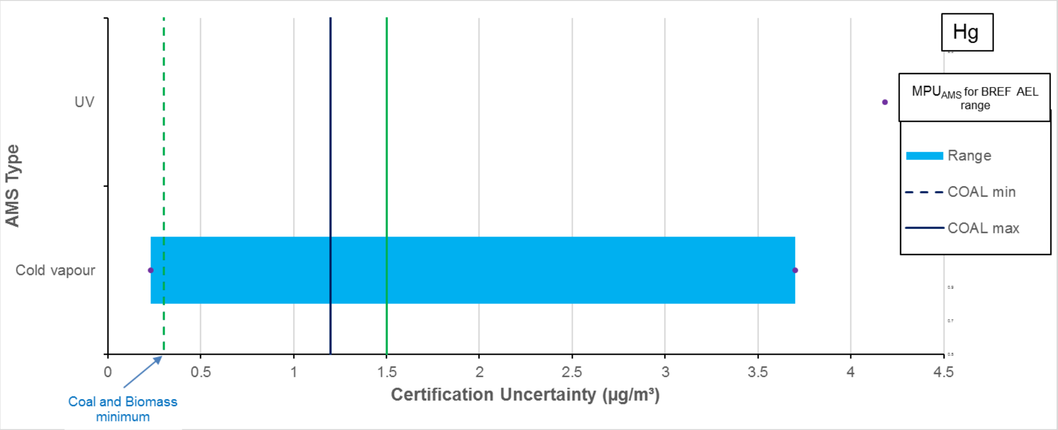


Figure A-8: Hg absolute uncertainty from certification

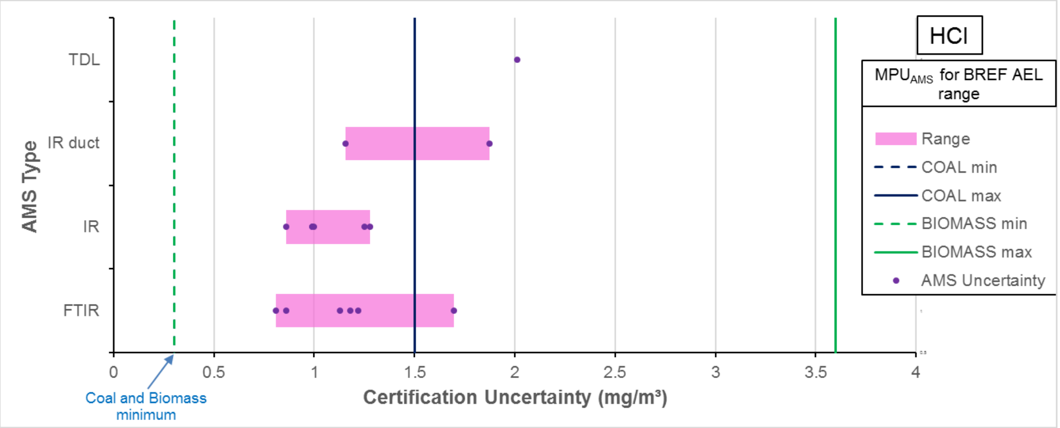


Figure A-9: HCl absolute uncertainty from certification

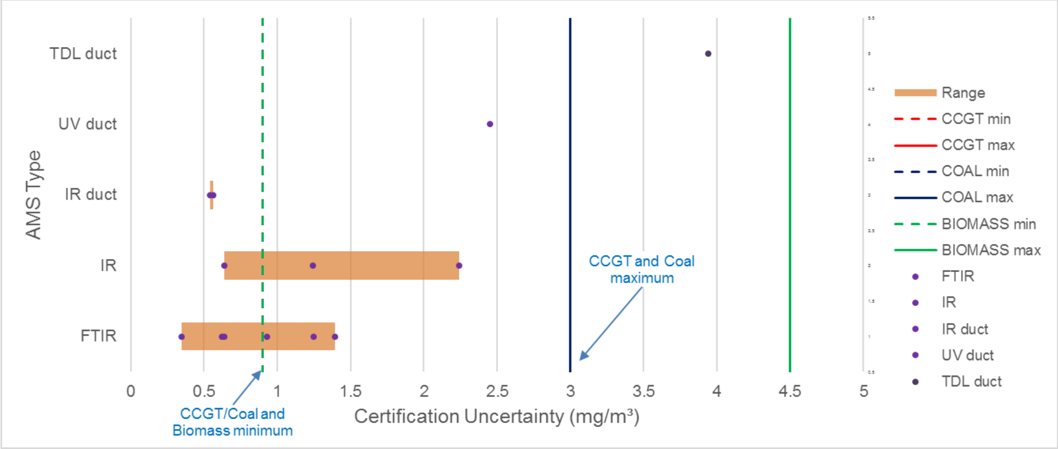


Figure A-10: NH$_3$ absolute uncertainty from certification

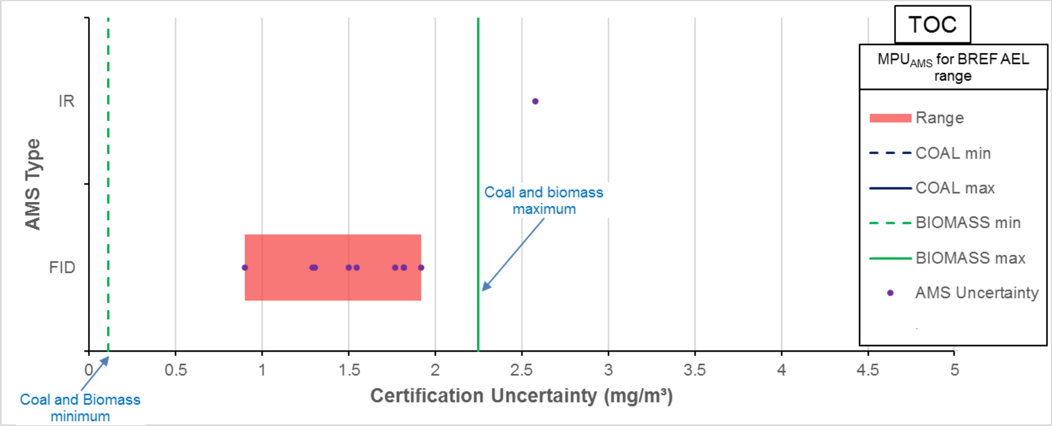


Figure A-11: TOC absolute uncertainty from certification

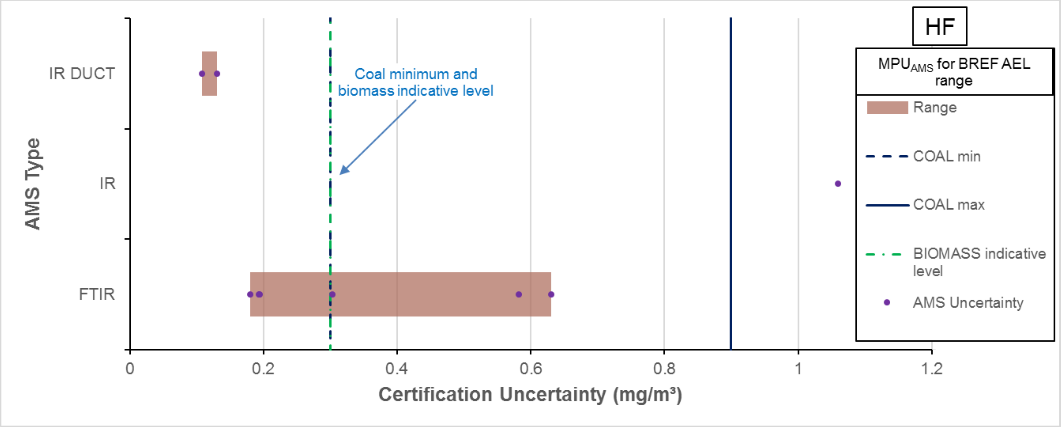


Figure A-12: HF absolute uncertainty from certification

A.3 REFERENCES

[A.1] EN 14181:2014, Stationary source emissions – Quality assurance of automated measuring systems, 2014.

[A.2] BS EN 15267-3:2007 Air quality. Certification of automated measuring systems. Performance criteria and test procedures for automated measuring systems for monitoring emissions from stationary sources, 2007.

[A.3] EN ISO 14956:2002 Air quality. Evaluation of the suitability of a measurement procedure by comparison with a required measurement uncertainty, 2001.

APPENDIX B

QAL2 (AMS CALIBRATION USING THE SRM)

B.1 ANALYSIS OF SRM PERFORMANCE CHARACTERISTICS

B.1.1 Background Information

The AMS is calibrated using the Standard Reference Method (SRM) during the QAL2 calibration. In general, the calibration then applies for five years. Effectively, this means that the AMS is forced to align with the SRM for a five-year period. The quality of the SRM measurements is therefore of paramount importance since the SRM uncertainty will be transferred onto the AMS. The performance characteristics of the European reference methods are provided in a suite of SRM standards. Note that the decimal separator is a comma (,) rather than a full stop (.) within this appendix, in line with the reference standards.

SRM performance characteristics, including repeatability and reproducibility, are derived from validation field test data, measured during the development of the standards. The field trial results and the associated statistical analyses, based on ISO 5725, are recorded in each SRM standard. The following information is provided in many SRM standards.

Repeatability is defined in ISO 5725-1, as '*precision under repeatability conditions*' which are, in turn, defined as '*conditions where independent test results are obtained with the same method on identical test items in the same laboratory by the same operator using the same equipment within short intervals of time*'. The '*repeatability standard deviation*, s_r, is *'the standard deviation of test results obtained under repeatability conditions'*. The '*repeatability limit*, r, is *the value less than or equal to which the absolute difference between two test results obtained under repeatability conditions may be expected to be with a probability of 95%'.* The *'repeatability limit'* is also referred to as the *'field repeatability'* within EN standards.

The exact definition of the repeatability limit, r, is not given in all SRM standards but it is defined within the SO_2 SRM (EN 14791) based on ISO 5725-2 and ISO 5725-6: $r = \surd 2 * t_{0.95;n-1} * s_r$ where $t_{0.95;n-1}$ is the student t-factor for a level of confidence of 95%, and a degree of freedom of n-1, and n is the number of paired measurements conducted by a single test laboratory.

For an SRM validation, the repeatability or 'intra-laboratory' uncertainty relates to the results of paired measurements conducted by the same test laboratory. It is assumed that the repeatability will be approximately the same for all Test Laboratories so that it is possible to establish one common value which will be applicable to any laboratory. However, any given laboratory can determine their own repeatability (under ISO 5725-6). The operating conditions and ambient conditions should be held as constant as possible during repeatability testing and the test equipment should not be recalibrated between measurements unless this is required for every single measurement.

Reproducibility is defined in ISO 5725-1 as '*precision under reproducibility conditions*' which are, in turn, defined as '*conditions where test results are obtained with the same method on identical test items in different laboratories with different operators using different equipment*'. The *reproducibility standard deviation*, s_R, is *'the standard deviation of test results obtained under reproducibility conditions'*. The '*reproducibility limit*, R, is *the value less than or equal to which the absolute difference between two test results obtained under reproducibility conditions* *may be expected to be with a probability of 95%'.* The '*reproducibility limit'* is also referred to as the *'field reproducibility'* within EN standards.

The definition of the reproducibility limit, R, is given in EN 14791 as: $R = \sqrt{2} * t_{0.95;np-1} * s_R$ where $t_{0.95;np-1}$ is the student t-factor for a level of confidence of 95%, and a degree of freedom of np-1, and n is the number of parallel measurements conducted by p laboratories.

For an SRM validation, the reproducibility uncertainty relates to results of parallel measurements conducted by different Test Laboratories. Whilst repeatability tends to be dominated by random uncertainty components, reproducibility incorporates both systematic and random uncertainty components. The 'inter-laboratory' standard deviation, s_L, tends to be dominated by systematic uncertainty, having removed the repeatability element, and this can be calculated from $s_L = \sqrt{(s_R^2 - s_r^2)}$. However, in reality, all of these quantities contain both random and systematic uncertainty contributions in different proportions.

Of course, an inter-laboratory comparison is normally conducted on identical material that is shipped to different analytical laboratories. In the case of a stack testing validation, there will be some process variability that is included within the results which is not separately assessed.

The reproducibility standard deviation is used to estimate the *expanded* uncertainty of a single measurement, U_R, defined in EN 14791 as: $U_R = t_{0.95;np-1} * s_R$.

For a large number of tests, $U_R \approx 2\,s_R$, $R \approx 2{,}8\,s_R$ and $r \approx 2{,}8\,s_r$. The reproducibility limit, R, describes the maximum difference between two test points so this is higher than the measurement uncertainty of a single measurement, U_R, which represents the overall method uncertainty across a range of test laboratories. For any given test laboratory, the individual laboratory test result *expanded* uncertainty, U_r, is calculated from the repeatability standard deviation in the same way [$U_r \approx 2\,s_r$].

B.1.1 Analysis Approach

With regards to QAL2 calibration, since at least 15 data points are obtained across at least three days of normal operation, any *random* uncertainty associated with the SRM will be reduced by a factor of 4 [$\approx \sqrt{15}$]. The residual *random* uncertainty is therefore given by $s_r / 4$. However, any *systematic* uncertainty will be transferred directly to the AMS via the QAL2 calibration.

Inspection of SRM validation field trial data indicates that the repeatability is arithmetically about 50% of the reproducibility, i.e., $s_r = s_R / 2$. The *systematic* inter-laboratory standard deviation is therefore: $s_L = \sqrt{(s_R^2 - s_r^2)} = \sqrt{(s_R^2 - (s_R/2)^2)} = \sqrt{(0.75\,s_R^2)} = 0.866\,s_R$. That is, the overall method uncertainty is dominated by *systematic* or inter-laboratory uncertainties.

If the residual *random* uncertainty is combined with the *systematic* inter-laboratory uncertainty, then the SRM uncertainty that is transferred to the AMS becomes 0.875 s_R. It would therefore reasonable to take the overall SRM *expanded* uncertainty to be an estimate of the QAL2 *expanded* uncertainty that is transferred to the AMS. This approach is taken below when comparing SRM uncertainty with the IED Confidence Intervals. However, it is likely that uncertainty that is classed as *systematic* may actually contain some *random* uncertainty components and, in some cases, there have been improvements in SRM implementation since the standards were validated. It is therefore suggested, in the main text, that 50% of the required SRM uncertainty should be used for uncertainty budgets unless better information is available, e.g., from additional SRM validation exercises.

In general the overall method uncertainty (U_R) is expressed as a linear function of the concentration (C) in SRM standards. However, this linear function overestimates the actual uncertainty at low concentrations. In the primary European SRM standards (NO_x, SO_2 and CO) all of the field test results are provided within the standards. In order to provide insight into the relationship between the SRM performance and Emission Limit Values (ELVs), represented by the BAT-AEL ranges, this data has been recalculated and shown graphically in the following sections for each LCP BREF pollutant species.

In each case, the relative *expanded* uncertainty [= U_R/C * 100%] is plotted against concentration and the relationship between relative *expanded* uncertainty and concentration is therefore always non-linear, as illustrated in Figure B-1. As expected, the relative uncertainty increases as the concentration decreases. Also, since the ranges of concentration from the SRM validation exercises are rather large, the concentration scale is logarithmic so that the results at the lowest concentrations, relevant to the BAT-AELs, can be inspected easily. In each case, the selected BAT-AEL range, combined with the IED Confidence Interval, is represented by a blue box, as also illustrated in Figure B-1.

For the key SRM standards, the original analysis was conducted by DNV and individual test results, not included in the standards, from within the quoted ranges of average values, are still available and have been used for recalculating the uncertainty functions. In each case, the linear uncertainty function, from the relevant standard, is plotted as a green line, and an improved power law function is plotted as a dark blue line, as again illustrated in Figure B-1.

The relative *expanded* uncertainty increases as the concentration is reduced but the IED Confidence Interval is defined as a fixed percentage of the Daily ELV. Due to the difficulties associated with assessing measurement uncertainty at very low absolute concentrations, an alternative approach, in which an absolute *expanded* uncertainty is used for compliance assessment, is used in The Netherlands. The absolute uncertainties are shown in Table B-1 as MPU_{min}, along with the threshold Daily ELVs below which the relative uncertainty associated with MPU_{min} would be higher than allowed, i.e., higher than the Confidence Interval (CI).

When this threshold D-ELV is within the BAT-AEL range, it is plotted as an orange square in the concentration plot for each species, as illustrated in Figure B-1. Otherwise, the orange square represents the threshold concentration below which the SRM measurement uncertainty exceeds the IED CI uncertainty. The orange dashed line in each plot simply indicates that the fixed absolute uncertainty results in an increasing relative uncertainty at concentrations lower than the threshold value.

Table B-1: Absolute uncertainty limits from The Netherlands

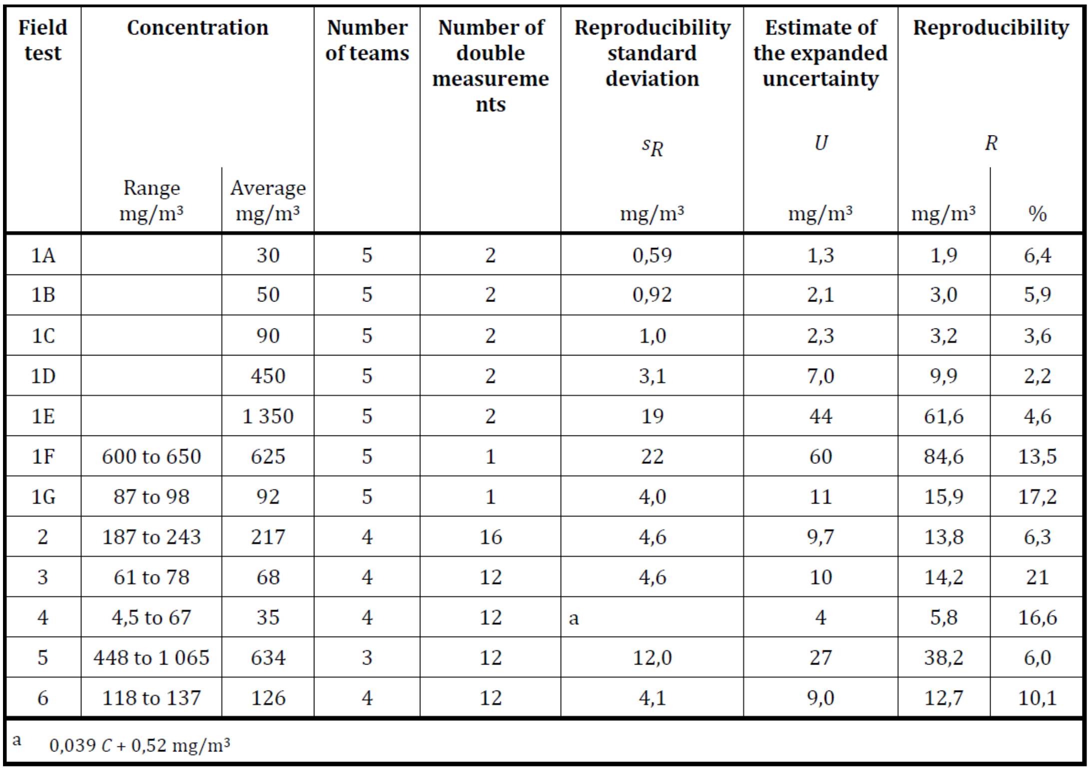
Species	**MPU_{min} mg/m^3**	**CI %**	**D-ELV mg/m^3**
NO_x	14.0	20%	70
SO_2	10.0	20%	50
CO	5.0	10%	50
Dust	1.5	30%	5
HCl	4.0	40%	10
HF	0.4	40%	1
Hg	0.004	40%	0.010
TOC	3.0	30%	10
NH_3	2.0	40%	5

B.3 NO_x

The field data for NO_x is provided in EN 14792, Annex A 'Validation of the method in the field' [B.1]. Table A.3 in that standard gives the Reproducibility in the field of the six field tests and also a column with the 'Estimate of the *expanded* uncertainty, U' and this table is reproduced as Table B-2 below. A linear function was derived for this uncertainty:
$U(C) = 0{,}038C + 4{,}4\ \text{mg/m}^3$ (Equation A.9 in EN 14792), where C is the mass concentration expressed in mg/m^3.

The NO_x concentration range from the lowest to the highest BAT-AEL, for Large Combustion Plant, is 15 - 165 mg/m^3. The NO_x concentration range in the EN field tests was considerably higher: 4.5 to 1350 mg/m^3. The results are plotted in Figure B-1. The green curve represents the linear uncertainty function from EN 14792. The blue curve is a 'power' function fit to all of the available data-points. Although this new function under-predicts the uncertainty at very low concentrations, below 10 mg/m^3, it is a much better representation of the data within the BAT-AEL concentration range.

Table B-2: EN 14792 Table A.3 (Reproducibility in the field)



Field test	Concentration Range mg/m³	 Average mg/m³	Number of teams	Number of double measurements	Reproducibility standard deviation s_R mg/m³	Estimate of the expanded uncertainty U mg/m³	Reproducibility R mg/m³	 %
1A		30	5	2	0,59	1,3	1,9	6,4
1B		50	5	2	0,92	2,1	3,0	5,9
1C		90	5	2	1,0	2,3	3,2	3,6
1D		450	5	2	3,1	7,0	9,9	2,2
1E		1 350	5	2	19	44	61,6	4,6
1F	600 to 650	625	5	1	22	60	84,6	13,5
1G	87 to 98	92	5	1	4,0	11	15,9	17,2
2	187 to 243	217	4	16	4,6	9,7	13,8	6,3
3	61 to 78	68	4	12	4,6	10	14,2	21
4	4,5 to 67	35	4	12	a	4	5,8	16,6
5	448 to 1 065	634	3	12	12,0	27	38,2	6,0
6	118 to 137	126	4	12	4,1	9,0	12,7	10,1

[a] $0{,}039\ C + 0{,}52\ \text{mg/m}^3$

The orange square in Figure B-1 is taken from the Dutch absolute uncertainty approach (70 mg/m^3 NO_x Daily ELV in Table B-1).

Figure B-1 shows that, at the concentration of the lowest BAT-AEL (15 mg/m^3) the relative *expanded* uncertainty is 30% from the standard linear formula which is unacceptably high. The newly calculated estimate of the uncertainty is circa 15% at 15 mg/m^3. Over most of the BAT-AEL range an *expanded* uncertainty of 10% is then maintained by the SRM in line with the maximum permissible *expanded* uncertainty for this SRM as referenced by the ROM (± 10%). The power law uncertainty function allows the threshold Daily ELV to be reduced to about 30 mg/m^3 in this analysis, as discussed in the main text (Section 5.2.2).

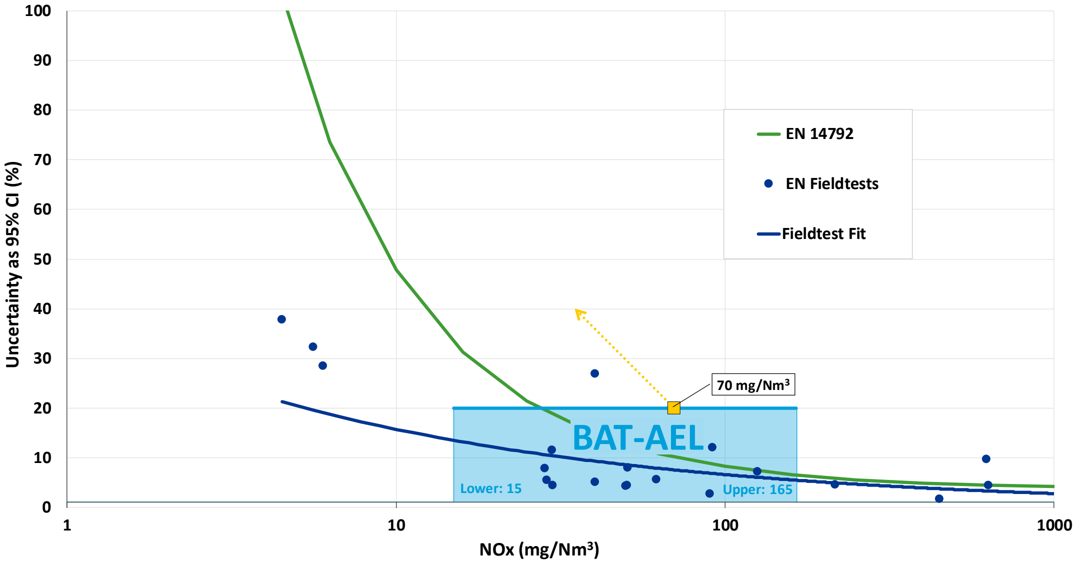


Figure B-1: NO_x performance from the field tests of EN 14792

B.3 SO_2 and CO

CEN also mandated extensive field tests for SO_2 and CO. The SO_2 SRM is based on extraction of a flue gas sample through impingers containing absorber solutions which are analysed subsequently by Ion Chromatography or the Thorin titration method. The results for the SO_2 SRM show substantially higher uncertainty compared with the direct measurement of NO_x by chemiluminescence.

The field data for SO_2 are provided in EN 14791, Annex A ‘Validation of the method in the field’ [B.2]. Table A.6 in that standard gives the Reproducibility in the field of the six field tests and also a column with the ‘Estimate of the *expanded* uncertainty’ for the Ion Chromatography method. A linear function was derived for this uncertainty: U(C) = 0,135C + 6,94 mg/m^3, where C is again the mass concentration expressed in mg/m^3. Table A.7 in the standard provides the same information for the Thorin titration method with U(C) = 0,168C + 1,617 mg/m^3 (noting that the standard contains a mis-print since it states that U(C) = 0,168C - 1,617 mg/m^3). Both *expanded* uncertainty functions were combined into one function U(C) = 0,152C + 2,662 mg/m^3.

Figure B-2 shows the results graphically using the same format as described previously.

Within the BAT-AEL range, from 25 to 165 mg/m^3, both the linear combined *expanded* uncertainty function, and the power law *expanded* uncertainty function, broadly achieve the 20% uncertainty requirement. This is in line with the maximum permissible *expanded* uncertainty for this SRM as referenced by the ROM (± 20%). The orange square defines a Daily ELV of 50 mg/m^3, below which the SRM does not formally comply with the IED and SRM uncertainty requirements of 20% based on both the linear and power law uncertainty functions. This aligns with the Dutch absolute uncertainty approach (50 mg/m^3 SO_2 Daily ELV in Table B-1).

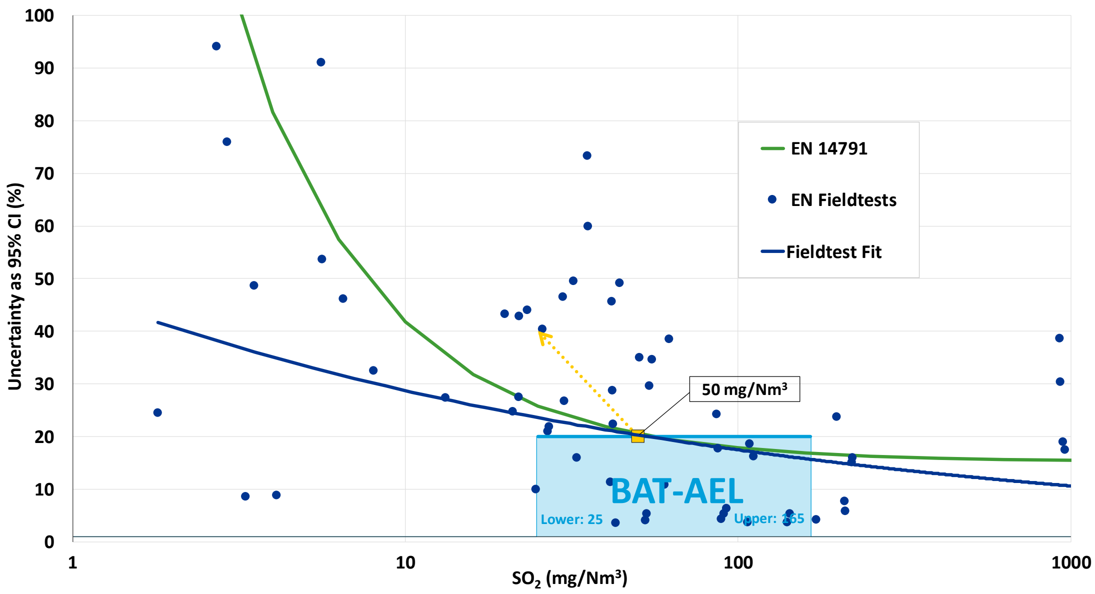


Figure B-2: SO_2 performance from the field tests of EN 14791

The field data for CO are provided in EN 15058, Annex A 'Validation of the method in the field' [B.3]. Table A.3 in that standard gives the Reproducibility in the field of the six field tests and also a column with the 'Estimate of the expanded uncertainty, U'. A linear function was derived for this *expanded* uncertainty: U(C) = 0,029C + 7,2 mg/m^3, where C is again the mass concentration expressed in mg/m^3. This relationship is plotted in Figure B-3 along with a power law fit to the original field trial data that is also shown in the graph.

Across most of the BAT-AEL range, from <5 to 100 mg/m^3, both the linear uncertainty function and the recalculated power law function do not attain the IED overall *expanded* uncertainty requirement of 10%. Neither are the results aligned with the maximum permissible SRM *expanded* uncertainty given in the SRM standard, as also referenced by the ROM (± 6%). Despite this, a lower minimum Daily ELV is specified in the Dutch approach (50 mg/m^3 CO Daily ELV in Table B-1). This may be because experience has shown that the method performance is generally better than indicated by the standard. However, the Dutch limit is also consistent with increasing the Confidence Interval from 10% to 20% as a number of countries allow for QA assessments.

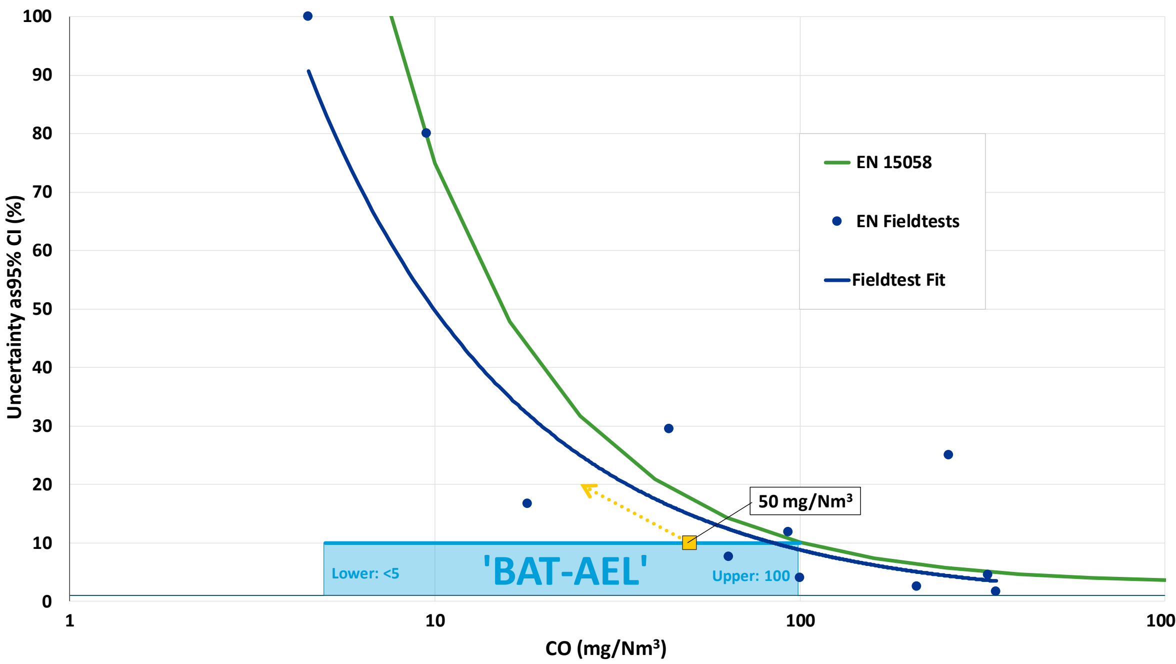


Figure B-3: CO performance from the field tests of EN 15058

B.4 DUST, HCl AND HF

The field data for Dust are provided in EN 13284-1, Annex A 'Performance characteristics of the method obtained in the method validation' [B.4]. Table A.1 in that standard gives the results of the validation tests. Only two field trials with 30 minutes sampling duration were performed. The data analysis provided a total Dust *expanded* uncertainty of 4.0 mg/m^3 at an average concentration of 6.4 mg/m^3 (ranging from 3 to 19 mg/m^3) and an *expanded* uncertainty of 1.8 mg/m^3 at an average concentration of 2.5 mg/m^3 (ranging from 0.3 to 6.8 mg/m^3). Using these results, it is possible to derive a linear function for the *expanded* uncertainty: U(C) = 0.56C + 0.39 mg/m^3, where C is again the mass concentration expressed in mg/m^3. This follows the approach in the other SRM standards as described above.

Within the BAT-AEL range from 3 to 11 mg/m^3 the linear uncertainty function does not attain the IED overall uncertainty requirement of 30%. Neither is this in line with the maximum permissible SRM *expanded* uncertainty referred to in the ROM (± 20%). This will typically be the case when sampling from 'wet' stacks containing water droplets. Sampling from 'dry' flue gas, i.e., when water is present only in the vapour phase, should result in significantly better performance, according to the standard. Increased the sampling duration from 30 min to 60 or 90 min, would also significantly improve the repeatability of the measurements. Even so, it will be difficult to achieve the IED uncertainty of 30% with the SRM at low Dust concentrations.

The orange square in Figure B-4 represents the Daily ELV of 5 mg/m^3, below which the IED uncertainty cannot be met by the SRM, under the most favourable SRM implementation, as demanded by EN 13284-1 and in line with the Dutch absolute uncertainty approach (5 mg/m^3 Dust Daily ELV in Table B-1). However, in many cases, this threshold Daily ELV is too low, resulting in QAL2 failures, as noted in the main text.

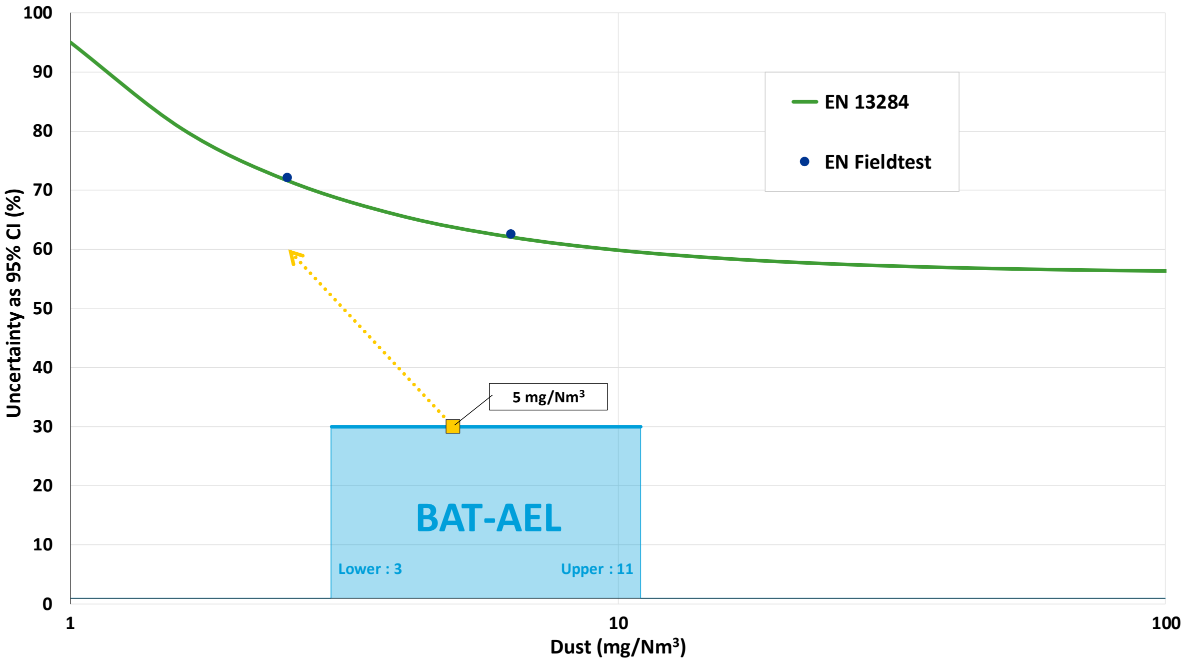


Figure B-4: Dust performance from the field tests of EN 13284-1

The field data for HCl are provided in EN 1911, Annex D ‘Performance characteristics of the whole measurement method’ [B.5]. Table D.1 in that standard gives the Reproducibility standard deviation which, when multiplied by a coverage factor of 2, gives the *expanded* uncertainty. Using these results, it is possible to derive a linear function for the *expanded* uncertainty: U(C) = 0,052C + 0,62 mg/m^3, where C is again the mass concentration expressed in mg/m^3. This follows the approach in the other SRM standards given above. However, a suitable power law fit can also be derived, albeit based upon limited data.

Below 2 mg/m^3, within the BAT-AEL range from (<)1 to 4 mg/m^3, the linear *expanded* uncertainty function does not comply with the overall IED uncertainty requirement of 40%. This increases to a threshold of 2.5 mg/m^3 in order to align with the maximum permissible SRM *expanded* uncertainty in the ROM (± 30%). The Daily ELV would need to be considerably higher than this in order to achieve an acceptable uncertainty across a meaningful concentration range, based upon the given SRM performance.

In this case, the orange square in Figure B-5 represents the threshold concentration below which the SRM measurement uncertainty exceeds the IED CI uncertainty (2 mg/m^3). However, it can be seen that the uncertainty relationships are based upon three widely scattered data points at about 4 mg/m^3 and these relationship are unlikely to be reliable. For that reason, a higher uncertainty threshold would be appropriate, e.g., that specified in the Dutch absolute uncertainty approach (10 mg/m^3 HCl Daily ELV in Table B-1). Further HCl validation work is clearly required as already proposed by CEN Working Group 3.

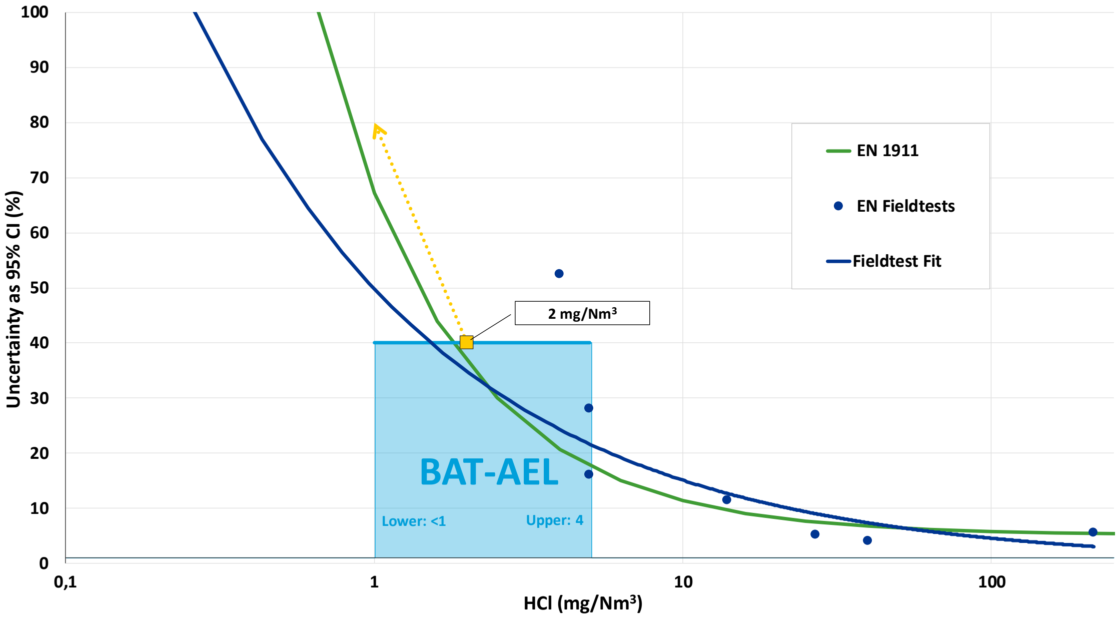


Figure B-5: HCl performance from the field tests of EN 1911

The CEN Technical Specification for HF (CEN/TS 17340 [B.6]) does not provide field test data. Annex E of that specification gives an example *expanded* uncertainty calculation at a concentration of 5 mg/m^3, giving U = 0,64 mg/m^3 for a single laboratory. However, the inter-laboratory uncertainty, which includes the variations associated with sampling and recovery of HF, will be substantially larger. To account for this, the overall *expanded* method uncertainty is estimated to be 2 * 0,64 = 1,28 mg/m^3 at 5 mg/m^3. At a lower concentration of 1 mg/m^3, it is estimated that this uncertainty will, at best, be half of 1,28 mg/m^3 , i.e., an *expanded* uncertainty of 0,64 mg/m^3 at 1 mg/m^3. These two estimates can be used to derive a linear uncertainty function: U(C) = 0,16C + 0,48 mg/m^3, where C is again the mass concentration expressed in mg/m^3.

Within the BAT-AEL range from (<)1 to 3 mg/m^3, this linear *expanded* uncertainty function does not attain the 40% uncertainty requirement. There is no stated maximum permissible *expanded* SRM uncertainty in the ROM. However, the analytical methodology and concentration range is similar to the HCl SRM. Only field test validation data or other inter-laboratory trials - at these low concentrations - can be used to derive the actual method performance.

In this case, the orange square in Figure B-6 again represents the threshold concentration below which the SRM measurement uncertainty exceeds the IED CI uncertainty (2 mg/m^3), although this is based on very limited data and the above assumptions. The Dutch absolute uncertainty approach specifies a very low Daily ELV (1 mg/m^3 HF Daily ELV in Table B-1) but this is likely to be an arbitrary assignment, noting that HF monitoring is uncommon and actual HF concentrations are vanishingly small such that the AMS is often calibrated using reference materials.

A full validation of the Technical Specification, focussing on very low concentrations, is clearly required.

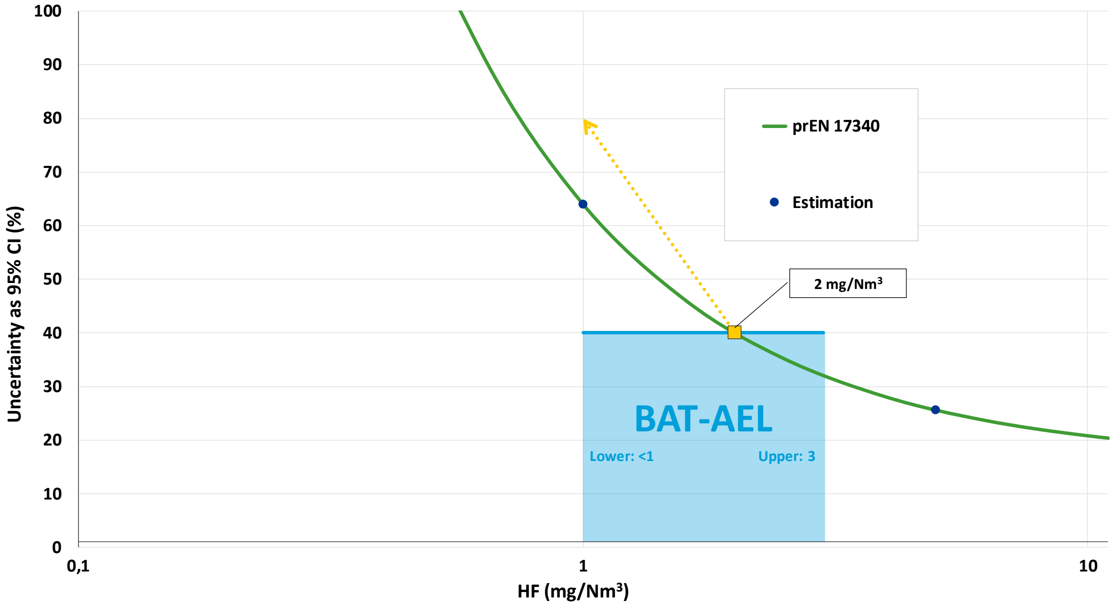


Figure B-6: HF performance from the uncertainty calculation in prEN 17340

B.6 MERCURY, HEAVY METALS AND Cd+Tl

The field data for mercury (Hg) is provided in EN 13211 [B.7] in ‘8.2 Performance characteristics’. The detection limit is calculated to be 2.6 µg/m^3. At this concentration the relative standard deviation of the validation results is 33% = 0.87 µg/m^3. The estimate for the *expanded* uncertainty is then 2 * 0.87 = 1.7 µg/m^3. The *expanded* uncertainty of 2.5 µg/m^3, in the concentration range 4 - 10 µg/m^3, is calculated from 12 parallel measurements. From these three points, a linear equation for the uncertainty function can be derived as follows:

$U(C) = 0.073C + 1.84\ \mu g/m^3$, where C is the mass concentration expressed in µg/m^3.

Within the BAT-AEL range from (<)1 to 4 µg/Nm^3 the linear function does not comply with the common specified *expanded* uncertainty requirement of 40%. This is not surprising as the trace Hg concentration is 1000 times lower than the other gas phase species considered. The inter-laboratory uncertainty can then easily be more than two times higher than this. The ROM does not give a maximum permissible *expanded* SRM uncertainty. Only validation field trial data or data from other inter-laboratory trials - at these low concentrations - can be used to derive the actual method performance.

In this case, the orange square in Figure B-7 represents the uncertainty target at the top of this BAT-AEL range (4 µg/m^3) which implies that the Daily ELV needs to be higher than this concentration, noting that the Dutch absolute uncertainty approach implies a Daily ELV of 10 µg/m^3 (Table B-1). However, the current method uncertainty is better than indicated by EN 13211, due to improvements in both sampling and analysis across the past 20 years, and a unilateral re-validation of the standard is underway in Germany, as sponsored by the German Environment Agency. This will also include validation of an alternative sorbent trap method defined in TS 17286:2019 [B.8].

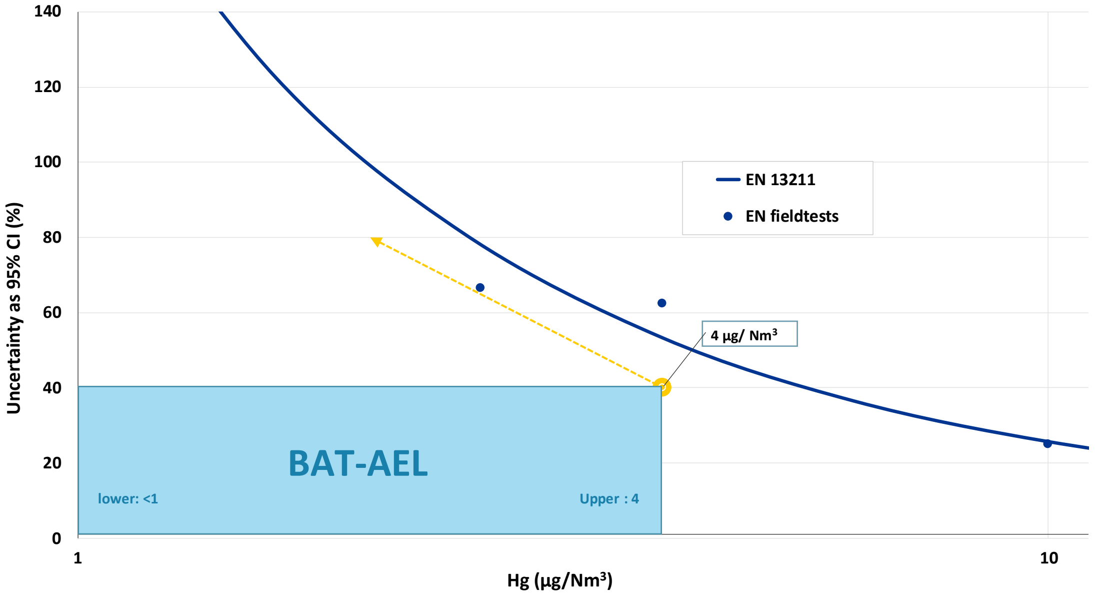


Figure B-7: Hg performance from the field test data in EN 13211

The field trial data for the sum of nine heavy metals, and (Cd+Tl), is provided in EN 14385 [B.9], in Annex D ‘Measurement results of two field tests’. Table D.3 in that standard (Reproducibility) gives the *expanded* uncertainty for all of the metals measured in both field tests.

The individual uncertainties of the nine heavy metals are squared and summed, then the square root is taken, to calculate the uncertainty of the sum of the nine heavy metals. The field test data are at relatively high concentrations (79 and 343 µg/Nm^3). DNV performs mass balances at coal fired power plant, at concentrations between 1 - 5 µg/Nm^3. At these low concentrations the uncertainty for the individual metals is estimated to be three times the concentration. Table B-3 provides the calculation for the sum of nine heavy metals.

Figure B-8 shows the three calculated uncertainties from Table B-3 in one graph.

The field test 2 result then has a much higher uncertainty (81%) than expected, despite the higher concentration, which is a cause for concern. However, it is evident that the uncertainty of the SRM is no better than 60%, across the BAT-AEL range, based on these limited data.

For Cd+Tl, the BAT-AEL range is from 5 to 6 µg/Nm^3. Field test 1 shows a calculated uncertainty of 72% at 3.3 µg/m^3. Within the range of the BAT-AEL, an *expanded* uncertainty of 60% would also be applicable based upon this data.

Table B-3: Field test data from EN 14385 and DNV mass balance data in µg/Nm^3

	First field test		**Second field test**		**Mass balance coal**	
	Average	**U**	**Average**	**U**	**Median**	**U**
As	3.2	9.4	1.4	3.5	0.08	0.24
Co	0.4	1.3	1.5	3.7	0.06	0.18
Cr	3.4	5.4	7.6	34.0	0.17	0.51
Cu	11.0	12.0	32.0	34.0	0.17	0.51
Mn	4.0	2.1	4.9	8.0	0.80	2.40
Ni	2.8	3.9	5.6	21.0	0.25	0.75
Pb	47.0	24.0	280.0	272.0	0.22	0.65
Sb	5.8	5.5	8.2	10.0	0.03	0.08
V	1.5	4.0	2.0	5.4	0.52	1.55
∑9HM	79.1	30.1	343.2	277.4	2.3	3.1
	Relative:	38%	Relative:	81%	Relative:	137%
Cd	2.9	2.3	7.6	11.0	0.005	0.025
Tl	0.4	0.6	13.0	50.0	0.010	0.050
Cd+Tl	3.3	**2.4**	20.6	51.2	**0.015**	0.056
	Relative:	72%	Relative:	249%	Relative:	373%

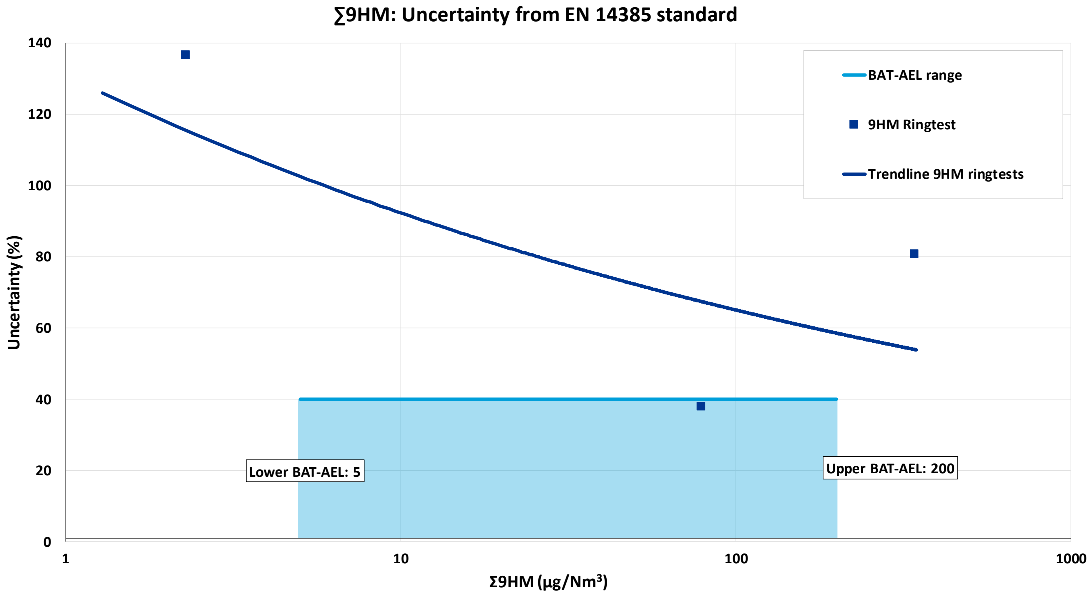


Figure B-8: Calculated performance data from EN 14385

B.7 REFERENCES

[B.1] EN 14792:2017 Stationary source emissions - Determination of mass concentration of nitrogen oxides - Standard reference method: chemiluminescence

[B.2] EN 14791: 2017 Stationary source emissions - Determination of mass concentration of sulphur oxides - Standard reference method

[B.3] EN 15058:2017 Stationary source emissions - Determination of the mass concentration of carbon monoxide - Standard reference method: non-dispersive infrared spectrometry

[B.4] EN 13282-1:2017 Stationary source emissions - Determination of low range mass concentration of dust - Part 1: Manual gravimetric method

[B.5] EN 1911:2010 Stationary source emissions - Determination of mass concentration of gaseous chlorides expressed as HCl - Standard reference method

[B.6] CEN/TS 17340:2020 Stationary source emissions – Determination of mass concentration of fluorinated compounds expressed as HF – Standard reference method

[B.7] EN 13211:2001 Air quality - Stationary source emissions - Determination of the concentration of total mercury

[B.8] CEN/TS 17286:2019 Stationary source emissions - Mercury monitoring using sorbent traps

[B.9] EN 14385:2004 Stationary source emissions - Determination of the total emission of As, Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, Tl and V

APPENDIX C

UNCERTAINTY RELATED TO THE SRM SAMPLING POSITION

C.1 IMPORTANCE OF REPRESENTATIVE SAMPLING

Obtaining a representative sample of flue gas is critically important for both the Automated Measuring System (AMS) and the Standard Reference Method (SRM) measurement system. The spatial deviation in pollutant concentration across a measurement plane must be taken into account when assessing the uncertainty of a measurement. Deviation from the mean at the AMS sampling location is corrected by the QAL2 calibration established under EN 14181 [C.1], provided that the SRM sampling location is fully representative. Deviation from the mean at the SRM sampling location depends on the type of SRM employed. If the SRM specifies a grid sampling approach, as is the case for most wet chemical methods and gravimetric Dust determination, it can be assumed that this spatial variation is accounted for.

However, when the SRM sample is extracted from a single point, the uncertainty related to the SRM location must then be considered. This is typically the case when the SRM is defined as an on-line instrumental method, such as NO_x, CO and O_2 SRMs, and the sampling location meets the requirements of the European stack gas sampling standard, EN 15259 [C.2]. This is also the case when a wet chemical SRM is replaced by an instrumental Alternative Method (AM) having first established equivalency with the SRM under EN 14793:2017 [C.3], as is commonly the case, in many European Member States, for acid gases such as SO_2. In some circumstances, even a wet chemical SRM does not require grid sampling, as is the case for mercury when the mercury content of the flue gas particulate can be neglected and sampling is conducted non-isokinetically [C.4].

The importance of representative sampling is highlighted in the IED in relation to Waste Incineration Plant which specifies that the Competent Authority is required to approve the sampling location.

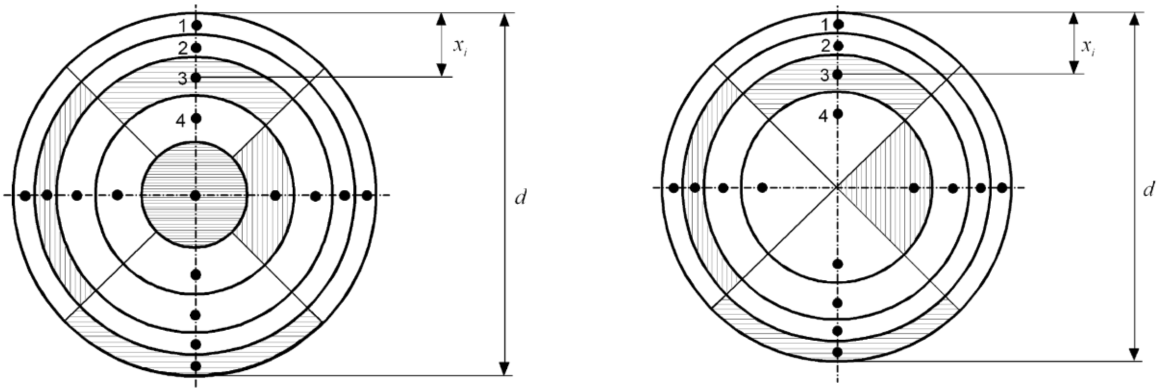
C.2 STANDARDS AND ACCEPTANCE CRITERIA

Prior to the adoption of EN 15259, relatively simple criteria were used for the assessment of sampling representativeness and these are considered first since they are relevant when considering the positional uncertainty, in the pollutant concentration, that is associated with single point sampling.

ISO 10396 [C.5] notes that, whilst it is important that the sampling point is not located near any obstructions that could seriously disturb the gas flow in the stack, the pollutant of interest may still have ‘cross-sectional variation’. ISO 10396 therefore requires that a stratification survey is conducted using an automated analytical method to measure the concentration of the pollutant (restricted to NO_x, SO_2 or CO), ***and*** the diluent concentration (O_2 or CO_2), at multiple points of equal area across the measurement plane (two minutes sampling duration at each point). The pollutant or diluent gas is considered to be ‘non-stratified’ if the concentration at all of the individual traverse points is within ±10% of the arithmetic average concentration. Temporal fluctuations are monitored by simultaneously sampling from the centre of the stack. If the gas concentration is non-stratified, any sampling point located between one-third and half of the stack diameter can be selected. If the gas concentration is ‘stratified’ an alternative monitoring location or a permanent multi-point grid sampling system is required.

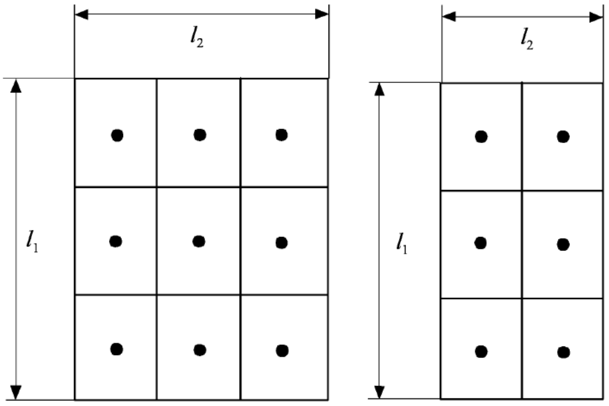
US EPA Method 7E [C.6] recommends that measurement planes are located at least eight stack diameters downstream and at least two diameters upstream of the nearest flow disturbances. Method 7E also requires a stratification survey is conducted, for a single pollutant ***or*** diluent, in order to determine the appropriate number of representative sampling points. The pollutant is considered to be 'non-stratified' if the concentration at all of the individual traverse points is within ±5% of the average concentration and is 'minimally stratified' if all of the traverse point concentrations are within ±10% of the average.

EN 15259:2007 [C.2] recommends that measurement planes are located at least five stack diameters (5D) downstream and at least two diameters (2D) upstream of the nearest flow disturbances. In common with the methods described earlier, for the purposes of conducting a duct survey, a stack of greater than 2m diameter (D), with a circular cross-section, is sub-divided into equal areas giving the sample points shown in Figure C-1, located at x_i. The larger the duct cross-sectional area, the larger the number of sampling points, noting that 20 points are considered to be sufficient for large stacks. A similar approach is adopted for rectangular exhaust ducts, as shown in Figure C-2.



a) General method (including centre-point) b) Tangential method (excluding centre-point)

Figure C-1: Sample point positions at centres of equal area in large circular ducts



a) $l_1/l_2 \leq 2$ b) $l_1/l_2 > 2$

Figure C-2: Sample point positions at centres of equal area in rectangular ducts

It should be noted that the recommended minimum lengths of straight ductwork, either side of the measurement plane, are focussed on flow uniformity, i.e., the avoidance of flow recirculation, swirling flow and extremes in maximum to minimum velocity ratios. These guidelines do not address inhomogeneity in gas concentration. If an abatement unit, such as a Flue Gas Desulphurisation (FGD) unit at a coal fired power plant, is located only 5 diameters upstream of the measurement plane then significant stratification/inhomogeneity in concentration may still be present.

EN 15259 specifies a different approach for assessing homogeneity of the gases when compared with previous standards. The standard deviation of the spatially varying concentration measured across the above traverse points, s_{grid}, is first calculated. This is compared with the standard deviation of the time-dependent concentration measured during the traverse at a fixed reference point, s_{ref}. The quantity s_{grid} nominally describes the spatial variation across the measurement plane but also incorporates the temporal variations that are described by s_{ref}. Both s_{grid} and s_{ref} include the analytical repeatability of the measuring instrument. If the concentration distribution is deemed to be homogeneous, an SRM sample can be extracted from any point within the measurement plane.

If the spatial variation is less than the temporal variation ($s_{grid} \leq s_{ref}$) then the distribution is automatically assumed to be homogenous. Otherwise, an F-factor is calculated as the ratio of the two variances (F-factor = s_{grid}^2/s_{ref}^2) and this must be less than a critical F-Factor ($F_{N-1;N-1;0,95}$) for the distribution to be deemed homogeneous. The critical F-factor is defined as a function of the number of grid points (N). For the most common power plant case of N = 20, that is, the maximum number of points within a large duct, the value of $F_{N-1;N-1;0,95}$ is 2.17. The distribution is then homogenous when $s_{grid}^2/s_{ref}^2 < 2.17$, equivalent to $s_{grid} < 1.47 * s_{ref}$. That is, the spatial variation cannot be more than about 50% higher than the temporal variation in order for the spatial distribution to be considered homogenous.

Because the EN 15259 acceptance criterion is based on the relationship between spatial and temporal deviations, rather than the absolute thresholds discussed previously, it is possible for this test to deliver a false FAIL when both the spatial and temporal (process) variations are very low. This is often the case at Combined Cycle Gas Turbine (CGGT) plant, requiring additional national guidance to address this issue. For example, in England the location is considered to be homogeneous when $s_{grid} < 5\%$ of the Daily ELV or $s_{grid} < 0.3\ \%O_2$ for oxygen [C.7]. The power industry has also highlighted the additional possibility of a false PASS of the homogeneity test when the spatial and temporal variations are both high [C.8].

Following a failure of the homogeneity test, there is a further test to determine the severity of the inhomogeneity. The *standard* uncertainty relating to the spatial deviation alone, i.e., the positional uncertainty, s_{pos}, is calculated by subtracting the time-dependent variance from the spatial variance: $s_{pos} = \sqrt{(s_{grid}^2 - s_{ref}^2)}$. This positional uncertainty is considered later.

The expanded positional uncertainty, U_{pos}, is then calculated using a Student t-factor, $t_{N-1;0,95}$, again defined in the standard as a function of the number of grid points, N. For the most common power plant case of N = 20, the value of $t_{N-1;0,95}$ is 2.093. The *expanded* uncertainty is then $U_{pos} = 2.093 * s_{pos}$. The t-factor is essentially a coverage factor that accounts for the finite number of traverse points. If the positional uncertainty, U_{pos}, is less than 50% of the maximum permissible uncertainty defined in EN 14181 [C.1], then the single measurement point closest to the average concentration can be selected, otherwise, grid sampling is required at that location. However, it needs to be recognised that the optimal sampling position may be different for different pollutants and a compromise sampling position may be required.

EN 15259 does not specify which pollutants are subject to a homogeneity survey and it is common practice to use a surrogate, such as O_2, to represent other pollutants. However, the O_2 homogeneity reflects the overall combustion process and is insufficient when considering homogeneity downstream of abatement systems, e.g., SO_2 assessment is required for coal fired power plant fitted with FGD in the UK.

C.3 POSITIONAL UNCERTAINTY

When considering the *standard* uncertainty that is applicable for a single SRM measurement taken from within a 'homogeneous' concentration distribution, the various tolerances and approaches within the relevant standards, described in Section C.2, can be considered. Table C-1 gives an overview of the applicable tolerances within the available regulatory documents and standards.

When a tolerance is defined, specifying that the grid point concentrations must be within ± 10% of the mean concentration, for example, it is standard practice to assume a rectangular probability distribution, i.e., the true spatial variation has an equal probability of falling anywhere within the tolerance. The tolerance half-width (10% in this example) is then divided by √3 [=1.732] in order to obtain the *standard* uncertainty, giving ± 5.8% for the same example. The range of maximum relative *standard* uncertainty based upon tolerances is then ± 2.9% to ± 5.8%.

It should be noted that the criterion in the national document, MID EN 15259, is applicable only in situations where the homogeneity test would otherwise fail, as noted in Section C.2 above.

Table C-1: Summary of homogeneity criteria and tolerances

Document	Pollutant and/or diluent	Description	Criterion	Coverage factor	Standard uncertainty
ISO 10396	NO_x, SO_2, CO and O_2 or CO_2	Non-stratified	± 10%	√3	± 5.8%
US EPA Method 7E	Any one pollutant or diluent	Non-stratified	± 5%	√3	± 2.9%
		Minimally-stratified	± 10%	√3	± 5.8%
EN 15259	Each relevant pollutant or a suitable surrogate	Homogeneous	$s^2_{grid}/s^2_{ref} < 2.17$	-	$\sqrt{(s^2_{grid} - s^2_{ref})}$
MID EN 15259	NO_x, SO_2, CO, TOC and O_2	Homogeneous	$s_{grid} < 5\%$	-	± 5.0%

The *standard* uncertainty defined in EN 15259 [$s_{pos} = \sqrt{(s_{grid}^2 - s_{ref}^2)}$] can be obtained directly from duct survey test results. However, in many situations the spatial and temporal variations are of a similar magnitude ($s_{grid} \approx s_{ref}$) and s_{pos} cannot be determined since only a positive square root can be evaluated.

In order to evaluate the spatial variation in all situations, both the reference and the grid concentrations are therefore first corrected to the standard oxygen reporting condition (O_{2rep}), i.e., 6 %O_2 dry for solid fuel firing and 15 %O_2 dry for CCGT. The oxygen correction is given in (Annex C, EN 15259):

$c_{grid,i,rep} = c_{grid,i} * (21 – O_{2rep}) / (21 – O_{2grid,i})$

and

$c_{ref,i,rep} = c_{ref,i} * (21 – O_{2rep}) / (21 – O_{2ref,i})$

Since the oxygen is continuously measured at every point, this takes account of variations that are solely related to dilution since these are eliminated when later correcting emissions for compliance reporting.

The grid values are then finally corrected for temporal (t) variations using the results from the fixed reference point, as follows, using the average of the oxygen corrected reference point measurements $\check{c}_{ref,rep}$):

$c_{grid,i,t} = c_{grid,i,rep} * \check{c}_{ref,rep} / c_{ref,i,rep}$

The standard deviation of the grid concentration distribution, having corrected for both temporal and oxygen variations, is then a direct measure of the *standard* uncertainty relating to the spatial variations alone ($s_{grid,t}$).

Compliant duct survey test data for SO_2 from 16 coal fired units fitted with wet limestone-gypsum FGD absorbers, and 5 units without FGD, are summarised in Table C-2. The relative standard deviations for both the grid and the reference points, based on raw concentration measurements, are presented, along with the positional uncertainty defined in EN 15259 (s_{pos}) for the cases where this quantity could be derived.

Taking the case of coal fired FGD units with sampling at the Stack (the first row of data in Table C-2), the average values of s_{grid} and s_{ref} are both 11.1% with maximum values of 20.0 and 22.0%, respectively. The positional uncertainty [$s_{pos} = \sqrt{(s_{grid}^2 - s_{ref}^2)}$] takes temporal variations into account and this has an average value of 5.9% and a maximum value of 10.5% across the 5 out of 9 cases where it was possible to calculate s_{pos}. The average value of the oxygen and time corrected standard deviation ($s_{grid,t}$), across all of the cases, is 4.8% with a maximum of 11.3% and this is very similar to the s_{pos} results. This confirms that the distribution of fully corrected grid concentrations provides a reasonable measure of the positional uncertainty. If the maximum value of $s_{grid,t}$ is removed as an outlier, the next highest value of 6.7% is much closer to the average value. The average and maximum SO_2 concentrations for this case are 213 and 331 mg/m^3, respectively.

These results for the best (Stack) sampling location suggest that the maximum *standard* uncertainty of ±5.8%, based on ISO 10396, is appropriate for abated acid gases, although the maximum uncertainties seen in practice can be higher. Even higher relative deviations, of up to 50%, are apparent when the outlet SO_2 concentration is very low (< 21 mg/m^3 or 7 ppm). However, these cases have been excluded from the current analysis, even though the homogeneity test was passed, since it is not possible to determine how much of the variation is related to the measurement uncertainty of the analyser at such low concentration levels. It follows that, as the monitoring technology improves, EN 15259 testing should be repeated.

Table C-2: Summary of SO_2 duct survey results from coal fired power station

SO_2			**RAW CONCENTRATION**							**CORRECTED FOR O_2 and t**			
Plant type	**SRM Location**	**No. units**	**s_{grid}**		**s_{ref}**		**s_{pos}**			**$s_{grid,t}$**		**$SO_{2\ grid}$ mg/m^3**	
			Mean	Max	**Mean**	Max	**Mean**	Max	#	**Mean**	Max	**Mean**	Max
Coal with FGD	Stack	9	**11.1%**	20.0%	**11.1%**	22.0%	**5.9%**	10.5%	5	**4.8%**	11.3%	213	331
Coal with FGD	FGD Outlet	7	**17.2%**	31.1%	**17.5%**	32.4%	**8.1%**	13.7%	3	**7.4%**	14.7%	298	715
Coal with FGD	FGD Inlet	15	**7.9%**	51.2%	**8.7%**	53.6%	**1.7%**	3.0%	9	**3.2%**	9.2%	1492	3638
Coal without FGD	Stack Inlet	5	**3.7%**	6.0%	**3.3%**	5.4%	**1.8%**	2.6%	5	**2.6%**	3.6%	919	1071

The results for the next case in Table C-2 contain a further 7 coal-fired units with sampling further upstream, between the FGD Outlet and the Stack location, and the positional uncertainties are unsurprisingly somewhat higher than the first case considered. The average value of s_{pos} increases from 5.9% to 8.1%, as shown in Table C-2. Higher values can be obtained in these non-ideal sampling locations, as illustrated by the two highest values in this data set of 12.3% and 14.7%. A *standard* uncertainty of ± 8.7%, equivalent to a tolerance of ± 15% across the sample plane, is more appropriate in these situations.

The remaining two cases in Table C-2 are related to higher absolute SO_2 concentrations at the FGD Inlet (measured at 15 units) or the Stack Inlet at the 5 unabated units. The uncertainties are lower, as expected, being of the order of 2 to 3% of the higher mean concentration.

Although variations in oxygen are largely taken into account in the above analysis, the variations in the oxygen concentration are shown separately in Table C-3. For the coal fired units, the relative positional uncertainty is about 2 to 4%, on average, with a maximum of about 6%. This is much lower than for Stack SO_2 for coal fired units with FGD. Variation in O_2 at the Stack location is governed by the residence time and fluid mixing between the Boiler and the Stack, in addition to air in-leakage. Variation in SO_2 at the Stack location is governed by the performance of the FGD absorber along with the lower residence time and reduced fluid mixing between the FGD Outlet and the Stack. It follows that O_2 is not a good surrogate for SO_2 in these processes but SO_2 is expected to be an acceptable surrogate for other acid gases, such as HCl and HF, which are also abated by absorption. This may also be the case for mercury since the oxidised portion of the mercury in the flue gas is absorbed in the FGD unit.

Table C-3: Summary of O_2 duct survey results from coal fired power stations

O_2			**RAW CONCENTRATION**							**CORRECTED FOR t**			
Plant type	**SRM Location**	**No. units**	**s_{grid}**		**s_{ref}**		**s_{pos}**			**$s_{grid,t}$**		**$O_{2\ grid}$ %vol**	
			Mean	Max	**Mean**	Max	**Mean**	Max	#	**Mean**	Max	**Mean**	Max
Coal with FGD	Stack	9	**3.5%**	8.8%	**3.4%**	8.4%	**1.4%**	2.4%	7	**2.1%**	3.6%	7.3	8.3
Coal with FGD	FGD Outlet	7	**6.8%**	13.5%	**5.6%**	10.6%	**3.7%**	7.7%	7	**3.0%**	5.5%	6.7	9.4
Coal with FGD	FGD Inlet	15	**4.5%**	13.2%	**4.5%**	12.3%	**1.9%**	5.5%	11	**3.0%**	5.1%	7.3	8.8
Coal without FGD	Stack Inlet	5	**4.8%**	10.6%	**3.9%**	8.8%	**2.9%**	4.8%	4	**3.7%**	5.2%	7.6	8.2

Compliant duct survey test data for NO_x from the same 16 coal fired FGD units and 5 unabated coal fired units are summarised in Table C-4. The final case in Table C-4 summarises data from an additional 34 CCGT units. As before, the relative standard deviations of both the grid and the reference points, based on raw concentration measurements, are presented, along with the positional uncertainty defined in EN 15259 (s_{pos}) for the cases where this quantity could be derived. Also presented are the relative standard deviation ($s_{grid,t}$) of the fully corrected grid concentrations, for all of the cases, along with the mean NO_x concentrations.

Table C-4: Summary of NO_x duct survey results from power stations

NO_x			**RAW CONCENTRATION**							**CORRECTED FOR O_2 and t**			
Plant type	**SRM Location**	**No. units**	**s_{grid}**		**s_{ref}**		**s_{pos}**			**$s_{grid,t}$**		**$NO_{x\ grid}$ mg/m^3**	
			Mean	Max	**Mean**	Max	**Mean**	Max	#	**Mean**	Max	**Mean**	Max
Coal with FGD	Stack	9	**3.3%**	11.5%	**3.2%**	11.2%	**0.8%**	1.9%	7	**2.2%**	3.7%	477	537
Coal with FGD	FGD Outlet	7	**5.3%**	7.7%	**6.6%**	11.7%	**2.6%**	3.1%	2	**3.9%**	9.8%	405	491
Coal with FGD	FGD Inlet	0	**-**		**-**		**-**			**-**		Not measured	
Coal without FGD	Stack Inlet	5	**6.0%**	19.1%	**5.8%**	19.8%	**2.0%**	2.4%	3	**2.5%**	3.9%	530	676
CCGT	Stack	30	**3.7%**	21.2%	**3.5%**	21.1%	**2.1%**	6.8%	17	**2.1%**	4.7%	34	69

None of the these units are fitted with NO_x abatement so, as might be expected, the average relative *standard* uncertainty is similar in all cases and this is about 2.5% (based on $s_{grid,t}$). On the same basis, the maximum uncertainty value is 9.8% for a single coal fired unit when sampling upstream of the stack but, once this is removed as an outlier, there are several $s_{grid,t}$ values at circa 5% amongst the other coal fired units. The maximum CCGT uncertainty of 4.7% corresponds with the only GT exhaust duct location within the data set and the next highest CCGT value of 4.3% (not tabulated) is from a supplementary fired Heat Recovery Steam Generator (HRSG) fitted with grid burners. In both of these situations, the homogeneity of NO_x concentration is expected to be worse than for the standard CCGT case.

In most cases, it has not been possible to obtain meaningful results for CO since emission concentrations tend to be either close to zero or high and variable. During normal operation, the behaviour of unabated CO emissions is expected to be close to that of unabated NO_x since both species are formed within the combustion system. However, greater variation in CO formation between individual burners is to be expected since, below a critical firing temperature, CO increases exponentially. For example, one of the CCGT units in this study was run at low load with an uneven outlet CO distribution, producing a fully corrected Stack CO concentration of 41 mg/m^3 and a relative standard deviation ($s_{grid,t}$) of 4.7%. The equivalent NO_x deviation was 2.5% thus illustrating the point that uneven CO production within the combustion system produces a higher variation at the Stack.

C.4 CONCLUSIONS

Positional uncertainty, related to a single SRM measurement taken at any random point within a sample plane that is deemed to be homogeneous according to EN 15259, can be characterised by the relative standard deviation of the grid concentrations obtained from a duct survey test, having fully corrected these for oxygen and temporal variations. This quantity is the most relevant for compliance purposes and is very similar in magnitude to the positional uncertainty obtained by direct calculation from the grid and reference point variations, as specified in EN 15259, which cannot be evaluated in all situations.

EN 15259 does not specify a maximum allowed deviation across the measurement plane but ISO 3096 specifies that all of the grid points must be within ±10% of the mean concentration. Assuming a coverage factor of √3 for this tolerance, based on an assumed rectangular probability distribution, this results in a *standard* uncertainty of ±5.8%.

Based on the duct survey data reviewed for multiple coal fired FGD units and multiple CCGT units, a *standard* uncertainty of ±5.8% is sufficient in most cases, including the measurement of abated species at coal fired plant, when sampling from the Stack location. Oxygen is not a suitable surrogate for abated acid gases such as SO_2. However, SO_2 is expected to be a suitable surrogate for other acid gases, such as HCl and HF, and possibly mercury. A *standard* uncertainty of ±5.8% is also sufficient to cover CO measurement at CCGT units, supplementary firing at CCGT units and also sampling from gas turbine exhaust duct locations during normal operation.

Higher uncertainties are applicable at sampling locations upstream of the Stack that are closer to the source of the emission variation, typically ±8.7% for abated processes which is equivalent to a tolerance of ±15% across the sampling plane. Lower uncertainties are applicable when sampling from the Stack from unabated processes, typically ±2.9%, equivalent to a tolerance of ±5% across the sampling plane.

It is not generally possible to obtain a meaningful uncertainty assessment for ultra-low or highly time-dependent concentrations. For example, ultra-low SO_2 concentrations from coal fired FGD units, ultra-low CO concentrations from CCGT units during normal operation or highly variable spatial and/or time-dependant variations in CO during abnormal plant operation.

The new plant sampling guidelines in EN 15259 do not guarantee complete homogeneity of concentration since this depends primarily on the proximity of the combustion or abatement system to the sampling location. It should be noted that it is usual practice to conduct only a single duct survey at base load operating conditions. Uncertainties related to changes in the concentration distribution as the plant load is varied, or year-on-year variation related to degradation of combustion or abatement systems has therefore not been considered.

C.5 REFERENCES

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[C.6] United States Environmental Protection Agency, Method 7E—Determination of nitrogen oxides emission from stationary sources (instrumental analyser procedure).

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