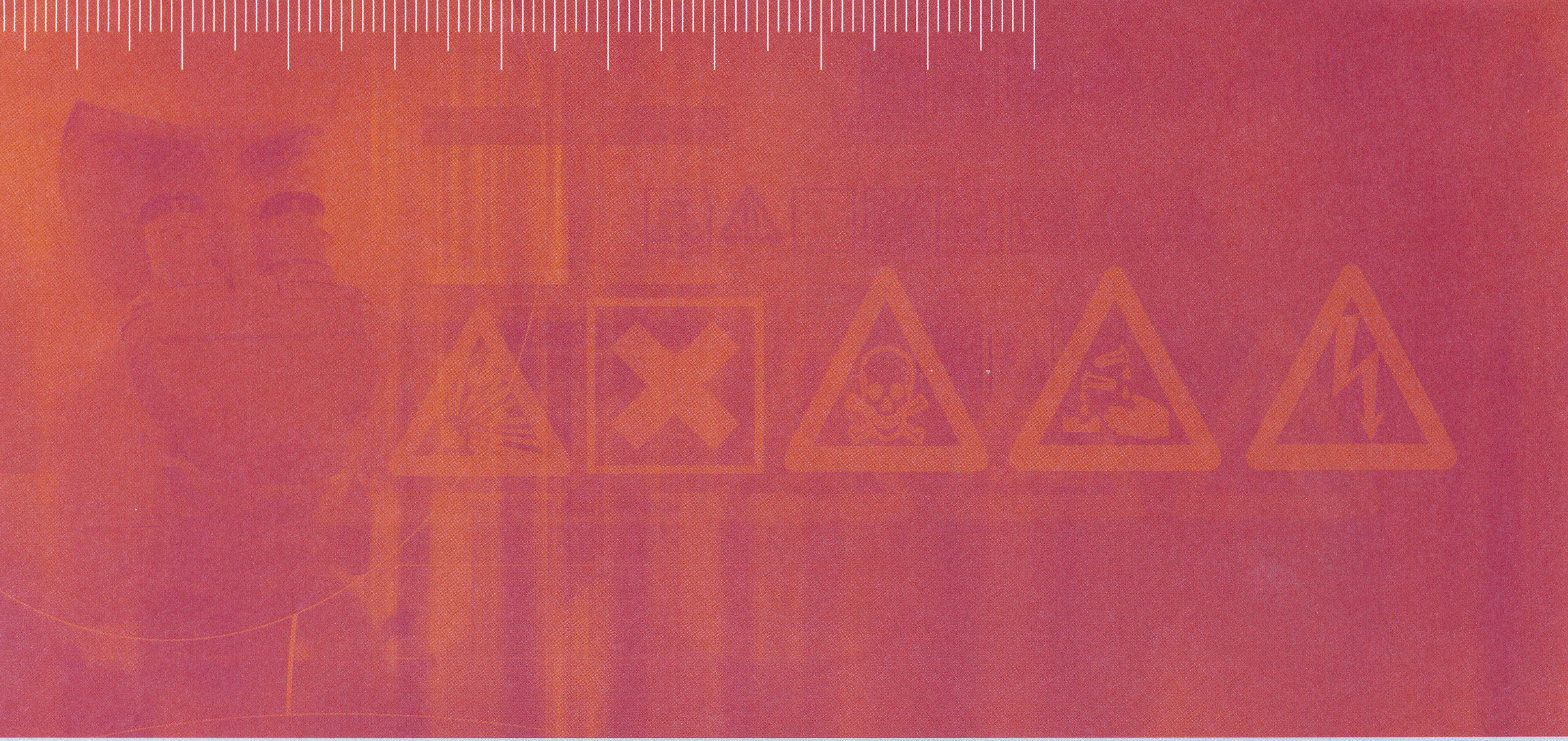

STUDY REPORT 10/11/2017

N° DRC-17-168319-02463B

Study of the performances of existing and under development AMSs (Automated Measuring Systems) and SRMs (Standard Reference Methods) for air emissions at the level of and below existing ELVs (Emission Limit Values) and BATAELs (Best Available Techniques Associated Emission Levels) for Waste Incineration, Co-incineration and Large Combustion Plants

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for sustainable development

Study of the performances of existing and under development AMSs (Automated Measuring Systems) and SRMs (Standard Reference Methods) for air emissions at the level of and below existing ELVs (Emission Limit Values) and BATAELs (Best Available Techniques Associated Emission Levels) for Waste Incineration, Co-incineration and Large Combustion Plants

CEWEP

Confederation of European Waste-to-Energy Plants

Avenue de Tervuren 113
1040 Brussels - Belgium

ESWET

European Suppliers of Waste-to-Energy Technology

Avenue Adolphe Lacomblé 59
1030 Brussels - Belgium

FEAD

European Federation of Waste Management and Environmental Services

Rue Philippe le Bon 15
1000 Brussels - Belgium

List of contributors to this study:

Amandine FIEVET – Nicolas KAROSKI – Jean POULLEAU – Cécile RAVENTOS

Cécile RAVENTOS and Jean POULLEAU, technical evaluators at COFRAC and respectively leaders of AFNOR X 43 B and X 43 E committees, have written this report. Jean POULLEAU leads CEN TC 264 WG 3 (HCl measurement) and WG 16 (O_2, CO, SO_2, NO_x, H_2O, etc. measurement) and is member of the TC 264 Emissions Task Force, tasked with prioritising TC actions.

FOREWORD

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Note: This report was peer reviewed by various European experts, whose input was included.

	Drafting	**Checking**	**Approval**
NAME	Jean POULLEAU	Cécile RAVENTOS / Isaline FRABOULET	Marc DURIF
Function	Unit Manager "EMIS" (Unit "Sources and Emissions") Chronic Risks Division	R&D Managers "EMIS" (Unit "Sources and Emissions") Chronic Risks Division	Department Manager Environment Characterisation Department " Chronic Risks Division
Visa			

TABLE OF CONTENTS

TABLES AND FIGURES LIST

DEFINITIONS

AMS: Automated Measuring System, measuring system permanently installed on site for continuous monitoring of emissions or measurement of peripheral parameters (like O_2, water vapour)

AST: Annual Surveillance Test, fourth quality assurance level; procedure of AMS quality assurance described in EN 14181 standard

The AST is a procedure which is used to evaluate whether the uncertainty of the measured values obtained from the AMS still meet the uncertainty criteria – as demonstrated in the previous QAL2 test. It also determines whether the calibration function obtained during the previous QAL2 test is still valid

BAT: Best Available Technique

BATAEL: Best Available Techniques Associated Emission Level, emission levels associated with the best available techniques

BREF or BAT reference document: Best Available Techniques REFerence document

EIPPCB: European Integrated Pollution Prevention and Control Bureau (or European IPPC Bureau) of the European Commission

ELV: Emission Limit Value

ELVd: Daily Emission Limit Value

GUM: Guide to the Expression of Uncertainty; see ISO/IEC Guide 98-3 in the references to standards below

IED: Industrial Emissions Directive, 2010/75/EU of 24 November 2010, merging 7 Directives including the LCPD, the WID and the IPPCD - Integrated Pollution Prevention and Control

ILC: Inter-Laboratory Comparison

LCPD: Large Combustion Plants Directive, merged with 6 other Directives into the IED in 2010

LoQ: Limit of Quantification

mg/Nm^3: Normal cubic meters expressed in standard conditions of temperature (273.15 K) and pressure (101325 Pa). According to IED Annexes V and VI, concentrations should be corrected as well for the water vapour content of the waste gases at a standardised O_2 content (6 % for solid fuels, 3 % for combustion plants, other than gas turbines and gas engines using liquid and gaseous fuels and 15 % for gas turbines and gas engines, 11 % or 3% for incineration and 10% for co-incineration).

P-AMS: Portable AMS used to implement an automated SRM

QAL1: first quality assurance level; quality assurance procedure for AMS, described in standard EN 14181.

The procedure consists in verifying that the total uncertainty of the AMS, calculated by appropriately summing up all the relevant uncertainty components arising from the individual performance characteristics, does not exceed 75% of the uncertainty required by the applicable legislation[1].

QAL2: second quality assurance level; quality assurance procedure for AMS, described in standard EN 14181.

QAL2 is a procedure for the determination of the AMS's calibration function as well as a test of the variability of the AMS-measured values compared with the maximum permissible uncertainty given by legislation[2].

ROM: JRC Report on Monitoring of emissions to air and water from IED installations

SRM: Standard Reference Method applied by laboratories; reference method prescribed by European or national legislation

WID: Waste Incineration Directive, merged with 6 other Directives into the IED in 2010

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[1] According to EN 14181:2014, § 3.15, note 2 : *In some EU Directives the uncertainty of the AMS measured values is expressed as half of the length of a 95 % confidence interval as a percentage P of the emission limit value E. Then, in order to convert this uncertainty to a standard deviation, the appropriate conversion factor is:* $\sigma_0 = P\,E / 1.96$.

It is the case of the Industrial Emission Directive which, in its Annex VI, Part 6, para. 1.3, provides, for the incineration relevant Automated Measuring Systems, the maximum values of the 95 % confidence intervals at the daily emission limit value level.

[2] Same as previous note.

REFERENCES TO STANDARDS

EN 14181: Stationary source emissions - Quality assurance of automated measuring systems

EN 15267: Air quality - Certification of automated measuring systems

Part 1: General principles

Part 2: Initial assessment of the AMS manufacturer's quality management system and post certification surveillance for the manufacturing process

Part 3: Performance criteria and test procedures for automated measuring systems for monitoring emissions from stationary sources

This European standard supports the requirements of EU Directives, among which the Waste Incineration Directive and the Large Combustion Plants Directives, which were recast into the Industrial Emissions Directive (IED).

EN ISO 14956: Air quality - Evaluation of the suitability of a measurement procedure by comparison with a required measurement uncertainty

ISO 11095: Linear calibration using reference materials

ISO/IEC Guide 98-3: Uncertainty of measurement -- Part 3: Guide to the expression of uncertainty in measurement (GUM: 1995)

NF FD X 43-132 (French implementation guide): Stationary source emissions -- Quality assurance of continuous emission monitoring systems - Application of EN 14181, EN 13284-2 and EN 14884

NF T 90-210 (French standard): Water quality - Protocol for the initial method performance assessment in a laboratory

EN 14789 (O_2): Stationary source emissions - Determination of volume concentration of oxygen (O_2) - Reference method – Paramagnetism

EN 15058 (CO): Stationary source emissions - Determination of mass concentration of carbon monoxide (CO) – Reference method – Non-Dispersive Infra Red Spectrometry

EN 14792 (NO_x): Stationary source emissions - Determination of mass concentration of nitrogen oxides (NOx). Reference method: Chemiluminescence

EN 12619 (COT): Stationary source emissions - Determination of the mass concentration of total gaseous organic carbon. Continuous flame ionisation detector method

EN 13284-1 (Dust): Stationary source emissions - Determination of the mass concentration of total gaseous organic carbon. Continuous flame ionisation detector method

EN 14791 (SO_2): Stationary source emissions - Determination of mass concentration of sulphur dioxide. Reference method

EN 1911 (HCl): Stationary source emissions - Determination of mass concentration of gaseous chlorides expressed as HCl. Standard reference method

NF X 43-304 (HF) (French standard): Stationary source emissions - Measurement of the concentration of fluorised compounds, expressed in HF – Manual Method

NF X 43-303 (NH_3) (French standard): Stationary source emissions - Determination of ammonia (NH_3)

EN 13211 (Hg): Air quality - Stationary source emissions - Manual method to determine total mercury concentration

NF X 43-329 (PAH): Stationary source emissions – Sampling and measurement of emitted polycyclic aromatic hydrocarbons

NF FD X43-135 (French document): Stationary source emissions - Adequacy and good practices for the implementation of standardized reference methods

NF XP X 43-554 (French standard): Determination of the mass concentration of non-methane gaseous organic compounds from measurements of total gaseous organic compounds and methane

STRUCTURE OF THE REPORT

After a brief background on the performances of measurement methods in general (Chapter 2), the report reviews (Chapter 3) the methodology implemented to characterise the performances of AMSs (online instruments) and SRMs (reference techniques used to calibrate the AMS) which are used when measuring the gases emitted in particular from waste incinerators and co-incinerators, large combustion plants and other waste treatment facilities.

The assessment of the uncertainties corresponding to the different methods in use are reviewed and discussed (see Chapter 4 and Annex E) for several substances, including those for which IED provides limit values and maximum uncertainties (as 95% confidence intervals). For each investigated substance, conclusions and resulting recommendations are given. A selection of onsite calibration test graphs (QAL2) illustrates the uncertainties observed at concentrations significantly lower than the IED daily ELVs (see Annex C).

The summary (Chapter 1) highlights several important findings of the study and, in Table 1, sums up the most relevant figures which led to the conclusions and recommendations of the study. In addition to Table 1 footnotes, a step-by-step explanation of the scientific approach and of how this Table was built is given for CO (see § 4.1.2).

1. SUMMARY

Within the context of the BREFs revision, many industrial associations, including CEWEP, ESWET and FEAD, have concerns on the capability of automated measuring systems (AMSs) and standard references methods (SRMs), that are available on the market, to fulfil new, increasingly low emission measurement requirements, especially in the field of waste incineration and large combustion plants.

For these associations, many questions are indeed relevant:

- What is the uncertainty level associated with operational data collected in order to establish BATAELs, and how to take this uncertainty into account during the BREFs revision process?
- What are the performances of air emission measurement instruments available on the market? In particular, in respect of the uncertainties required by EU-legislation and standards.
- What is the procedure for competent authorities to set the installation's ELVs, based on the BATAEL range given in the BREFs (Daily ELV measurement must be performed with the appropriate uncertainty, both for self-monitoring through an AMS, for which the IED sets uncertainty thresholds, and for periodic measurements or AMS calibration, performed by control laboratories)?

Good practice is also that measurement ranges are adapted to a Limit of Quantification (LoQ) that is low enough, compared to the ELV.

INERIS was therefore asked to assess:

- The level of uncertainty of emissions data that can currently be collected from installations, especially when measured values are significantly lower than the IED's ELVs;
- The performances, in particular with regards to uncertainty associated with best available AMSs and the challenges related to simultaneously complying with EU legislation and standards;
- The limits of the measurement methods applied by control laboratories among others when calibrating AMSs and when checking compliance with ELVs during periodic measurement;
- Whether measurement instruments' evolution will enable improving measurement and lowering the measurement uncertainty in the future.

The study is based on:

- AMSs performance data given in certification documents for certified instruments;
- Experience of control laboratories' measurement uncertainties when they calibrate AMSs (see the 2 approaches described below);
- Data from QAL2 control reports for waste incineration installations in Europe, supplied by the industrial associations.

The quality of both the AMSs' and SRMs' performances is mainly evaluated through 2 characteristics:

- Measurement uncertainty at the ELVs level;
- And the ratio between the ELV and the LoQ, a good practice that is not yet applied everywhere in European Member States, that aims at minimising the risk that an ELV exceedance is not noticed, or that an ELV exceedance is erroneously detected or to declare as incompliant an AMS during a QAL2 test.

Measurement data based on the AMS must comply with the uncertainty requirements of the IED, which are expressed as 95% confidence intervals on daily ELVs,

As a reminder, two methods are available to estimate measurement uncertainty:

- Firstly, the GUM approach which is to calculate, for each pollutant, the expanded uncertainty of one measuring system from the evaluation of the uncertainty components arising from its individual performance characteristics determined by an independent metrology laboratory, according to EN 15267-3 and EN ISO 14956 (certification process).
- The GUM approach (ISO/IEC Guide 98-3 "Uncertainty of measurement -- Part 3: Guide to the expression of uncertainty in measurement (GUM: 1995)"), is systematically applied during the procedure of certification of an AMS (in accordance with EN 15267-3), in order to estimate the uncertainty of the AMS before it is put up on the market. The plant owner has to check during the "QAL1" control (quality assurance procedure for AMS, described in standard EN 14181) that $U_{GUM,AMS} < 0{,}75\ U_{max,IED}$ i.e. that the AMS uncertainty is smaller than 75% of the max uncertainty given in IED (the additional 25% uncertainties correspond to the correction of measured values to standardized conditions of pressure, temperature, O_2, moisture),
- The GUM approach is also implemented by control laboratories which have to show, in their on-going process of accreditation, that their measuring system fulfils the requirement of uncertainty of the standard reference methods (SRMs) used for periodic measurements and for QAL2. They have to check that $U_{GUM,SRM} < U_{max,SRM}$ (for each dELV which applyies to the activity).

- The second approach uses the information from Inter-Laboratory Comparisons (ILCs), where the results of various measurement systems fulfilling the requirements of uncertainty for standard reference methods (SRMs) and implemented by accredited control laboratories are compared. It should be noted that this approach is applied today only for the comparison of different equipment implemented by laboratories of control, that is to say, for SRMs.

  During ILCs, the influencing factors do not all vary or vary in a narrower range than the default ranges given in EN ISO 14956 Standard (GUM approach) and used during certification, which should minimise the uncertainty estimate compared to a calculation with relatively larger ranges. However, since the uncertainty components linked to the implementation of different "measurement systems" and to the implementation by different teams of control laboratories have a large influence, the uncertainties estimated based on the reproducibility variance of the ILCs generally are higher than those given by the GUM approach, as shown in the summary sheets by substance (see Annex E and §4). The final estimation of uncertainty using ILCs includes all influencing factors (see Table below) and therefore provides a more truthful picture of the performance of measurement systems.

As an example, in the revised version of EN standard for the determination of dust concentration (EN 13284-1) an uncertainty requirement of 30% has been fixed. This means that each accredited laboratory has to show to its accreditation body that it fulfils this requirement by providing an uncertainty calculation at the lowest daily limit value it can encounter in its subsequent missions, by using the GUM approach. However, this does not mean that the actual uncertainty of the SRM used by this laboratory is limited to 30% of this lowest daily limit value when it is used in the field by several accredited laboratories: indeed, during the validation of the standard, 4 laboratories were involved, each of them simultaneously using two sampling systems, working in parallel and the estimation of expanded uncertainty at 5 mg/m^3 was between 50 and 70 %. This means that the estimation of expanded uncertainty around the IED ELV of 10 mg/m^3 is approximately 50% to be compared with a value lower than 30% determined by GUM.

ILCs approach is a necessary complement to the GUM approach:

	GUM	**ILC**
Applies to	One measuring system at a time, fulfilling the requirement of uncertainty of the standard reference methods (SRMs) or to be used for self-monitoring (AMSs) Applies to any concentration	Several measuring systems fulfilling requirements of uncertainty for standard reference methods (SRMs), implemented in parallel by several control laboratories. Could be applied as well to AMS, even if not done up to now because not required by the standard and difficult to implement. Applies to any concentration
Method	‘Quadratic Sum’ of a list of standard uncertainties (equal to the sum of variances) corresponding to standardized ranges of variation of several factors (voltage, …) See EN 15267-3 and EN ISO14956	Dispersion of measured values obtained by different measuring systems and accredited teams on a same flue gas. See ISO 5725
Completeness	Does not include uncertainties due to sampling, DAHS (Data Acquisition and Handling System), nor the ones due to human factors. For AMS it also does not include the uncertainty of the SRM which is used for the calibration of the AMS.	Includes all sources of uncertainties but does not cover the full ranges of variation of the factors covered in GUM.
Pros	Possibility to see the relative influence of the different components of standardised uncertainty components.	Provides an overview of the overall uncertainties. Considers the influence of human factors, of using different equipment and of DAHS (Data Acquisition and Handling System).
Cons	Does not consider the uncertainties due to human factor, variability of equipment and DAHS (Data Acquisition and Handling System), nor, for AMS, the uncertainty of the SRM used to calibrate the AMS.	Availability of ILCs on representative matrices for all parameters. (a real matrix with hot and wet conditions is highly recommended).

	Need to model the measurement to identify influence parameters of measurement and relationship between these parameters and the measurand. Necessity to be able to quantify the performance characteristics, including the effect of influencing quantities.	No possibility to quantify the individual contribution of each influence parameter or metrological performance.
Findings	Shows often low uncertainty values compared to the ILCs approach	Shows significant higher uncertainty values (when ILCs are carried out on actual flue gases)

The relative uncertainty linked to a measurement result is constant for the upper part of the concentration range and then grows in a non-linear manner for the lower part when concentration decreases. This means that if the legislator reduces the ELVs, the associated uncertainty expressed in relative value shall be increased significantly, thus possibly preventing available techniques to comply with the requirements of legislation and standards in respect of uncertainty. The following table summarises the main results of the AMS's characteristics in terms of LoQ, and SRMs and AMSs' uncertainties.

The ELVs and maximum allowed uncertainties taken into consideration in the table are the Daily ELVs and the 95% confidence intervals that are associated to them in Annex VI of the IED (on incineration and co-incineration)[3]. These ELVs are in fact the lowest ones mandated by the IED, which only sets Daily and Half-hourly ELVs (and in option a 10-min ELV for CO) for these sectors.

In the framework of a reduction of Daily ELVs, the LoQs and uncertainties are reported, on one hand, for the median of all the EU-Standard certified AMSs and, on the other hand, for the 3 best AMSs.

The IED's SRM uncertainty requirements are also recalled. The comparison between the relative uncertainties of the AMS and of the SRM, U_{AMS} and U_{SRM}, allows checking if the pre-requisite of QAL2 calibration, implicitely described in EN 14181, $U_{SRM} << U_{AMS}$,[4] can be complied with.

It is important to note that, for self-monitoring, only Automated Measuring Systems are used while SRMs can, depending on the substance, either be "automated" methods using analysers (O_2, CO, NO_x, TOC) or "manual" methods, involving the collection of the gaseous or/and particulate phase of the pollutant on appropriate media which are analysed later by a control laboratory (for dust, HCl, HF, NH_3, SO_2, Hg, PAH, Dioxins-Furans, PCB).

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[3] For substances that are also regulated for LCPs, the 95% confidence intervals given in IED Annex V are the same as those for incineration and co-incineration.

[4] The linear regression used for QAL2 tests is the application of the least squares general method which can be applied under certain conditions (See http://www.inrp.fr/Tecne/Acexosp/Savoirs/Stathtm1.htm). The method only minimises the differences between the regression line and the experimental points (AMS), thereby following the X axis. This implies that the uncertainty on the value shown in Y (SRM) must be nil or negligible in comparison of the one of the AMS. This requirement, well-known by metrologists, is evoked in EN 14181 Standard, among others in notes 2 and 3 of the § 8.6 regarding the variability test:

"NOTE 2: 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 a false failure of the variability test). The procedure for determination of uncertainty is not in accordance with GUM (ISO/IEC Guide 98-3).

NOTE 3: This method implies that the quality of the application of the SRM influences the result of the test. It will be noted, however, that it is the result that determines a pass or failure and that in some cases a better application of the SRM could change the result from fail to pass."

Table 1: Study Results Summary[5]

***"Min ELV" (5):** ELV reachable by best-performing AMSs*

"U$_{ILC,SRM}$ << U$_{certif,AMS}$" ***(10):** Required condition to make a QAL2 test*

"Min ELV to comply with U$_{GUM,\ maxSRM}$ " ***(11):** ELV for which the uncertainty required by the SRM is actually in robust conditions reached (coming from Inter-Laboratory Comparisons)*

1	2	3	4	5	6	7	8	9	10	11	12
Substance **(0)**	**Current Daily ELV** **(1)**	**AMS's LoQ (2)**	**AMS's LoQmin-LoQmed (3)**	**Min ELV = (5*LoQmin - 5*LoQmed) (4)**	**Target U$_{GUM,max\ SRM}$ (5)**	**Target U$_{GUM,\ maxAMS}$ (6)**	**Min-Med U$_{certif,AMS}$ (7)**	**U$_{ILC,SRM}$ (8) at current ELV**	**U$_{ILC,SRM}$ << U$_{certif,AMS}$ (9)**	**Min ELV to comply with U$_{GUM,\ maxSRM}$ (10)**	**Conclusion and recommendations**
CO	50 mg/Nm^3	0.03 - 2.8 mg/Nm^3	0.07 mg/Nm^3 0.8 mg/Nm^3	0.35 mg/Nm^3 4.0 mg/Nm^3	6%	7.5%	3.8 % 7.4%	12%	No	120 mg/Nm^3	The objective of uncertainty of the SRM is not achieved in practice below 120 mg/Nm^3 Search for a better-performing SRM
NO$_x$	200 mgNO$_2$/Nm^3	0.02 - 8 mg/Nm^3	0.04 mg/Nm^3 0.8 mg/Nm^3	0.2 mg/Nm^3 4.0 mg/Nm^3	10%	15%	4.7 - 9.1%	6%	Yes for C > 75 mg/Nm^3	75 mg/Nm^3	The objective of uncertainty of the SRM is achieved in practice over 75 mg/Nm^3 when the ratio NO$_2$/NOx is < 5%. The higher NO$_2$/NOx is, the bigger the uncertainty.
TOC	10 mgC/Nm^3	0.012 - 0.06 mgC/Nm^3	0.013 mg/Nm^3 0.04 mgC/Nm^3	0.065 mg/Nm^3 0.2 mgC/Nm^3	15%	23%	8.7 - 12.3%	30%	No	50 mgC/Nm^3	The objective of uncertainty of the SRM is not achieved in practice below 50 mg/Nm^3
Dust	10 mg/Nm^3	0.0002 - 0.9 mg/Nm^3	0.0061 mg/Nm^3 0.06 mg/Nm^3	0.035 mg/Nm^3 0.3 mg/Nm^3	20%	23%	3.3 - 6.4%	60%	No	50 mg/Nm^3	The objective of uncertainty of the SRM is not achieved in practice below 50 mg/Nm^3 Significantly increase sampled volumes for SRM in order to lower the measurement uncertainty. No Alternative method available
SO$_2$	50 mg/Nm^3	0.06 - 3.7 mg/Nm^3	0.19 mg/Nm^3 0.6 mg/Nm^3	0.95 mg/Nm^3 3.0 mg/Nm^3	20%	15%	4.6 - 10%	16%	No	150 mg/Nm^3	The objective of uncertainty of the SRM is achieved in practice above 150 mg/Nm^3 If a manual SRM is used, possibility to increase sampling volume in order to lower the measurement uncertainty. Alternative automatic methods to the SRM available (U$_{GUM}$ 13%)
HCl	10 mg/Nm^3	0.0078 mg/Nm^3 1.08	0.019 mg/Nm^3 0.18 mg/Nm^3	0.095 - 0.9 mg/Nm^3	30%	30%	7.9 - 11.8%	100%	No	50 mg/Nm^3	The objective of uncertainty of the SRM is not achieved in practice below 50 mg/Nm^3 If manual SRM is used, increase significantly the sampling volume.

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[5] Between the first publication of this report (July 2016) and the second (July 2017) a more detailed analysis spread on 3 years of ILCs campaigns was performed and therefore the values in this table were updated accordingly.

1	2	3	4	5	6	7	8	9	10	11	12
Substance (0)	**Current Daily ELV** (1)	**AMS's LoQ** (2)	**AMS's LoQmin-LoQmed** (3)	**Min ELV = (5*LoQmin - 5*LoQmed)** (4)	**Target $U_{GUM,max SRM}$** (5)	**Target $U_{GUM, maxAMS}$** (6)	**Min-Med $U_{certif,AMS}$** (7)	**$U_{ILC,SRM}$** (8) **at current ELV**	**$U_{ILC,SRM}$ << $U_{certif,AMS}$** (9)	**Min ELV to comply with $U_{GUM, maxSRM}$** (10)	**Conclusion and recommendations**
		mg/Nm^3									A validation of an automatic measurement method (TS 16429) is in progress and may reduce the uncertainty level .

Table 2: Study Results Summary

"Min ELV" (5): *ELV reachable by best-performing AMSs*

"$U_{ILC,SRM}$ << $U_{certif,AMS}$" ***(10):*** *Required condition to make a QAL2 test*

"Min ELV to comply with $U_{GUM, maxSRM}$ " ***(11):*** *ELV for which the uncertainty required by the SRM is actually in robust conditions reached (coming from Inter-Laboratory Comparisons)*

1	2	3	4	5	6	7	8	9	10	11	12
Substance (0)	**Current Daily ELV** (1)	**AMS's LoQ** (2)	**AMS's LoQmin-LoQmed** (3)	**Min ELV = (5*LoQmin - 5*LoQmed)** (4)	**Target $U_{GUM,max SRM}$** (5)	**Target $U_{GUM, maxAMS}$** (6)	**Min-Med $U_{certif,AMS}$** (7)	**$U_{ILC,SRM}$** (8) **at current ELV**	**$U_{ILC,SRM}$ << $U_{certif,AMS}$** (9)	**Min ELV to comply with $U_{GUM, maxSRM}$** (10)	**Conclusion and recommendations**
HF	1 mg/Nm^3	0.006 - 0.2 mg/Nm^3	0.025 - 0.096 mg/Nm^3	0.125 - 0.48 mg/Nm^3	20%* *desirable	30%	10.7 - 24.6%	no data available	No		No robust data available. Changing the SRM is not possible. Increasing the samples volumes for the SRM will reduce the LoQ and the uncertainty; but the targets will remain difficult to fulfil with a Daily ELV = 1 mg/Nm³
NH_3	No IED ELV. ELV often found (cf. § 4.1.9): 10 mg/Nm^3 In France: 30 mg/Nm³	0.012 - 0.88 mg/Nm^3	0.037 - 0.21 mg/Nm^3	0.185 - 1.05 mg/Nm^3	20%* *desirable	30%	5.4 - 9.4%	100%	No	50 mg/Nm^3	The objective of uncertainty of the SRM is not achieved in practice on the studied range 0-50 mg/Nm^3 Increasing the sampling volumes for SRM will reduce the LoQ and the uncertainty. To fulfil targets at a Daily ELV = 10 mg/Nm³, a solution may be to use an automatic TDLAS method with a reliable calibration instead of the SRM.
Hg	50 µg/Nm^3 (periodic)	0.02 - 0.7 µg/Nm^3	0.10 - 0.14 µg/Nm^3	0.5 - 0.7 µg/Nm^3	-	-	7.8 - 9.6%	30%	No	-	Although no criterion is fixed, the manual SRM's uncertainty level at the current Daily ELV level (30% at 50 µg/Nm³) is high. Increasing sampling times would lower the uncertainty. Alternative manual methods with solid absorbing traps should allow a much larger gas volume sampling and thus lower significantly the uncertainties (method under developpement in CEN TC264 WG8).
PAH	-	-	-	-	-	-	-	Cf. § 4.1.11	-		No AMS. Too little information to make recommendations.

(0): To ease understanding, find for instance at § 4.1.2 (CO) references to the columns of this table and explanations on how the figures have been calculated (for CO).

(1): Daily Emission Limit Value from IED (Industrial Emissions Directive) Annex VI. The Daily ELVs are generally the lowest ELVs and it is why the IED requires to prove that the uncertainty requirements are fulfilled at the level of daily ELVs.

(2): Ranges of EU Standard-certified AMS's (Automated Measuring Systems) Limits of Quantification (LoQs).

(3): LoQmin: Average of LoQs from the 3 EU Standard-certified AMSs with the lowest LoQs.

LoQmed: Median of LoQs from all EU Standard-certified AMSs.

(4): Minimum ELV for LoQmin and LoQmed, on the basis that it should not be under 5 times the AMS's LoQ (cf. § 2.3.2).

(5): SRM's relative expanded uncertainty target, as defined in the Standard describing the SRM or in the draft revised Standard for Dust (cf. § 2.3.3), or desirable in the cases of HF and NH_3, substances for which the measurement method Standard does not set an uncertainty requirement.

(6): AMS's relative expanded uncertainty target from EN 15267 Standard, corresponding to 75% of the confidence interval set by the IED (cf. § 2.3.3).

(7): EN 15267-certified instruments' relative expanded uncertainties (estimated by an uncertainty budget approach). Minimum value of expanded uncertainty of certified AMSs, taken equal to the average of the 3 lowest expanded uncertainties. Median values of expanded uncertainties of certified AMSs.

(8): Expanded uncertainty coming from ILCs (Inter-Laboratory Comparisons) organised by INERIS of for Standards validation (cf. summary sheets in Annex E and in § 4), therefore when various laboratories implement the method on site.

(9): Fulfilment of the condition that the SRM's uncertainty must be significantly lower than that of the AMS (cf. § 2.3.3).

(10): Minimum ELV fulfilling the SRM's uncertainty target set in the Standard describing the SRM.

Colour code in Table 1

Red: describes a non-satisfactory situation, such as:

- $U_{ILC,SRM}$ is higher than $U_{GUM,SRM}$ mandated by the SRM at the current Daily ELV, the second to last column shows from which concentration the SRM's requirement is not fulfilled anymore.
- The $U_{ILC,SRM} << U_{certif,AMS}$ condition, necessary for a reliable calibration function, is not fulfilled.

Green: describes a satisfactory situation, such as:

- $U_{ILC,SRM}$ is lower than $U_{GUM,SRM}$ mandated by the SRM at the current Daily ELV, the second to last column shows from which concentration the SRM's requirement is fulfilled.
- The $U_{ILC,SRM} << U_{certif,AMS}$ condition, necessary for a reliable calibration function, is fulfilled.

Table 1 shows that the performance of SRMs are often not as good as it is required and therefore, for installed AMS (that must be calibrated using SRM) it proves remaining challenging to comply with uncertainty requirements in some cases:

- As mentioned above, using an ordinary least squares slope for AMS calibration by SRM implies having SRMs with much lower uncertainties than the ones required by the IED for the values given by the AMS. However, given thus the collected data, this prerequisite for calibration is not fulfilled (except for NO_x), impacting the quality of current QAL2 results. The non-respect of this rule causes a calibration of poor quality and therefore a higher uncertainty of the measurements given by the AMS. Nevertheless, European experts chose as SRMs the most performing methods available at the time of writing the European Standards. For some substances, CO, TOC, Dust, HCl, HF or NH_3, the actual uncertainty of the SRM (estimated from ILCs) at the current Daily ELVs is higher than the uncertainty required in the standard describing the reference method. This shows that the GUM approach, which assesses the suitability of the measuring system according to the SRM, does not reflect the actual uncertainty in the field. This real uncertainty affects the quality of the QAL 2 performed[6].

This situation can be solved in some cases by improving or changing the SRMs. However:

- There is no alternative for TOC, for which the FID method has been the reference for decades and it is unclear whether another index, infrared for instance, would limit the uncertainty.
- For substances in particulate-form, Dust and HF, and the other substances for which the SRM is manual, an improvement consists in significantly increasing the sampled volumes. As a reminder, increasing sampling time enables increasing the sampled gas' volume and increasing the quantity of trapped substance, thus reducing respectively the relative uncertainty associated with the sampled gas' volume and with the analysis' result, and hence of the measured concentration. However, when referring to the Horwitz Model, which links the relative reliability figures in an analysis method to the analyte's concentration, multiplying the sampling time by 4 provides an improvement of only 20% of the measurement uncertainty. On the other hand, if longer-time compliance and QAL2 checks were applied, then the number of samples taken should be limited so that the costs of these operations would not raise unduly (the EN 13284 Standard "Determination of low range mass concentration of dust – Part 2, AMS" accepts QAL2 comparisons with 5 long-term measurements instead of 15).
- For SO_2, there is an alternative to the EN 14791 method (Determination of mass concentration of sulphur dioxide. Reference method), which is the use of an automated analyser: a CEN TC 264 WG 16 technical specification is being finalised on this topic.
- For HCl and NH_3, it would be good to use an alternative to methods described in the EN 1911 (Determination of mass concentration of gaseous chlorides expressed as HCl. Standard reference method) and NF X 43-303 (Ammonia (NH_3) Determination) Standards. The EN TS 16429 (Sampling and determination of hydrogen chloride content in ducts and stacks. Infrared analytical technique) describing the automatic method for HCl was drafted and its validation is ongoing.

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[6] No exercise of inter-laboratories comparisons concerning the calibration QAL2 of AMS having been realized in Europe, it is difficult to know the risk led by the uncertainty associated to measures of the SRM on the conclusions of conformity of the AMS during the operations QAL2 and AST.

> We have shown that the relative uncertainties of measurements increase when the concentrations are decreasing. Caution is necessary when SRM or AMS data are used as benchmarking if emission levels are low because the uncertainty can be very high in relative value.

Also, the uncertainty linked <u>to an individual measurement</u> from an AMS calibrated through a QAL2 does not take into account:

- the intra and inter laboratories' variabilities which both are influence factors;
- the potential bias linked with the AMS data transfer to the data handling system;
- the uncertainty linked to data handling (potential moisture, temperature, pressure and oxygen content corrections with data that is not always calibrated).

It should be noted that EN 14181 provides a variability test to ensure that the uncertainty at the daily ELV is lower than the maximum uncertainty allowed by IED. However, because of the nature of the variability test formula, when the measured concentrations are much lower than ELV, the variability test always passes, even if values are very scattered. In other words, the fact that the variability test is successful gives no information on the actual uncertainty when emission concentrations are much lower than the ELV.

As it can be seen in Annex A of the report thishappened for many calibration tests of the QAL2 reports which were investigated in the study for which the measured concentrations were very low: although the calculated calibration functions do not show good correlations sometimes, the variability tests were always satisfied: for example if a daily ELV equals to 10 mg/Nm^3 with related maximum uncertainty of 20%, then the variability test will accept a difference of up to 2 mg/Nm^3 between the reading of AMS and the value measured by the SRM which, for instance, could be 3 mg/Nm^3. In this case:

- the uncertainty level at 3 mg/Nm^3 is much higher than 20% (2/3 = 67%)
- and since it provides no information on the differences between AMS and SRM readings at 10 mg/Nm^3 the test does not give any idea on the level of uncertainty actually performed at 10 mg/Nm^3.

It is also important to note that for certain substances that are not continuously monitored by an AMS, the values given by the operator are based on one or two periodic measurements obtained with SRM during the year. In these conditions, it is difficult to assess their time representativeness and hence to consider their impact on the associated measurement uncertainty.

In SRM test reports they produce, most control laboratories give uncertainties calculated with a GUM approach. They do not include the differences due to the different equipments used by control organisations or due to the human factor in their estimation. This often leads to an important underestimation of the displayed uncertainty compared to the real uncertainty.

In conclusion, it is important to be very cautious when handling data from AMSs or SRM's, and reporting to the competent authorities, because:

- the measurement uncertainty associated with these AMSs' data is in general not given,
- or the one evaluated for a periodic measurement is underestimated because of the additional contributions mentioned above.

Since the uncertainty associated to a given concentration becomes higher – as a relative value – when the measurements are close to 0, decision-makers have to be cautious when interpreting the data or when fixing new ELVs. An adequate level of uncertainty must be associated to these new ELVs. We must note that the compliance of an installation or the accuracy of an AMS will be more difficult to assess if ELVs decrease.

Any lowering of the Daily ELVs using the same measuring methods may lead to a higher risk of invalidation of the installation or of the installation's AMS. New reference methods for control organisations must be found to reduce these risks. Alternatively, standards can support the new legislation.

New technologies for automatic SRMs are already emerging and could decrease the measurement expanded uncertainty, in particular, when they can supersede manual methods. For manual methods, to lower measurement uncertainty and to reach the objective of uncertainty of the SRM, a very significant increase in sampling times is necessary or/and an improvement of the collection media must be found, which often will lead to a cost impact on services provided by control organisations. For substances for which it is not possible to get varied concentration levels during QAL 2, a calibration with a reduced number of parallel measurements (AMS/SRM) could be considered (e.g. 5 instead of 15), which would not affect too much the robustness of the calibration lines thus obtained. This would require a modification of EN 14181.

This study, through examining about 40 QAL2 reports carried out in Europe, provides the following findings:

- The QAL2 test aims at ensuring that the AMS is reliable (in terms of repeatability and trueness) under real, on-site operating conditions, and that it complies with the required uncertainty at the Daily ELV level. The variability test on the QAL2 test is meaningful only if there are enough data near the Daily ELV. If, during the QAL2 step, it was not possible to vary the concentrations and if the tested level remains low, the differences between the AMS and SRM measurements may become important in relative value (for instance, differences of the same magnitude as the measured concentrations). However, these differences will remain low in absolute values compared to the Daily ELV and the test will still be fulfilled.

- In the case where the cloud of points is at low concentration levels, the test is irrelevant because one cannot conclude on the behaviour of the equipment with measurements near the Daily ELV. For this reason, where concentrations are under 30% of the Daily ELV, the French Guide FD X 43-132 proposes, for the determination of the calibration function, to combine with AMS/SRM data those obtained when a span gas is injected to the AMS at zero and another one at the concentration of the Daily ELV. Thus, required uncertainty at the Daily ELV will be better respected and the AMS will more likely show a correct value around the daily ELV, if the installation was to emit at this level of concentration. A similar procedure (known as method C) is provided in the revised version of Standard EN 14181 (December 2014). It is important to note that using span gas does not help improving the uncertainty at very low concentrations where the effect of interfering substances can be significant. A selection of graphs presenting the measurements [AMS;SRM] during QAL2 controls and calibration lines can be found in Annex C. They highlight the important increase and difference in measurement results between AMS and SRM in relative value when concentrations are much lower than IED daily ELVs.
- Laboratories already often use calibration gases in combination with results of comparison (AMS/SRM), and sometimes more extensively than what is allowed by EN 14181, e.g. at concentrations much higher than the daily ELV. There are some limitations to the use of calibration gases, mainly because they may not exist at very low concentrations and that diluting a calibration gas with a level of concentration would introduce an additional source of uncertainty. Moreover, using reference materials is not always possible, e.g. for dust calibrations.

When reference materials exist and when the level of emission concentration is very low compared to ELV, a combination of the results of a limited number of measurement results (AMS/SRM) and of the results of the adjustment of the AMS by the reference material is an acceptable procedure to obtain a realistic calibration function (see EN 14181 § 6.4.3 c). But the use of reference material only, which was the common practice before EN 14181 was launched, is no more accepted by this standard.

Clarification

1) As indicated above, the values shown as minimum ELV for compliance with the $\mathbf{U_{GUM,SRM}}$ rule (see 11th column of table 1) are those obtained during Inter-Laboratory Comparisons organized on the INERIS test bench (See § 2.1.3).

The last columns of tables 1 and 2 conclude on the quality of the SRM at the existing ELV and provide recommendations to reduce the current $\mathbf{U_{GUM,SRM}}$ uncertainty levels.

2) A high measurement uncertainty is observed at significantly lower concentrations than the IED's ELVs; it would not fulfil the IED's and SRM standards requirements in terms of confidence intervals if the ELVs were lowered at those emission levels with the same uncertainty requirements.

However, despite a higher uncertainty level than the one targeted in the Standards, given that the measured concentration levels are far lower than the IED's ELVs, there is no concern on the effective compliance with those ELVs.

2. BRIEF BACKGROUND ON MEASUREMENT METHODS' PERFORMANCES

Both AMS and SRM measurement quality performances are based on:

- Daily ELV measurement uncertainties;
- Ratio between the ELV and the LoQ.

The main requirement for SRM, is to ensure that the supplied measurements, used among others to check an installation's compliance with ELVs, contain an "acceptable" uncertainty. For AMS, the main requirement is that the supplied measurements corrected by the calibration function fulfil the uncertainties required by legislation. For a given substance, an SRM's acceptable uncertainty level comes from the necessity that the uncertainty is significantly lower than the uncertainty required for the AMS by the IED. It is hence a mathematical pre-requisite to enable calibrating the AMS in comparison with SRM. The ISO 11095 "Linear calibration using reference materials" Standard, on which the EN 14181 Standard is based, indeed assumes that there is no error in the reference materials' values (for QAL2 controls, the SRMs are used as "reference materials"), a hypothesis validated if the reference material's uncertainty – that of the SRM – is significantly lower, compared to the errors of these materials's measured values (i.e. AMS' values).

2.1 ABOUT UNCERTAINTY ESTIMATION METHODS

Measurement uncertainty is a parameter associated with the measurement result, which characterizes the dispersion of values that may be attributed to the measurand (quantity to be measured: concentration, flow, etc.). This parameter characterizes the quality of the measuring system implemented to determine the measurand. To guarantee this quality:

- the European Commission has fixed maximum uncertainties for emission values measured by plants to control and monitor their emissions to the atmosphere, and has mandated CEN to define the different quality assurance levels necessary to achieve this objective (QAL1, QAL2, QAL3 and AST of EN 14181).
- each SRM (Standard Reference Method) used for periodic measurements of emissions from stationary sources or calibration of AMS (Automated Measuring Systems), has, according to the standard which defines it, to meet a fixed maximum uncertainty objective.

The compliance with these objectives must be demonstrated at the lowest emission limit value which applies to the plant where the characterization takes place.

How to determine the uncertainty linked to a measurement result?

To determine this uncertainty, a precise definition of the measurand is necessary, as well as the knowledge of all parameters that can influence the measurand.

Following is a description of 2 widely used approaches to assess measurement uncertainty in the field of stationary sources.

2.1.2 PROPAGATION OF UNCERTAINTY APPROACH, DESCRIBED IN EN ISO 14956 OR ISO/IEC GUIDE 98-3 (GUM: GUIDE TO THE EXPRESSION OF UNCERTAINTY)

This approach is implemended to estimate the measurement uncertainty of AMS.

The suitability evaluation of an AMS and its operating procedure are described in EN 15267-3[7] and EN ISO 14956[8] where a methodology is given for calculating the expanded uncertainty (total uncertainty) of concentrations measured by AMS.

This uncertainty calculation approach is commonly called a “GUM approach” which provides an uncertainty calculation for the specific measurement system.

This expanded uncertainty is calculated from the identification of all components that influence the measurement (often called the uncertainty budget), and a quantification of the uncertainty associated to each component. The method includes many sources of uncertainties with a large range of variation of influence factors but not the human factor, not considered because it would require tests of implementation by users (which is not possible in particular in case of certification).

Variability of equipment, and DAHS (Data Acquisition and Handling System) in case of automated methods, are not either taken into account. Thus:

- the uncertainty is estimated for the studied AMS, only;
- data are recorded and handled, but the performance of the AMSs is evaluated only for the measurement equipment and the associated sampling line when the measurement is extractive; the influence of the acquisition and handling system is not included in the uncertainty budget.

The certification process described by the EN 15267 Standards series provides in Part 3 the conditions of tests (procedures, number of tests, levels of concentration and values of the influence parameters) to determine the AMSs’ performance characteristics. These characteristics are determined by an accredited body that is independent of the measurement system supplier / manufacturer.

This GUM approach is implemented during the procedure of certification of AMSs for the QAL1 control (Quality Assurance Level 1) to check the conformity of the AMS with the regulatory requirement of uncertainty. A more precise calculation may be carried out by the plant owner who wants to determine an estimate corresponding to its own plant or willing to demonstrate that – at the requested emission limit value level - his Automated Measurement System is fit for controlling and monitoring emissions to the atmosphere with the appropriate level of uncertainty fixed by IED.

This GUM procedure is also applied by control laboratories involved in periodic measurements which, in their on-going process of accreditation, must estimate the uncertainty associated to their results when they implement a SRM, and to demonstrate the conformity of their implementation of the SRM to the uncertainty criteria defined in the SRMs that they use for periodic measurements and for QAL2 calibration.

The compliance with the objectives of uncertainty for AMS and SRM must be demonstrated at the level of the lowest emission limit value which apply to the plant where the characterization takes place.

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[7] EN 15267-3 ”Air quality — Certification of automated measuring systems — Part 3: Performance criteria and test procedures for automated measuring systems for monitoring emissions from stationary sources”: defines the performance criteria and test procedures for performance testing of AMS used to monitor emissions from stationary sources

[8] EN ISO 14956 ”Air quality – Evaluation of the suitability of a measurement procedure by comparison with a required measurement uncertainty”: specifies the procedures to determine the measurement uncertainty of an individual measurement result, using relevant performance characteristics of the measuring method, and to check compliance with the requirements of the measuring task

Modelling Equation

The first step is to determine the modelling equation. The modelling equation describes the mathematical relation between the measurand (the considered substance's concentration) and all parameters influencing the measurement result.

The modelling function is used to calculate the measurement result, based on measured values and to obtain the standard uncertainty, composed of the measurement result to which the propagation of uncertainty is applied.

The modelling equation relative to the $C_{\mathrm{pollutant}}$ pollutant's volume concentration can be expressed as a sum of C_i individual contributions, as given in Formula (1):

$$C_{\mathrm{pollutant}} = \sum_{i=1}^{N} C_i \quad (1)$$

C_i individual contributions stand for volume concentration read by the analyser and the corrections linked with the biases due to the analyser's performance characteristics and to the influence quantities.

The certification process described by the EN 15267 Standards series provides the parameters to determine the AMSs' characteristics. These characteristics are determined by an accredited body that is independent of the measurement system supplier. The usually-determined characteristics are given in the following table.

Table 3: C_i contributions to measurement uncertainty

Performance characteristic	**Symbol** C_i	**Standard Uncertainty** u_i
Volume concentration signal from analyser	C_{sig}	u_{sig}
Repeatability	C_{r}	$u_{\mathrm{r}} = s_{\mathrm{r}}$
Lack of fit	C_{lof}	u_{lof}
Zero drift	$C_{\mathrm{d,z}}$	$u_{\mathrm{d,z}}$
Span drift	$C_{\mathrm{d,s}}$	$u_{\mathrm{d,s}}$
Cross-sensitivity (interference)	C_{i}	u_{i}
Influence of ambient temperature at span	C_{t}	u_{t}
Influence of atmospheric pressure at span	C_{ap}	u_{ap}
Influence of sample gas pressure	C_{p}	u_{p}
Influence of sample gas flow	C_{d}	u_{d}
Influence of supply voltage	C_{v}	u_{v}
Adjustment (span gas)	C_{adjust}	u_{adjust}

Combined standard uncertainty

The $C_{\mathrm{pollutant}}$ pollutant's concentration's combined standard uncertainty $u_{\mathrm{c}}(C_{\mathrm{pollutant}})$ is obtained by applying the propagation of uncertainty to the uncertainty Formula (1), leading to the quadratic sum (sum of squares) of u_i standard uncertainties shown in Table 3:

$$
\begin{aligned}
u_{\mathrm{c}}\left(C_{\text{pollutant}}\right) &= \sqrt{\sum_{i=1}^{N}\left[\left(\frac{\partial C_{\text{pollutant}}}{\partial C_i}\right)^2 u^2\left(C_i\right)\right]} \\
&= \sqrt{\sum_{i=1}^{N} u^2\left(C_i\right)} \qquad (2) \\
&= \sqrt{\sum_{i=1}^{N} u_i^2}
\end{aligned}
$$

Contributions to the u_i uncertainty are quantified based on the measurement system's performances, on repeated measurement's dispersion data, on influence quantities data or on data provided by the calibration certificates.

Expanded uncertainty

In general, the uncertainty linked to the measurement result is expressed as an expanded uncertainty corresponding to the combined standard uncertainty multiplied by a coverage factor k. The coverage factor's value is chosen based on the confidence level required for the interval $C_{\text{pollutant}} - U\left(C_{\text{pollutant}}\right)$ to $C_{\text{pollutant}} + U\left(C_{\text{pollutant}}\right)$.

One can assume that in most cases using a factor $k = 2.0$ gives an interval with a confidence level of about 95% (note that this is approximately twice the standard deviation of dispersion, corresponding to half a confidence interval of 95.45% in the case of a standard distribution of measurement values).

The $U\left(C_{\text{polluant}}\right)$ expanded uncertainty of the $C_{\text{pollutant}}$pollutant's volume concentration is then determined through Formula (3):

$$U\left(C_{\text{pollutant}}\right) = 2\, u_{\mathrm{c}}\left(C_{\text{pollutant}}\right) \qquad (3)$$

2.1.4 INTER-LABORATORY COMPARISON APPROACH DESCRIBED IN ISO 5725 (ACCURACY OF MEASUREMENT METHODS) AND IN EN 17043 AND ISO 13528 (PROFICIENCY TESTING BY INTERLABORATORY COMPARISON)

An inter-laboratories comparison consists of the simultaneous implementation by the participants, of measurement systems which comply with the SRMs standards.

As far as possible the comparisons must be performed on the most representative possible matrices of those met on-site. Different levels of concentrations are provided to obtain an estimation of the uncertainty at various concentrations.

Participants are generally required to simultaneously implement two measurement systems to determine their intra-laboratory variance and the average repeatability variance of participants. Repeatability and inter-laboratory variances are combined to determine the reproducibility variance from which is calculated an estimate of the actual uncertainty of the results obtained with the SRM.

Simultaneous participation of many control bodies also allows determining the measurement method's reproducibility variance S_{Rj}^2 for a j concentration level, based on S_{rj}^2 repeatability variance and the S_{Lj}^2 inter-laboratory variance. During Inter-Laboratory Comparisons organised by INERIS[9], repeatability and inter-laboratory variabilities variances are determined by a robust estimation following the ISO 5725-5 Standard's procedure.

$$S_{Rj}^2 = S_{rj}^2 + S_{Lj}^2 \tag{4}$$

U, the expanded uncertainty measurement is estimated from the reproducibility variance at the j concentration level is given by Equation (5):

$$U = t_{1-\frac{\alpha}{2}} \times S_{Rj} \tag{5}$$

where $t_{1-\frac{\alpha}{2}}$ is the fractile of order $\left(1-\frac{\alpha}{2}\right)$ of the Student Law at (p-1) degrees of freedom; we take $\alpha = 0.05$ for a 95% confidence interval.

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[9] In the field of stationary sources emissions, INERIS is mandated by the French ministry of Environment to organise interlaboratory comparisons (ILCs) on a test bench during which the participants implement the standardised monitoring reference methods, "automated methods" by means of specific gas analysers, and "manual methods" including a sampling phase on an appropriate material and a post analysis by an analytical laboratory,

The ILCs are made in the frameworlk of issuing approval certificates to accredited bodies carrying out the regulatory controls of air emissions from installations classified for environment.

The INERIS test bench generates combustion gas which can be heated, moisted and more or less enriched in different pollutants. This provides the ability to reproduce sampling in conditions of real materials and to simulate for instance gases generated by combustion plants or incineration plants. The gas used are produced by fuel-oil- natural gas- or biomass-fired furnaces.

The aim of tese ILCs is also to maintain or improve the quality of services provided by the participant bodies which are challenged not only to show that they know well the standards and reference rules but also that they actually master their implementation.

The bench can accomodate 12 participants at a time. A statistical analysis of the participants' data allows to evaluate the repetability and reproducibility confidence intervals of the implemented reference methods at different concentration levels. The participants' measurement bias is calculated by means of performance statistics as well as a benchmark of their results versus the reference value. Finally, suspicious values can be identified by outliers testing

2.1.5 COMPLEMENTARY APPROACHES

ILCs approach is a necessary complement to the GUM approach:

	GUM	ILC
Applies to	One measuring system at a time, fulfilling the requirement of uncertainty of the standard reference methods (SRMs) or to be used for self-monitoring (AMSs) Applies to any concentration	Several measuring systems, fulfilling requirements of uncertainty for standard reference methods (SRMs) implemented in parallel by several control laboratories. Could be applied as well to AMS, even if not done up to now because not required by the standard and difficult to implement. Applies to any concentration
Method	'Quadratic Sum' of a list of standard uncertainties (equal to the sum of variances) associated to metrological performances and to influence parameters, applying standardized ranges of variation of several factors (voltage, …) See EN 15267-3 and EN ISO14956	Dispersion of measured values obtained by different measuring systems and accredited teams on a same flue gas. See ISO 5725
Completeness	Does not include uncertainties due to DAHS (Data Acquisition and Handling System), nor the ones due to human factors. For AMS it also does not include the uncertainty of the SRM which is used for the calibration of the AMS	Includes all sources of uncertainties but does not cover the full ranges of variation of the influence factors covered in GUM.
Pros	Possibility to see the relative influence of the different components of standardised uncertainties	Provides an overview of the overall uncertainties. Considers the influence of human factors, of using different equipment and of DAHS (Data Acquisition and Handling System)
Cons	Does not consider the uncertainties due to human factor, variability of equipment and DAHS (Data Acquisition and Handling System), nor, for AMS, the uncertainty of the SRM used to calibrate the AMS. Need to model the measurement and to identify influence parameters of measurement and relationship between these parameters and the measurand. Necessity to be able to quantify the performance characteristics, including the effect of influencing quantities	Availability of ILCs on representative matrices for all parameters. (a real matrix with hot and wet conditions is highly recommended) No possibility to quantify the individual contribution of each influence parameter or metrological performance

Findings	Shows often lower uncertainty values than that of the ILCs ‘approach	Shows significant higher uncertainty values (when ILCs are carried out on actual flue gases)

Comments on Propagation of Uncertainty law approach (GUM)

The approach described in the GUM which is to use the characterisation results of a unique measurement system does not consider the human factor, which reflects the variability linked with a procedure executed by various persons or teams. This minimises the uncertainty where many teams are likely to intervene and could lead, in extreme cases, to erroneously invalidate an AMS (for instance if an AST is made by another organisation than that which performed the QAL2).

This uncertainty calculation approach (GUM) is systematically applied for AMS during QAL1 as well as for SRMs. For “automatic” SRMs (called P-AMS), those made with an analyser (O_2, CO, NOx, VOC), performance characteristics considered are roughly the same as for AMS, listed in Table 3 but the performance criteria given in the measurement method Standards or in the EN 15267-4 are more challenging than those usable for AMSs (EN 15267-3). For “manual” SRMs, those involving a sampling on a specific trapping device that is later analysed in a control laboratory (for dust, HCl, HF, NH_3, SO_2, Hg, PAH, Dioxins-Furans, PCB), the performance characteristics considered are those from the equipment that enables determining the volume of sampled gas, as well as those of the analysis.

For AMSs, the uncertainty calculation is made by certification bodies who do not know on which site the AMS will be installed (QAL1). The influence variation factors are hence maximised as well as the uncertainty resulting from it and from the instruments’ certificates (cf. influence parameters’ default variation table, given in the EN ISO 14956 Standard). On a given site, the influence factors’ variations can be more limited (for instance, concerning the ambient air temperature, supply voltage or other interferences), thus reducing the determined uncertainty.

For SRMs, the laboratory can potentially detail the influence parameters’ variation ranges according to the site, when they are known.

Inter-Laboratory Comparison approach (ILCs)

This approach is in fact only used for SRMs.

The Inter-Laboratory approach, by definition, considers the variability of the intervening teams and of the used equipment. These equipments must individually fulfil performance criteria fixed by the Standards describing the measurement method, as indicated before. But within the compliance range, the performances and influence parameters sensitivities may differ from one equipment to the other, thus increasing the inter-laboratory variability.

However, during Inter-Laboratory Comparisons, the influence factors do not all vary or vary in a lower range than the default variation ranges mentioned in the EN ISO 14956 Standard (GUM approach) and applied upon certification, which reduces the uncertainty compared to a calculation of relatively large variation ranges.

In practice, the uncertainty components linked to the different “equipment” used by participants, and to the “human factor”, have a strong influence; and the uncertainties estimated from the inter-laboratory comparisons’ reproducibilities are generally higher than those given by the GUM approach, as show the summary sheets by substance (cf. Chapter 4 and Annex E).

2.1.6 CONTROL BODIES' PRACTICES WHEN SUPPLYING UNCERTAINTIES IN THEIR TEST REPORTS

Virtually all control bodies (laboratories) show uncertainties calculated on an uncertainty budget (i.e. according to the GUM approach, combining uncertainties linked with various influence parameters to the method's performances) in their test reports. Indeed, they do not include differences linked to DAHS, equipment or human factor in their estimation, which often leads to an important underestimation of the displayed uncertainty compared to the effective uncertainty. Some control bodies propose a calculation made for each concentration result and for each measured parameter. Others show uncertainty tables per covered concentration range.

Very few control bodies show uncertainty estimation tables linked to the concentration level coming from the Inter-Laboratory Comparisons connected to the validation of an EU Standard or from Inter-Laboratory Comparisons organised for instance by INERIS (F), TNO (B) or HLUG (D) and which they took part in,. These uncertainty levels are significantly more important than those obtained by uncertainty budgets (GUM), explaining that the latter are the ones supplied to clients in the laboratory reports.

Finally, the Inter-Laboratory Comparisons' philosophies vary from country to country. The INERIS test bench generates real, hot, humid emissions, enriched (spiking) with the target compounds. The laboratories' result dispersions and hence the resulting estimated uncertainties are more important than those obtained on TNO or HLUG test bench, where the substances to be measured are often generated one by one in simple air, which masks some interfering effects, and at a close to ambient temperature, avoiding for instance the condensation risks when sampling, and hence losses of some compounds (see 3.1.2 for more info on INERIS test bench).

2.1.7 QUALITY OF DATA GIVEN TO AUTHORITIES BY OPERATORS

We can easily estimate the uncertainty linked to an individual measurement given by an AMS. The GUM approach allows checking that the uncertainty is under 75% of the maximum uncertainty required by the IED at the current Daily ELVs. The EN 15267-3 standard indeed requires that a margin of at least 25 % of the accepted maximal uncertainty is allocated to the contributions to the uncertainty of the site peripheral measurement (pressure, temperature, determination of the content in vapour of water and oxygen, the results of which are used to pass from a concentration expressed on the real conditions in concentrations expressed in the reference conditions). Another requirement of this standard is to take into account the AMS' implementation on site (for instance, the fact that measurement is made in one point of the measurement section for Dust).

The QAL2 calibration in principle globally validates that this level is respected at the level of the Daily ELV under site operating conditions. However, Inter-Laboratory trials carried out on similar measurement systems operated by control laboratories (when the SRM is an automatic method) show that the uncertainty can grow significantly, as a relative value, when the concentration level decreases (cf. the following example for CO).

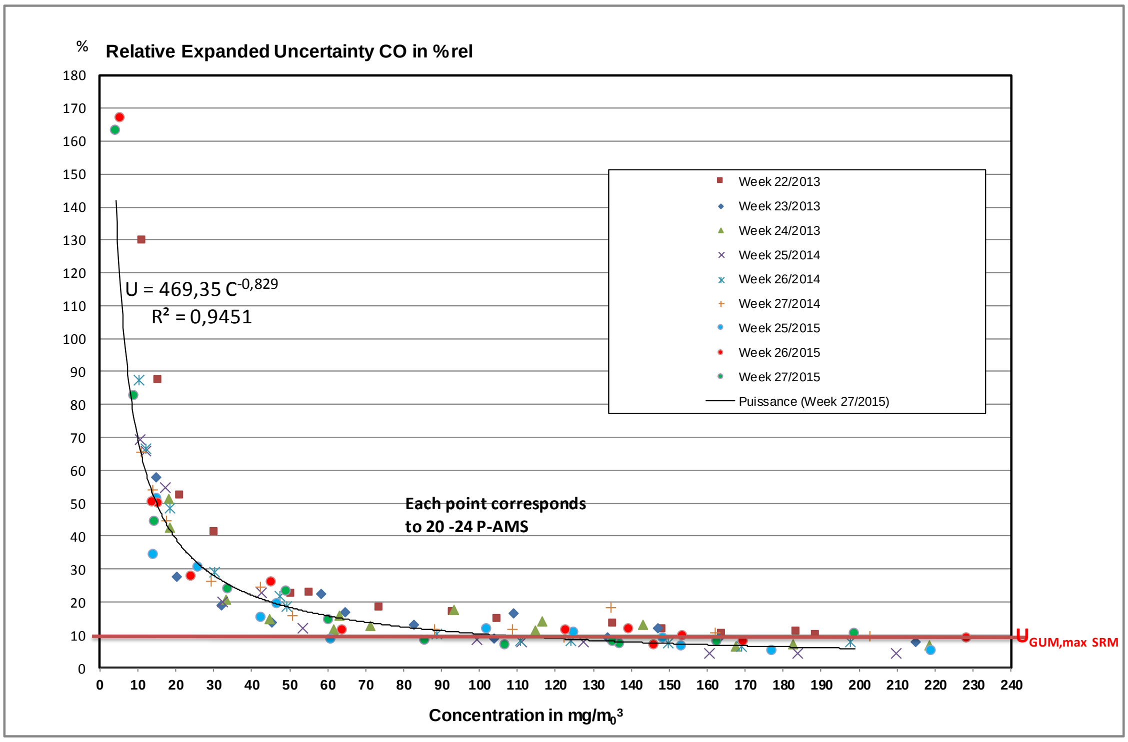


Figure 1: Evolution of the relative expanded uncertainty in function of the concentration. Example of ILCs on CO (INERIS test bench, 9 campaigns 2013-2015).

Note: The results shown in Figure 1 are resulting from INERIS' Interlaboratory comparisons. Each of the 9 weeks, 10 to 12 different laboratories were implementing between 20 and 24 different SRM equipment at different concentrations. Each point on the figure corresponds to the average of the relative expanded uncertainty obtained by those 20 to 24 SRMs. When the concentration decreases, the relative uncertainty increases. The red horizontal line recalls the maximum relative uncertainty required by the SRM standard for CO (EN 15058).

Since concentration levels given by AMSs on site, are nearly always below the Daily ELV, each individual measurement may include a significantly higher uncertainty, in relative value, than the level required by the IED at the Daily ELV. The above example shows that the relative uncertainty at 10 mg/Nm³ is almost 4 times as big as at the Daily ELV of 50 mg/Nm³.

We know, however, that the uncertainty linked to an <u>individual measurement</u> does not take into account in the QAL2 calibration operations:

- the intra-laboratory variability of the "control body" that did the site calibration (estimated during ILCs by the interlaboratory variance), and the inter-laboratory variability with regard to other laboratories,
- the potential bias linked with the AMS data transfer to the data logger;
- the uncertainty linked to data handling (potential moisture, temperature, pressure and oxygen content corrections with data that is not always calibrated).

It is also important to note that for certain substances that are not continuously monitored by an AMS, the values given by the operator are based on one or two periodic measurements a year obtained with SRM. In these conditions, it is difficult to assess their time representativeness and hence to consider their impact in the associated measurement uncertainty.

In conclusion, because of the widespread underestimation of uncertainties, a great care must be paid particularly when data much lower than the existing ELVs are used to set future limits, whatever the method used to measure them, e.g. from AMS's or SRM's. Particular care should be used on very low operational emission data since the uncertainty associated with tthis data is commonly not known/reported.

2.2 ABOUT LOQ DETERMINATION

Various Limit of Quantification (LoQ) method definitions exist. They are not all exactly identical, but mainly LoQ corresponds to the smallest value of a measurand that can be quantitatively determined in defined measurement conditions, with a defined uncertainty.

2.2.1 MANUAL METHODS (SRM)

For manual methods, the LoQ of the method is calculated based on the LoQ of the analysis part (noted $LoQ_{analysis}$) divided by the volume V of the sampled gas expressed in the ELV conditions.

$$LoQ = \frac{LoQ_{analysis}}{V} \qquad (6)$$

The measurement LoQ can therefore be lowered by increasing the sampled gas volume, which often requires increasing the sampling time.

A presumed value for the analytical LoQ can be determined by applying the formula:

$$LoQ_{analysis} = 10 \text{ x } Sr_0 + C_{avg,blank} \qquad (7)$$

Where Sr_0 is the blank values' dispersion standard deviation and $C_{avg,blank}$ is the average of the blank values.
In most cases, $C_{avg,blank}$ is negligible compared to 10 x Sr_0, leading to:

$$LoQ_{analysis} = 10 \text{ x } Sr_0 \qquad (8)$$

2.2.2 AUTOMATIC METHODS (SRM AND AMS)

For the automatic methods, the LoQ are determined following the EN 15267-3 or 4 Standard:

$$LoQ = 4 \text{ x } Sr_0 \qquad (9)$$

Where Sr_0 is the zero-repeatability standard deviation.

2.3 GOOD PRACTICES

2.3.1 UNCERTAINTIES FIXED TO THE LOQ

The NF T 90-210 Standard recommends that, after having estimated the LoQ according to what is described in § 2.2.1, at this level of concentration, the estimated LoQ ± $2.S_{LoQ}$ (S_{LoQ}: standard deviation of estimated LoQ), be within [LoQ ± 60% LoQ]. The 60% value was defined by convention in this Standard. If this is not the case, the selected LoQ is the concentration level fulfilling the requirement that the uncertainty is smaller or equal to 60%.
Some European Standards for the methods selected as reference for air emission measurements refer to a water analysis Standard because many gaseous substances are trapped in aqueous solutions. Therefore, it is possible that the NF T 90-210 Standard's procedure to analyse samples is used by certain laboratories.

2.3.2 MINIMUM ELV/LOQ RATIO

Minimum ELV/LoQ ratio for AMS

The lower end of the BATAEL range given in the BREFs must at least be equal to the LoQ, thus guaranteeing that a measurement uncertainty can be associated to this concentration level.

Since the measurement uncertainty is generally high at the LoQ level, a good practice is to require a minimum ratio between ELV and LoQ.

In Table 1, a minimum ratio of 5 was used.

In France, a minimum ELV/LoQ ratio of 10 is also demanded for reference methods (cf. following paragraph).

Minimum ELV/LoQ ratio for SRM

As for AMS, SRMs must have LoQ that are sufficiently lower than the site Daily ELVs where they are applied.

There is no minimum ELV/LoQ ratio required at the European level but a minimum ratio of 10 between ELV and the field blank is commonly used, which often corresponds to the same level of requirement.

For “manual” SRMs, a good practice which could be introduced when European Standards are revised is that the sampling time or the use of an analysis technique fulfilling the requirement that the LoQ is lower than 10% of the ELV (a ratio of ELV/LoQ > 10 is considered as providing an acceptable measurement uncertainty at the Daily ELV,) for the target measurand (which can be an individual substance or a sum of substances).

> Note: For a manual method, for which the concentration is a sum of concentrations obtained from different phases (for instance, for HF, with the particulate and gaseous phases), coming from various compartments or trapping devices (for Dust, with Dust trapped on a filter and in the probe-rinsing solution), and/or coming from various compounds (for instance, PAH, metals, dioxins), it is the sum of concentration-expressed LoQ, in the same unit as the ELV and calculated for each phase/instrument and/or substance, that must be below 10% of the ELV.

If the requirement, mandated by the French legislation, that LoQ < 10% of the ELV is generalised, it will lead to an increase in each sampling time, which could have an impact on the cost of mandatory controls if the number of measurements is not reduced.

As shown in § 2.2.2, for “automatic” methods, the LoQ is 4 times the repeatability standard deviation at zero point. It is hence linked to the equipment’s performance, which must be selected accordingly.

2.3.3 $U_{MAX\ SRM} << U_{MAX\ AMS}$

To ensure that the compliance check is of sufficient quality, the IED mandates uncertainty thresholds for data read by the AMSs, considering what the available AMS technology allows. They are given in Table 4.

Note that the EN 14181 Standard (version 2014) mandates that AMSs be certified according to the EN 15267-1, -2 and -3 Standards. The Standard’s part 3 recommends, as already explained in § 2.1.7, that the AMS’ uncertainty, should be **at least 25% under the maximum admissible uncertainty. This 25% corresponds to** the uncertainty brought by the correction of data which must be expressed in the same conditions as the ELV (correction of O_2, and, if applicable, water vapour).

	Relative Expanded Uncertainties of half-confidence intervals imposed to AMS by the IED $U_{IED,max\ AMS}$
CO – Carbon monoxide	10%
SO_2 – Sulphur dioxide	20%
NO_{xx} – Nitrogen Dioxide	20%
Dust	30%
TOC – Total organic carbon	30%
HF – Hydrogen fluoride	40%
HCl – Hydrogen chloride	40%

Table 4: Uncertainty thresholds required by legislation on self-monitoring of air emissions (IED Annex VI, Part 6, 1.3)

Maximum uncertainty levels of other substances have been set in national legislation. This is the case in French legislation for NH_3: The decree of 3rd August 2010 order on incineration and co-incineration mandates an uncertainty threshold of 40% for a Daily ELV of 30 mg/Nm³.

One can notice that the **IED does not set uncertainty levels for peripheral measurements of O_2 and water vapour** (these substances not being polluting substances). Nevertheless, these measurements are necessary to express the results in the same conditions as the ELV, including the O_2 reference level, and on dry gas, in case the AMS measurement technique leads to a reading on wet gas. These uncertainties hence contribute to the concentration uncertainty expressed in the site reference conditions.

The 2014 version of the EN 14181 Standard states that the AMSs measuring O_2 and water vapour may be calibrated with AMS/SRM parallel measurements like other substances, without however stating the uncertainty levels and the values to consider as "ELV" for the variability test.

In France, the FD X 43-132 Guide to apply the NF EN 14181 Standard recommends using AMSs, measuring O_2, whose measurement uncertainty at the site reference value does not exceed 15%, and AMSs measuring water vapour whose measurement uncertainty does not exceed 30% on the covered concentration range. Annex D determines the impact on uncertainty of correction from wet to dry gases and on correction from the real oxygen content correction to a reference oxygen content.

What uncertainty to mandate for SRMs used in periodic measurement or to calibrate AMSs?

The EN 14181 Standard was elaborated based on the ISO 11095 Standard that uses SRMs to calibrate AMSs. It states that, to be relevant and efficient, the QAL2 calibration operations require the following:

- **Have the possibility to get data on the whole AMS range;**
- **The SRM's uncertainty must be significantly lower than that of the AMS.**[10]

---

[10] The linear regression used for QAL2 tests is the application of the ordinary least squares general method which can be applied under certain conditions (See http://www.inrp.fr/Tecne/Acexosp/Savoirs/Stathtm1.htm). The method only minimises the differences between the regression line and the experimental points (AMS), thereby following the X axis. This implies that the uncertainty on the value shown in Y (SRM) must be nil or negligible in comparison of the one of the AMS. This requirement, well-known by metrologists, is evoked in EN 14181 Standard, among others in notes 2 and 3 of the § 8.6 regarding the variability test

Unfortunately, the first condition is not always respected, which leads FD X 43-132 to allow combining AMS/SRM comparison data with those of the zero / span gas injection, and when the concentration level cannot vary and remain at a low level, also with a span point (concentration different than 0), to obtain an AMS calibration line that is not unsuitable.

For the second condition, considering that very often, the AMS and SRM measurement equipment is not very different, it has appeared relevant in France to recommend that SRM have a measurement uncertainty not exceeding 50% of those enforced to the AMSs.

However, this principle is not always respected: Standards describing the reference methods set uncertainty limits that can be well above this target (cf. Table 5), including for ELVs corresponding to concentration levels required for the former LCP and WI European Directives (now recast into the IED, Annexes V and VI).

The Inter-Laboratory Comparisons organised for instance in France dedicated to control laboratories calibrating AMSs and periodic measurement compliance check for installations, or Inter-Laboratory implementation trials by CEN for Standards validation, show that, for some substances, **it is not possible with current methods and available equipment, to lower the measurement uncertainties to this target level of 50% of the uncertainty enforced to the AMSs when they must comply with ELVs fixed in the former LCP and WI European Directives (recast into the IED). Even when the SRM enable reaching the required relative measurement uncertainty at the level of the Daily ELVs, they do not comply with them anymore at lower concentration levels (cf. Figures and Tables of summary sheets in § 4).**

	SRM uncertainty targets: 50% of the uncertainty required for calibrated value given by the AMSs	Uncertainty required by the European ELV legislation, or reference value for (O_2) / water vapour concentration
CO	± 5%	± 6% (EN 15058)
SO_2	± 10%	± 20% (EN 14791)
NO_x	± 10%	± 10% (EN 14792)
Dust	± 15%	± 20% (draft revision pr EN 13284-1)
TOC, CH_4	± 15%	± 15% (XP X 43-554)
HF	± 20%	-
HCl	± 20%	± 30% (EN 1911)
Water vapour	-	± 20% (EN 14790)
O_2	-	± 6% (EN 14789)

Table 5: Uncertainty targets for SRMs

“NOTE 2: 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 a false failure of the variability test). The procedure for determination of uncertainty is not in accordance with GUM (ISO/IEC Guide 98-3).

NOTE 3: This method implies that the quality of the application of the SRM influences the result of the test. It will be noted, however, that it is the result that determines a pass or failure and that in some cases a better application of the SRM could change the result from fail to pass.”

3. METHODOLOGY USED TO CHARACTERISE SRMS' AND AMSS' PERFORMANCES

Summary sheets show the SRMs' and AMSs' characteristics (cf. Annex E and Chapter 4).

3.1 SRMS' CHARACTERISTICS

3.1.1 SRM CHARACTERISTICS' DATA

Summary sheets provide the following SRMs' characteristics:

- The uncertainty level required at the Daily ELV level;
- An estimate of the method's LoQ;
- A calculation of the minimum ELV based on this LoQ and complying with the good practice of LoQ being under 10% of the ELV.

For manual methods, we assumed a 1-hour sampling period, a bubbling flow rate of about 2 l/min to fulfil the trapping efficiency requirements. The analytical LoQ, from which the LoQ of the method was calculated, is also given.

Time and number of samplings during periodic regulatory controls: common practice in most European countries

Time: the sampling time depends on the site's Daily ELV concentration levels. The minimum sampling time is 30 minutes and can be increased to try obtaining a higher result than the method's LoQ. Therefore, sampling time can be doubled or tripled but generally does not exceed 2 hours (except for Dioxins, where the very low ELV concentration level requires a sampling time of 6 to 8 hours).

Number of samplings by compound: 1 to 3 samplings, depending on the country.

In France, the 10 March 2010 decree requires adapting the sampling volume or times, so that the LoQ < 10% of the Daily ELV, with a minimum of 30 minutes for gaseous substances and 1 hour for particulate substances. It also requires 3 samplings per substance, unless the expected concentration is under 20% of the Daily ELV; in this case, a single sampling for a longer time (usually no longer than 2 hours) is required.

In Germany, all samplings (except PCDD/F) are limited to 30 minutes.

Significantly increasing the sampling time will also lead to significantly more expensive control procedures, unless the required number of samplings is adapted. When quadrupling, the time spent on site, the control service's costs due to the time spent on site will increase by about 100%, and the uncertainty will be reduced by 20%.

For automatic methods, few analysers are certified as SRM and the values of their repeatability standard deviation at zero point are hence rarely available in a certificate. When a control laboratory uses a non-certified analyser, it can nevertheless determine the repeatability at zero point by following the EN 15267-3 Standard's procedure or by getting it from a metrology laboratory. This determination is now mandatory in France for accredited control laboratories. For the present study, the median value obtained by the AMSs fulfilling the SRM measurement principle was chosen as default LoQ for these methods, to calculate the minimum ELV equalling 10 times the LoQ. For some substances, instruments' performances that could enable an evolution of the Daily ELVs in the future, are however mentioned.

Common practice in European countries is to make samplings for compounds measured with automated methods during the duration of the whole site sampling plan.

3.1.2 INTER-LABORATORY COMPARISONS DATA

As mentioned in § 2.1.2, for each trial corresponding to one concentration level j, repeatability $S_{rj}{}^2$ and inter-laboratory $S_{Lj}{}^2$ variances are determined by a robust estimation following the ISO 5725-5 Standard's procedure:

U, the expanded uncertainty of measurement is estimated from the reproducibility variance at the j concentration level:

$$U_{ILC,SRM} = t_{1-\frac{\alpha}{2}} \times S_{Rj} \tag{10}$$

where $t_{1-\frac{\alpha}{2}}$ is the fractile of order $\left(1-\frac{\alpha}{2}\right)$ of the Student Law at (p-1) degrees of freedom; we consider $\alpha = 0.05$ for a 95% confidence interval (p: number of participant laboratories).

and $$S_{Rj}{}^2 = S_{rj}{}^2 + S_{Lj}{}^2 \tag{11}$$

3.1.2.1 INERIS TEST FACILITY

The bench is designed to generate gaseous effluents of identical composition for each of the 12 sampling ports. Prior to their introduction into the loop, the gases provided by combustion in one of the three boilers fueled with gas, light fuel oil or biomass can be, if necessary, heated, moistened and enriched by some pollutants injected through a generation system with mass-flow controllers (CO, NO, SO_2, HCl, HF, CH_4, C_3H_8, etc.) or liquid (specific VOC) to simulate gas matrices with very similar characteristics to those of industrial facilities burning fuels or waste.

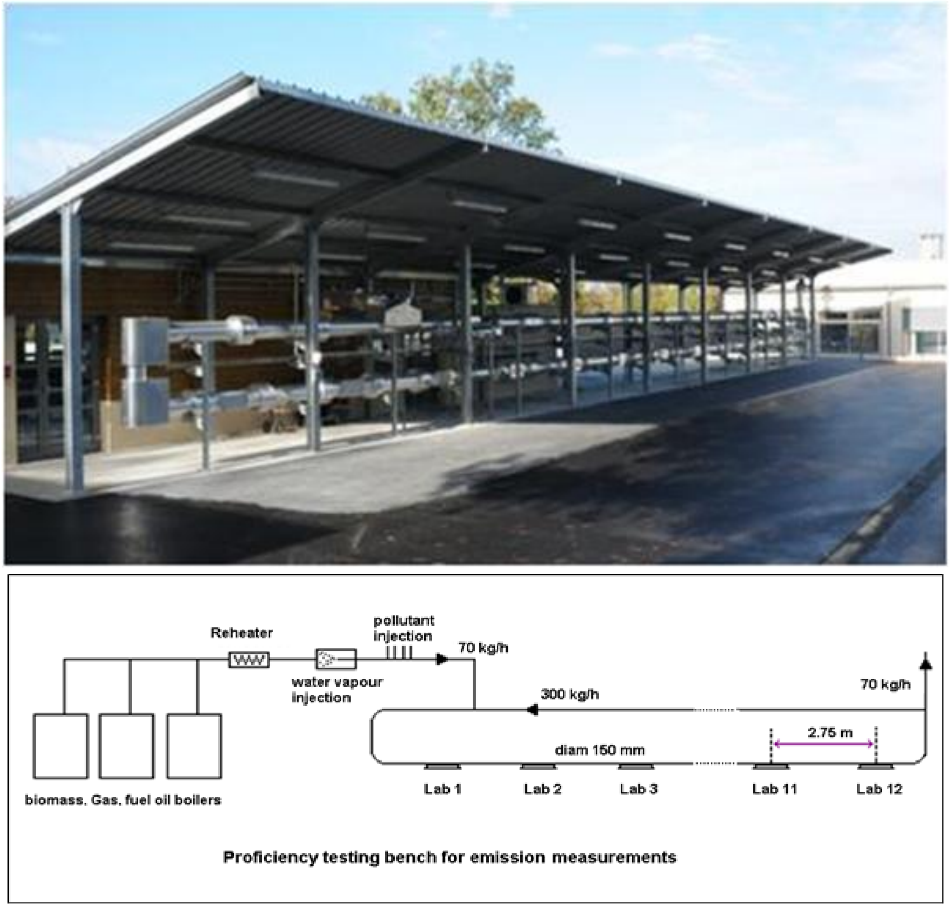


Figure 2: INERIS test bench

The concentration levels generated are monitored by a FTIR (Fourier transform infrared spectroscopy) instrument which allows to adjust the level of concentrations. The generated gases enter a loop made of steel, internally protected by a PFA coating, where a 400 kg/h flow-rate circulates. This loop is maintained in temperature by electric tracing. The inside diameter of the duct is 150 mm.

INERIS is accredited by COFRAC (n° 1-2291 - scope of accreditation on www.cofrac.fr/en/home) for the organization of inter-laboratory campaigns according to EN/ISO/IEC 17043.

3.1.2.2 INERIS ILC PROGRAMME

The programme of ILCs is relative to the implementation of reference methods for measurement of gas compounds or dust from stationary sources emission. It has been defined in consultation with the members of the Steering Committee, in agreement with the Ministry in charge of Environment.

The trials are carried out during 3 days. The programme changes every 3 years.

The purpose of the ILCs is to enable **each participant laboratory** to know:

- The trueness of its results to the assigned value (taken as the “reference” value),
- The onsite repeatability of its measurements through the simultaneous implementation of two measurement equipments complying with applied standard.

ILCs are also used:

- To determine the confidence intervals of repeatability and reproducibility in the implementation of the measurement methods; reproducibility confidence intervals especially allow to evaluate if the uncertainty associated with the the measurement results being implemented by laboratories during the calibration of automated measuring systems (AMS) is sufficiently low in comparison with the required uncertainties required on the latter by regulation,
- To follow the evolution of the quality of the implementation of the standardized procedures by accredited and “approved” laboratories working in France, year after year.

  Most of laboratories are French with a few Belgian and German laboratories.

Most of the results shown in this study come from campaigns organised between 2013 and 2016 as shown on the graphs presenting the relative expanded uncertainties for different substances. The participants from France and other European countries (Belgium and Germany) are accredited according to EN 17025 and have got the “agrément” from the Minsitry of Environment to perform emission for regulatory purposes on the French territory. The list of participants can be found in the French arrêté:

…https://www.legifrance.gouv.fr/eli/arrete/2016/12/15/DEVR1635228A/jo

3.1.2.3 STATISTICAL TREATMENT OF TRIALS RELATED TO O_2, CO, NO_X, TVOC, NMVOC, CH_4, CO_2, SO_2, DUST MEASUREMENTS

The statistical treatment of the data leads to the determination of:

- The value taken as a "reference" (assigned value) of each compound for each trial, and its associated uncertainty;
- The bias of each participant by comparison with the values taken as a "reference" (performance statistics);
- The outliers of participants;
- Confidence intervals of repeatability and reproducibility for each compound.

ILCs are performed on real effluent arising from the boiler and spiked prior to being circulated in the loop.

The value taken as a “reference” or assigned value on which to base, to evaluate the performance of laboratories in terms of trueness and precision must therefore be calculated from the consensus values of participating laboratories. The value taken as a "reference" is determined by robust analysis of data, as described in the standards ISO 13528 and ISO 5725-5. Robust analysis consists in applying to the data, a calculation algorithm that allows, by successive iterations, to give less weight to the extreme values of the series of data processed, until the process converges.

3.1.2.4 INTERPRETATION OF RESULTS

In annex E are presented ILCs available data. Most of them are coming from INERIS’ILCs. Some data from the validation of SRMs may complement the INERIS information.

For each measuring campaign, several levels of concentrations of each studied substance are generated. Each point of the graph corresponds to the average of the relative expanded uncertainty provided by the 20 to 24 measurement systems of 10-12 participant laboratories.

On Figure 3, the results of 9 campaigns on CO are presented and a trend curve is calculated. It is generally an exponential curve which gives the highest determination coefficient R^2 value and the best estimate of the expanded uncertainty expressed in absolute or in relative unit.

A red line recalls the maximum level of uncertainty required by the SRM: $\mathbf{U}_{\mathbf{GUM,maxSRM}}$, calculated with the GUM approach.

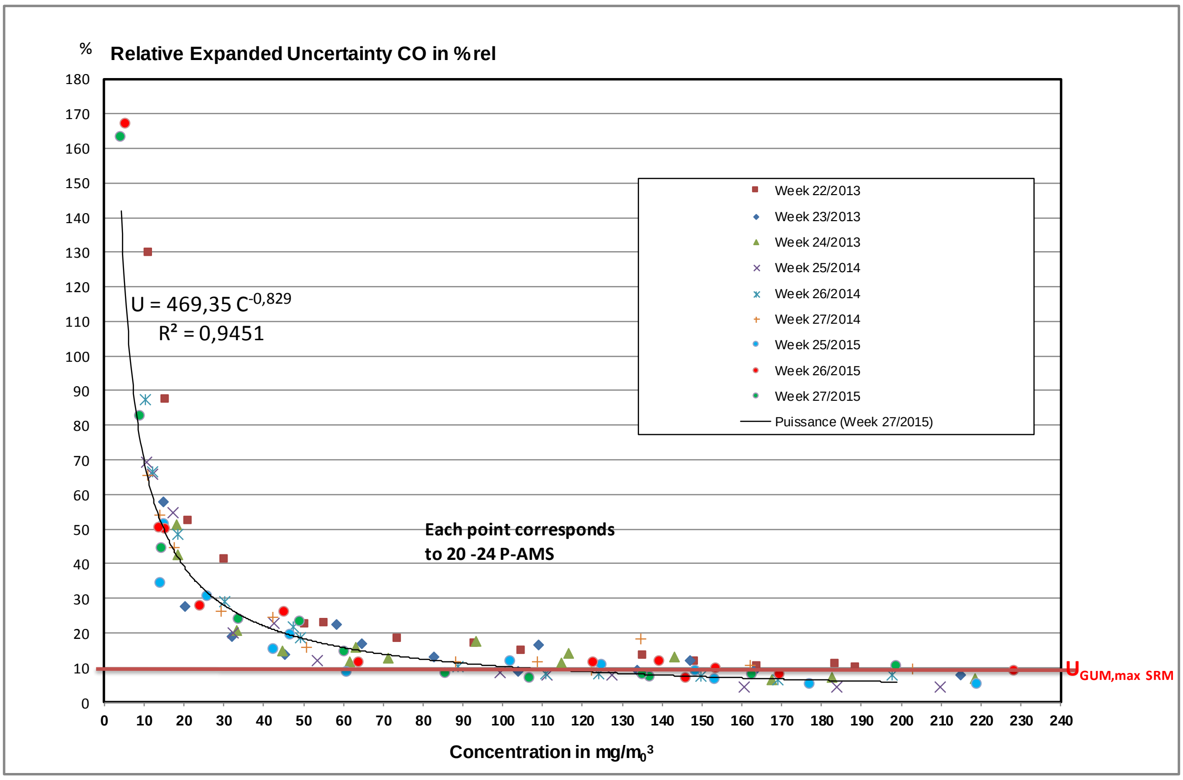


Figure 3: Example of the estimate of the expanded uncertainty ***U*** *as a function of the concentration (drawn from ILCs data)*

3.2 AMSS' CHARACTERISTICS

3.2.1 CERTIFICATION DATA

In Europe, the AMSs' certification (QAL1) is currently done or coordinated by:

- The Environmental Agency of England and Wales, which has developed a Monitoring Certification Scheme (MCERTS), implemented by the CSA group;
- And the *UmweltBundesAmt* (UBA), the German Environmental Protection Agency, which certifies instruments based on characterisations made by TÜV Rheinland.

The certified AMSs' certificates (QAL1) mentioned in this report are available online at:

- http://www.qal1.de/en/
- http://www.csagroupuk.org/wp-content/uploads/2015/12/MCERTSCertifiedProductsCEMS.pdf

It is important to note that:

- The choice of the AMS's certified range is in general set according to the installation's Daily ELV for which the instrument will be used; for instance, for CO, the certification is in general made for a range up to 75 mg/Nm³ (which is 1.5 times the Daily ELV of 50 mg/Nm³, for incineration (cf. § 5.2 of the EN 15267-3)). Some AMSs are certified for several ranges.
- The expanded uncertainty is calculated at the IED's (or formerly, the LCP and WI Directives) Daily ELV, or at the lowest ELV imposed on the installation for which the instrument is used, for instance at 50 mg/Nm³ for CO. For a lower concentration level, the relative expanded uncertainty (in %) will be higher. However, as it can be seen on Figure 3, it does not vary in a linear way with concentration, because some components of the uncertainty have a constant contribution, regardless of the concentration level: therefore, the uncertainty may be higher at that level. Under a certain concentration level, the chosen certified range may also not be suitable anymore. (The larger the range, the lower the accuracy at low concentration.)

Measurement uncertainty

When certifying AMSs, the GUM approach is used (an uncertainty budget is established). The certificate systematically provides the relative expanded uncertainty and, in most cases, also the absolute uncertainty (in mg/Nm³ or in % of volume, according to the substance), thus mentioning the concentration level for which the relative uncertainty was determined.

When this concentration level is not specified, it is assumed to be equal to the concentration indicated in the summary sheet (cf. Chapter 4 and Annex E).

This uncertainty $\mathbf{U_{certif,AMS}}$, can be compared to the maximum uncertainty for the AMS $\mathbf{U_{GUM,maxAMS}}$ to fulfil the variability test made during the QAL2 control (cf. Chapter 4).

Limit of Quantification

It is calculated based on the repeatability standard deviation at zero point and following the formulas given in § 2.2.

Note: the certificates given by the certification bodies do not always give the value of the repeatability standard deviation at zero point with the accuracy needed to determine a precise LoQ. For instance, some certificates show a standard deviation of 0.0 mg/Nm³. In this case, we have assumed that the number of digits after the comma was giving the measurements' accuracy and hence that the repeatability standard deviation at zero point was < 0.05 mg/Nm³.

Minimum ELVs fulfilling an ELV/LoQ = 5 ratio for AMS

When certifying an AMS, the repeatability standard deviation at zero point is determined, and it must not exceed 0.2% volume for O_2 and 2% of the certified measurement range for the other substances. The EN 15267-3 Standard shows that the LoQ is 4 times the repeatability standard deviation at zero point (cf. §2.2).

For each certified AMS, its LoQ and the minimum ELV equal to 5 times this LoQ were calculated.

3.2.2 AMS'S CHARACTERISTICS RESULTING FROM QAL2 CALIBRATIONS

3.2.2.1 QAL2 CONTROL PRINCIPLE

Important reminder to ease the understanding of the data shown in paragraphs 3.2.2.2 and 3.2.2.3:

The QAL2 control, mandated by the EN 14181 and EN 15267-3 Standards, for all continuous measurements, is to determine the calibration function of the AMS, against the SRM, based on parallel AMS / SRM measurement and to check the variability of the AMS.

The calibration function is calculated based on data pairs [AMS; SRM], in the AMS's measurement conditions: for instance, on wet gas if the AMS measures on wet gas.

The variability test aims at validating the AMS's ability to provide measurement results, at the ELV level, with an uncertainty fulfilling the legislation. When legislation does not set a threshold, a possibility is to set an uncertainty, double that of the SRM, at this same ELV level.

The test consists in testing the AMS's reliability with respect to the legally-binding uncertainty threshold, by checking that the S_D standard deviation of the differences between the calibrated AMS measurements (to which the determined calibration function was applied) and the SRM measurements is under the legal uncertainty (expressed as standard uncertainty), weighted by a k_v factor, taking into account the number of data pairs.

In the test, the AMS and SRM measurements are expressed in the site's reference conditions, as is the ELV, meaning that the test also takes into account the peripheral measurement variability (measurement of O_2 and, where applicable, of water vapour).

$$S_D \leq \sigma_0 \times k_v \qquad (12)$$

With $$\sigma_0 = \frac{\mathrm{U}_{\mathrm{IED,max\ AMS}} \times \mathrm{ELV}}{1.96} \qquad (13)$$

Where:

S_D: Standard deviation of the differences between AMS and SRM measurements, in mg/Nm^3 dry, 11% O_2

σ_0: Standard uncertainty that the AMS must fulfil, in mg/Nm^3 dry, 11% O_2

k_v: Weighting factor; between 0.8326 for 3 data pairs and 0.9824 for 20 data pairs

$U_{IED,maxAMS}$: Legally-binding uncertainty threshold that the AMS must fulfil, corresponding to an expanded uncertainty, expressed in % (for example 30 % for Dust, 10 % for CO…)

ELV: Emission Limit Value, in mg/Nm^3 dry, 11% O_2

NOTES:

- The 2014 version of the EN 14181 Standard mentions that only the values under the ELV must be considered for the variability test (in the former version, this point was not mentioned, however it was applied in France because it was mentioned in FD X 43-132 of 2007).
- In France, since 2007, the FD X 43-132 offers the possibility of combining, with the parallel AMS/SRM measurements, the addition of span gas measurements, to determine the calibration function when the measured concentrations are low or when the range of concentrations tested are limited; this possibility was added in the 2014 version of the EN 14181 Standard.

  The combination of comparative SRM/AMS data and of measurements at the Daily ELV level with span gases avoids issues when the QAL2 data provides only a cloud of AMS/SRM points at low concentration levels. In this case, an unlimited number of slopes can go through a cloud of points, without any physical meaning.

  Therefore, for QAL2 controls performed before 2015, there can be a difference in the data handling, depending on where the QAL2 was performed.
- As specified in the 2014 version of the EN 14181 standard, the calculated variability takes into account the uncertainty components associated with the repeatability of the AMS and SRM, but does not take into account all of the uncertainty components of the SRM. Thus, an insufficient SRM performance may lead to a worse apparent variability for the AMS.

3.2.2.2 ESTIMATION OF THE ELV THRESHOLD UNDER WHICH THE VARIABILITY TEST IS NOT FULFILLED

A first proposal is to calculate the minimum ELV under which the variability test is not fulfilled, according to the legally-binding uncertainty threshold $\mathrm{U}_{\mathrm{IED,max\ AMS}}$.

A priori, this calculation could simply be made based on the QAL2 control reports, by applying the following calculation, based on Equations (14) and (15):

$$\mathrm{S_D} \leq \frac{\mathrm{U}_{\mathrm{IED,\,max\ AMS}} \times \mathrm{ELV}}{1.96} \times \mathrm{k_v} \tag{14}$$

Therefore $\mathrm{ELV_{min}} \approx \frac{\mathrm{S_D} \times 1.96}{\mathrm{U}_{\mathrm{IED,max\ AMS}}}$ if the k_v factor is neglected (15)

However, for the sake of verification, a data reprocessing was made for the examples from QAL2 reports given by the industrial associations.

It appears that the value, obtained by this calculation, may be biased, compared to the one given by data reprocessing, for the following reasons:

- The ELV_{min} calculated based on Equation (4) can be lower than the concentrations measured on site; however, the variability test is “normally” made with concentrations lower than the ELV. Data reprocessing could lead, in such cases, to a limit ELV not because the variability test is not fulfilled, but because of the lack of remaining data pairs to make the test.

  In this case, it is not possible to really check the compliance of the AMS with the requirements at ELV levels lower than the measured concentrations.

  The calculated ELV must therefore not be lower than the lowest measured concentrations on site during the QAL2 control. If this is the case, no conclusion can be drawn on the performance of the AMS under these levels.

- During data reprocessing, the ELV is progressively lowered and, in some cases, some data pairs are no more taken into account, because they are above the tested ELV. The S_D value can therefore vary with the considered ELV. However, in the calculation approach, S_D is considered as constant.

The summary sheets (see Annex E) show:

- The average concentration measured by the SRM;
- The number of parallel SRM/AMS measurements made;
- The minimum ELV obtained by data reprocessing or according to Equation (14);
- The minimum ELV obtained according to Equation (14) In the case where data reprocessing eliminates data pairs in the variability test causing a change of the S_D value.

The detailed calculation tables are given in Annex A.

3.2.2.3 ESTIMATION OF THE SITE ELV'S UNCERTAINTY THRESHOLD UNDER WHICH THE VARIABILITY TEST IS NOT FULFILLED

Based on Equation (3), the lowest uncertainty threshold for which the variability test is fulfilled can be calculated, so that this can be compared to the uncertainty defined in the instruments' certificates.
For QAL2 controls, the uncertainty threshold is obtained in specific instrument installation conditions and matrix characteristics.

3.2.2.4 QAL2 CONTROL CALIBRATION FUNCTIONS ANALYSIS

It has been useful to examine several QAL2 control reports, supplied by the industrial associations and performed in various EU Member States, in order to evaluate:

- if the supplied SRMs and AMSs measurements were consistent,
- if the given calibration functions were relevant
- and if difficulties in implementing calibrations of the AMSs' against SRMs' according to the emitted concentration levels and the current Daily ELVs, have been observed.

Remark on the variability test's relevance

The variability test is made with all the AMS's and SRM's calibrated measurements, expressed in mg/Nm³ dry at 11% O_2. The dispersion standard deviation of the difference between these measurements is then determined. This S_D differences standard deviation is then compared to $\sigma_0 \times k_v$, where σ_0 is the legally-binding uncertainty threshold, expressed as an absolute standard uncertainty value ($\sigma_0 = \frac{U_{IED, max\ AMS} \times ELV}{1.96}$), and k_v is a weighting factor according to the number of data pairs taken into account for the variability test.

Since the comparison is made between 2 data expressed as absolute values, **this variability test is meaningful only if there are enough data near the Daily ELV, because the uncertainty, to which S_D is compared, is calculated at the concentration level corresponding to the Daily ELV.** During the QAL2, if it was not possible to vary the concentrations, and the tested level has remained low, important differences between the AMS and SRM measurements expressed as relative values can be seen (for instance, close to the measured concentration). Nevertheless, these differences remain low in absolute values, compared to the Daily ELV, and therefore the S_D standard deviation is well below σ_0 and the test is always fulfilled. **In this case, with a cloud of points at low concentrations, the test is not relevant because one cannot confirm that the test was conclusive with measurements near the Daily ELV.**

4. SUMMARY SHEETS FOR SRMS’ AND AMSS’ PERFORMANCE CHARACTERISTICS

To facilitate the understanding of this chapter and the summary, references are made, for instance here for CO (see § 4.1.2), to the summary sheet in Annex E and to Table 1 in the summary.

4.1 OVERVIEW OF THE CURRENT SITUATION

4.1.1 O$_2$

Those comments are based on the Summary sheet in Annex E. To facilitate the understanding of the sheets, they are gathered at the end of the report. They can easily be printed in A3 format.

The EN 14789 Standard describes the SRM: Paramagnetic Method.

LoQ:

The LoQs calculated for paramagnetic AMSs (the method corresponding to the SRM) are between 0.00 and 0.06% volume, with a median value of 0.02% volume. Although not all certified instruments are suitable for measurements as P-AMS by laboratories, this indicates the LoQ that can be reached by this measurement method. Taking into account all the certified AMSs, 50% of the instruments have a LoQ ≤ 0.03% volume, with a rather large LoQ range, between 0.01 and 0.25% volume.

For Waste Incineration installations with an O$_2$ reference level at 11% volume, and concentrations generally very close to this level, the instruments’ LoQs are suitable.

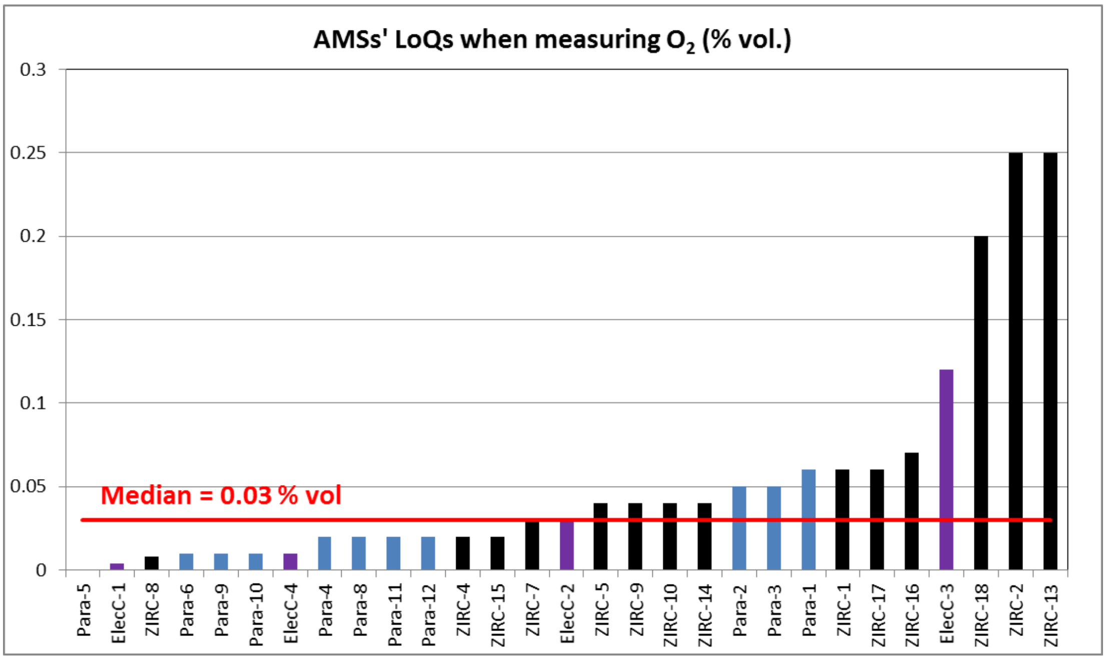


Figure 4: Certified AMSs’ LoQs when measuring O$_2$

Measurement uncertainty:

For the SRM applied by control laboratories, the expanded uncertainty mandated by the EN 14789 Standard, via an uncertainty budget, is of 6% rel. at the measured concentrations’ level. It can easily be reached by all the certified paramagnetic analysers available on the market; the relative expanded uncertainty is between 0.28 and 4.2 rel. %, with a median value of 2.3 rel. % and an average value of 2.2 rel. %.

The estimation of the expanded uncertainties coming from the SRM implementation during the ILCs, leads to a very close value: 2.3 relative %, which means that the implementation of the measurements on site and the variability between laboratories only have a weak impact on the uncertainty.

Remark: Figure 6 shows that the estimate of uncertainty may differ from one week to another, for the same level of concentration. This is linked to the implementation of the laboratories. The consequence is a low determination coefficient.

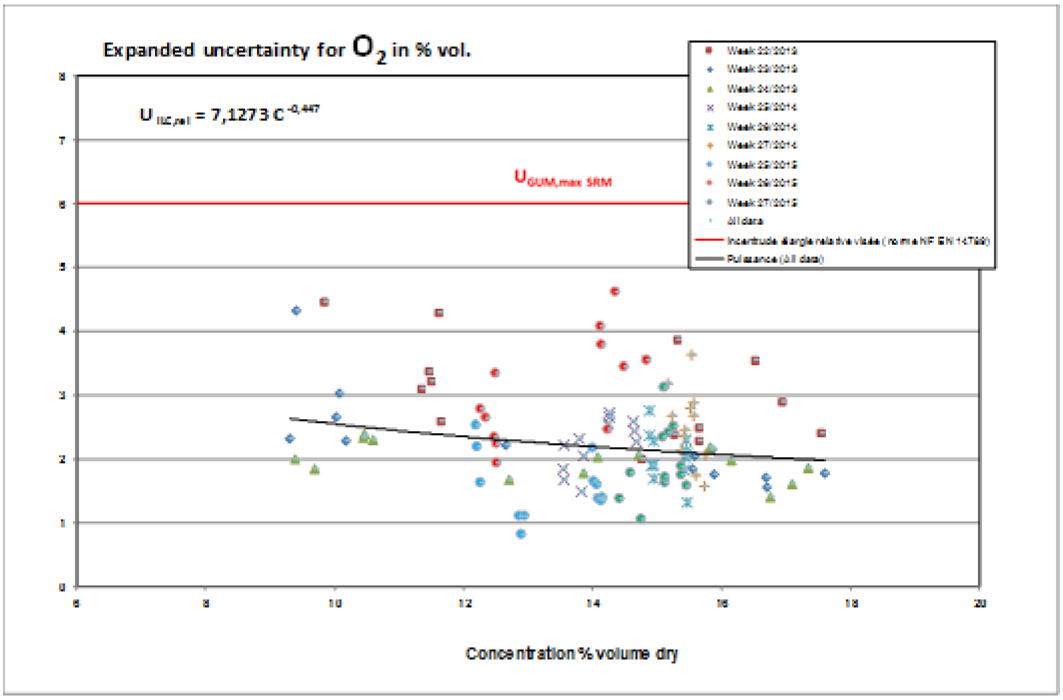


Figure 5: Estimation of actual uncertainty using ILC, when measuring O_2

For AMSs, the legislation does not require a maximum relative uncertainty level. The French FD X 43-132 application guide recommends using instruments with a relative expanded uncertainty not exceeding 15%. Considering all the methods used by the various certified AMSs, the relative expanded uncertainty median value is very close to that of paramagnetic instruments alone, with a median value of 2.4 rel. % and an average value of 2.3 rel. %.

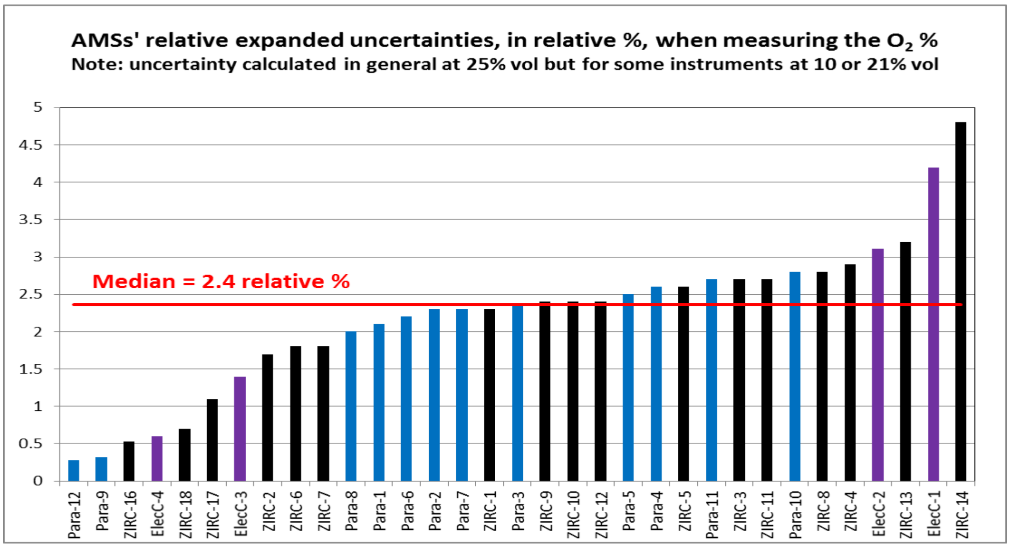


Figure 6: Certified AMSs' relative expanded uncertainties when measuring O_2

If the average LoQ and SRM measurement uncertainty performances are rather satisfying, they are on average equivalent or near those of the AMSs, leading to QAL2 implementation conditions that are not ideal: the $U_{\textbf{max SRM}} << U_{\textbf{max AMS}}$ condition is not fulfilled;

Additionally, the O_2 concentration variation condition during QAL2, is likely to be difficult to fulfil for some installations.

Nevertheless, the QAL2 calibration on oxygen remains necessary to detect a potential (malfunction) failure of the AMS on site (air leak, for instance) or an inappropriate probe positioning (for instance, an unrepresentative sampling point).

Conclusion for O_2

The paramagnetic reference method has very good performances. The instruments used for SRM and the AMSs often are very robust and there is limited maintenance. The situation is hence satisfactory for oxygen contents found in the Waste Incineration Plants and Large Combustion Plants sectors, although the AMSs' calibrations based on QAL2 are made with SRMs whose performance in terms of measurement uncertainty, is only equivalent to that of the AMSs.

Note that zirconia sensors are unsuitable for effluents where the matrix gas is rich in reducing gases (CO, H_2S, etc.). Electrochemical cells are not suited for all matrices (not recommended for some gases such as H_2S, halogenated compounds, metals, etc.) and their capacity to continuously operate must be checked.

Finally, instruments with the lowest uncertainties must still be favoured in all cases, both for SRMs and AMSs. This is because O_2 measurement uncertainty has an impact on the controlled substances' concentration values, expressed under site's reference conditions (especially when the measured O_2 concentration is high, see Annex D). It therefore impacts the declaration of compliance/incompliance with the ELVs as well as the fulfilment of the calibration function validity test, performed during the QAL2 and AST controls.

4.1.2 CO

The comments below are based on the summary sheet found in Annex E.
To ease understanding of the evaluation of the performance of the AMSs and SRMs and their impact on the feasibility of lowering the ELVs for gaseous substances, details are given here for CO, in a step by step approach, showing references to the CO summary sheet in Annex E and references to Table 1.

The EN 15058 Standard describes the SRM: non-dispersive infrared spectrometry and its variations method (GFCIR).

LoQ:

The LoQs calculated for AMSs using infrared techniques (the method corresponding to the SRM) are rather variable (0.03 to 2.8 mg/Nm³) [see CO summary sheet in Annex E: LoQs of NDIR-1 and of GFCIR-6 // see range given in Table 1, col. 3], with a median value of 0.8 mg/Nm³ [cf. Figure 7 /// and LoQmed value given in Table 1, col. 4]. For a better representativeness, one could consider as a minimum LoQ, the average of the 3 lowest LoQs, being 0.07 mg/Nm³ [see LoQmin in Table 1, col. 4]. To fulfil the ELV/LoQ = 10 ratio recommended for SRMs, this leads to a minimum ELV of 8 mg/Nm³. Taking into account all certified AMSs, half of the instruments have a LoQ ≤ 0.6 mg/Nm³) [17 out of 30 available LoQ values; see CO summary sheet in Annex E]. The overall median value is lower, among other reasons, because of the FTIR instruments' lower LoQs [shown by a blue bar on Figure 7]. However, DOAS and electrochemical cells methods [in green and orange on Figure 7] do not appear suitable.

These LoQs of AMS using infra-red techniques (0.07 to 0.8 mg/Nm³) would lead to minimum ELVs, based on the ELV/LoQ = 5 ratio principle, for use as AMS, comprised between 0.35 and 4 mg/Nm³, [values given in Table 1, col. 5).

Following the analysis of 10 QAL2 test reports [see CO summary sheet in Annex E, column "Min ELV by data reprocessing"] however leads to minimum ELVs, enabling the fulfilment of the variability test, that are much higher than this median value of 4 mg/Nm³: from 6 to 29.2 mg/Nm³. For 5 of these control tests, the minimum ELV obtained by data reprocessing is maximised, because of on-site concentration levels between 15-20 mg/Nm³, which hinders lowering the ELV because of a lack of sufficient data to make the test (cf. § 3.2.2.2). Considering instead the minimum ELVs estimated by calculation, they are lower for one instrument [GFCIR 1 and 2], representing 2 QAL2 test reports, but for the others they are of the same order.

The minimum value of 4 mg/Nm³, based on 5 times the median value of LoQs, appears low for instruments currently used on sites, given the QAL2 control test results. This is also likely to be linked to the fact that the QAL2 control, and hence the variability test, is also impacted by the SRM's performances and not only by those of the AMS.

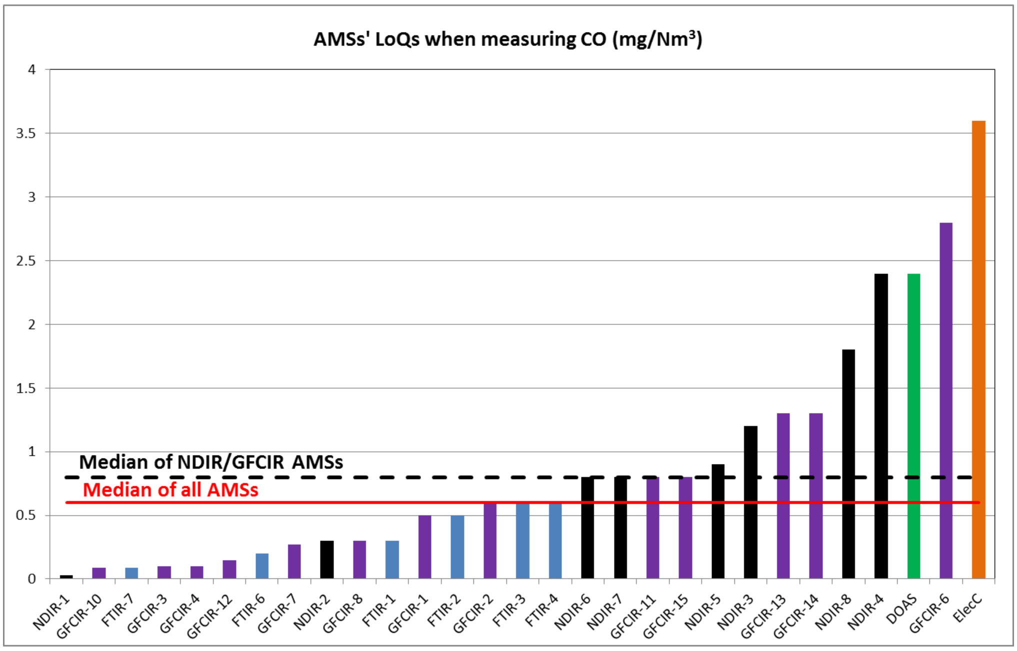


Figure 7: Certified AMSs' LoQs when measuring CO

It is desirable to have analysers that can be used as SRM and for which the LoQ is sufficiently low, for example less than 0.5 mg/Nm³ so that the average concentrations on site, which in steady operation are very low, can be precisely determined.

<u>Measurement uncertainty:</u>

Regarding uncertainty, the value mandated by the EN 15058 Standard describing the SRM, via an uncertainty budget, is of 6% at the Daily ELV level [see Table 5 // value given in Table 1, col. 6]. The IED mandating a 10% uncertainty threshold for the values given by the AMSs [see Table 4], the uncertainty budget should not exceed 7.5% [see § 2.3.3 // value given in Table 1, col. 7].

The uncertainty obtained for AMSs, at 50 mg/Nm³, varies according to the analysis principle [see CO summary sheet in Annex E]:

- NDIR: 7.3 to 8.5%; average: 7.6%
- GFCIR: 3.5 to 12.5%; average: 7.1%
- FTIR: 2.8 to 9.8%; average: 7.1%
- DOAS: 6.9%
- Electrochemical cells: 20.6%

As shown on Figure 8, the median of all the AMSs is the same as that of the NDIR and GFCIR only: 7.4% [value given in Table 1, col. 8 // The min value in Table 1, col. 8 (3.8%) is the average value of the uncertainties of the 3 AMS with the lowest uncertainties].

Two thirds of the 31 certified instruments fulfil the 7.5% uncertainty criteria for the current Daily ELV level of 50 mg/Nm³. However, the relative uncertainty will increase if the ELV is lowered; with the optimistic hypothesis that the uncertainty varies linearly with the concentration, the best-performing certified instrument (FTIR-6) could not fulfil the 7.5% threshold under 19 mg/Nm³. As for the LoQ, the electrochemical cell instrument does not show a suitable performance in terms of uncertainty.

Analysing a few QAL2 test reports shows that the lowest uncertainty levels, enabling the fulfilment of the variability test, match those determined by an uncertainty budget.

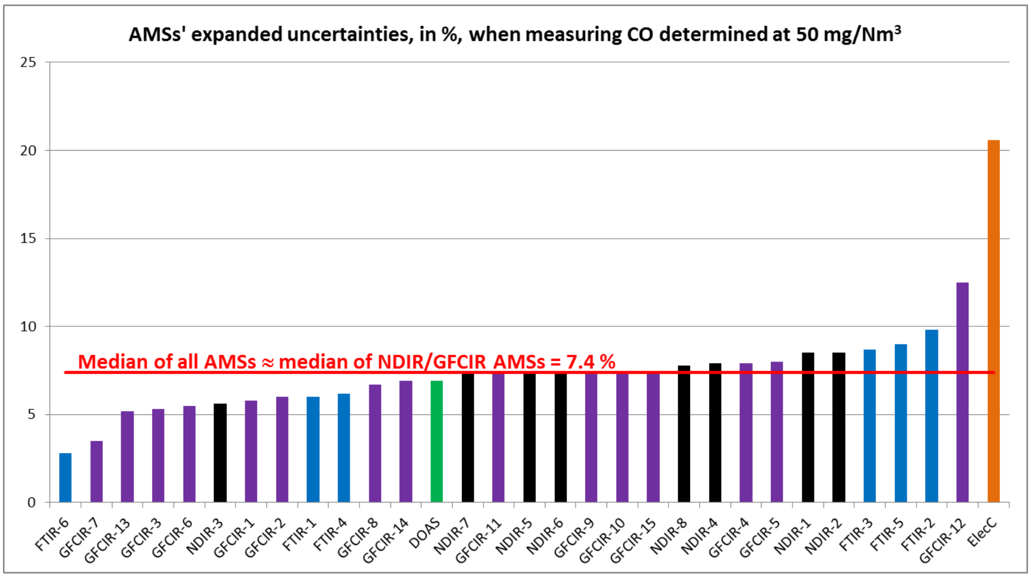


Figure 8: Certified AMSs' relative expanded uncertainties when measuring CO

Analysing the certificates (QAL1) shows that for NDIR and GFCIR AMSs, those using the method corresponding to the SRM, an uncertainty of 6% can only be reached by a small number of AMSs: Servomex 4900, Horiba 250 (when referring to the MCERTS certificate; the TÜV obtaining a significantly less favourable uncertainty), SICK SIDOR or MCS 100E HW or 100E PD, Environnement SA MIR-IS. Some of those instruments are not portable and can hardly be used as an SRM.

Besides, the ILCs show that this 6% uncertainty value is not reached in practice on site below 120 mg/Nm³ [see Figure 9 or CO summary sheet in Annex E, graph on top left // "No" value given in Table 1, col. 10] and that the NDIR technology, even in its GFCIR variation, has an insufficient specificity. The relative uncertainty sharply rises when the concentration decreases (39% at 20 mg/Nm³ and 70% at 10 mg/Nm³) [see Figure 9]. The ILCs aiming to evaluate the SRM's implementation performance show that the target uncertainty of 6% mandated by the European Standard will in practice only be reached on the site for concentrations above about 120 mg CO/Nm³ [see Figure 9 // Value given in Table 1, col. 11].

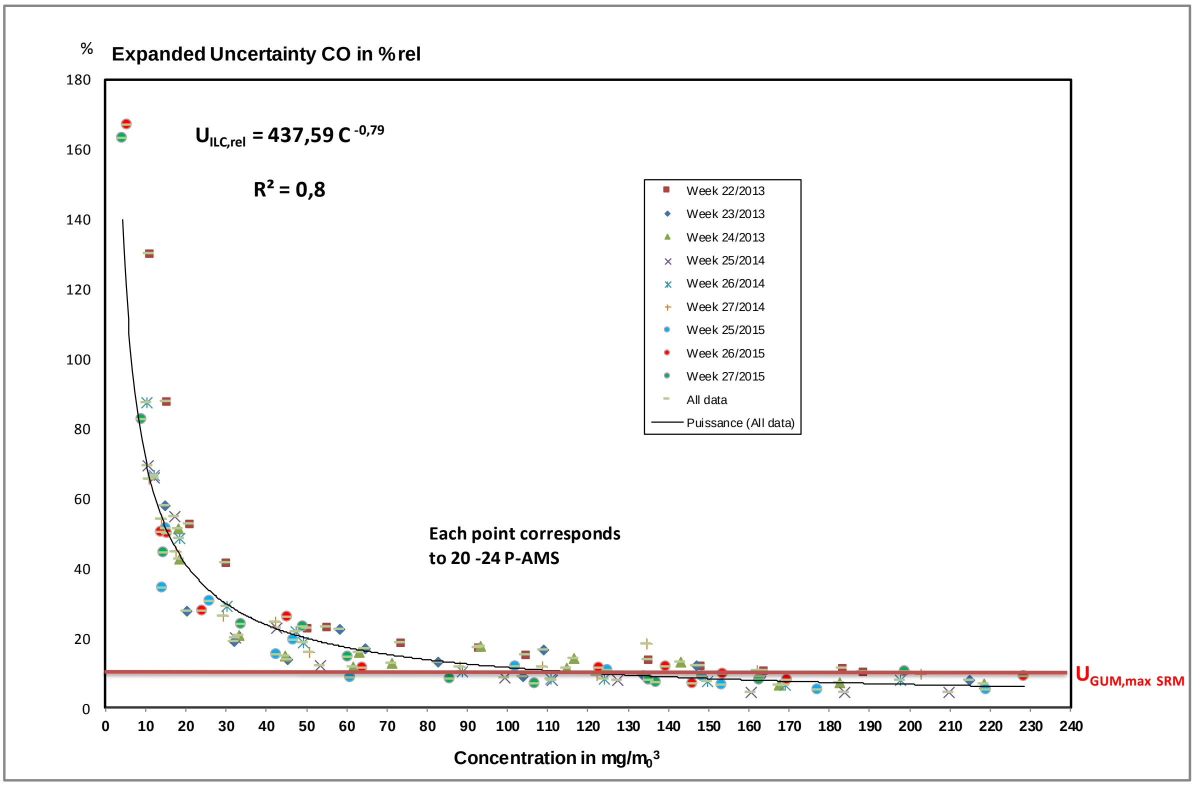


Figure 9: Relative expanded uncertainties when measuring CO (ILCs)

If many AMSs could be tested in parallel and for concentration levels under 120 mg/Nm³, the relative expanded uncertainty would most probably also be higher than that given in the certificates for one single AMS's model. **The $U_{max\ SRM}$ << $U_{max\ AMS}$ condition that should be fulfilled for AMSs' calibration by SRMs is hence not fulfilled; this can affect the calibration function and therefore the accuracy of the results given by the AMS** [information 'no' given in Table 1, col. 10].

Comparison of the AMS / SRM measurements during QAL2 controls:

Analysing 28 QAL2 reports, corresponding to the control of 42 AMSs (cf. Annexes B: summary of results as tables and C: QAL2 test reports Analysis: Graph representation of measurements [AMS;SRM] and calibration function), shows that the average concentration levels during these tests are under 10 mg/Nm³. **When the concentration levels are above this value, the concentrations measured by AMS and SRM are in general consistent and the calibration functions have a slope close to 1. However, on sites with lower concentrations, significant differences between AMS and SRM measurements are often observed, and less "good" calibration functions are obtained (slope significantly different to 1 and/or high intercept point compared to the site concentration level, R² << 1). When the calibration function is still of "good quality", this is in general linked to the addition of measurement results coming from span gas injection for calibration but this does not improve the accuracy of the points at low concentration.**

Conclusion for CO

Some instruments usable as AMS or SRM can reach, according to their certificates, performances that could be accepted in terms of LoQ and in terms of uncertainty at the current Daily ELV level of 50 mg/Nm³. This would not be true if the ELV was lowered.

The ILCs organised to evaluate the SRMs also show that the required uncertainty is in fact not always fulfilled in real measurement conditions; **even for a Daily ELV of 50 mg/Nm³, the measurement uncertainty is too high: 18 % relative for a target of 6 %. A Daily ELV of 120 mg/Nm³ would provide a minimised risk when declaring whether an AMS is compliant or non-compliant.**

The $U_{max\ SRM}$ << $U_{max\ AMS}$ condition that should be fulfilled for AMSs' calibration by SRMs is hence not fulfilled, this can affect the calibration function and therefore the accuracy of the results given by the AMS.

Analysing QAL2 test reports also shows that the average concentrations measured by the AMSs and the SRMs are not always comparable (it is not possible to tell if the bias comes from one or the other measurement), with a relative difference increasing when the concentration decreases. This also impacts the AMS's calibration function.

Lowering the ELV under the current value of 50 mg/Nm³ therefore may lead to biased ELV compliance/incompliance declarations, because of measurements with an uncertainty higher than the IED's 10% confidence interval.

The TDLAS-CRDS techniques have potential and could maybe get a better specificity than the techniques applied nowadays. However, no instrument using this technique is currently certified for CO.

4.1.3 NO_x

The comments below are based on the summary sheet in Annex E.

Concentrations noted in "mg/Nm³" correspond to mg equivalent NO_2 per Nm³.

The EN 14792 Standard describes the SRM: Chemiluminescence method.

LoQ:

The LoQ calculated for the certified Chemiluminescence AMSs, corresponding to the SRM method, are between 0.08 and 7.2 mg/Nm³, therefore very variable LoQs. The highest LoQ is that of an instrument that was evaluated on a higher range than those of the other AMSs, which may partly explain this value, but the LoQ remains however very high compared to the performances that may be reached by the other instruments. Note that not all of these instruments are portable and usable for SRM (P-AMS), but this still gives an estimate of the performance that Chemiluminescence analysers can reach. The LoQ median value is 0.8 mg/Nm³ if we consider all the analysers.

The certified AMSs' LoQs, all measurement methods included, vary between 0.02 (GFCIR-7) and 8 mg/Nm³, a very wide range. This is partly linked to the fact that the instruments were evaluated on different ranges, the instruments were reclassified into 2 categories according to the certified ranges, cf. Figure 11 and Figure 12. The certified range impacts the LoQ, and the median value significantly increases for AMSs certified for the highest ranges. To choose a site-specific instrument, a comparison of instruments' performances must be made, the site's concentration levels must be known and the certified range must be taken into account. The LoQ median value is equal to 0,4 mg/Nm³ on a 20 and 90 mg/Nm³ range, and to 1,6 mg/Nm³ on a 100 and 250 mg/Nm³ range.

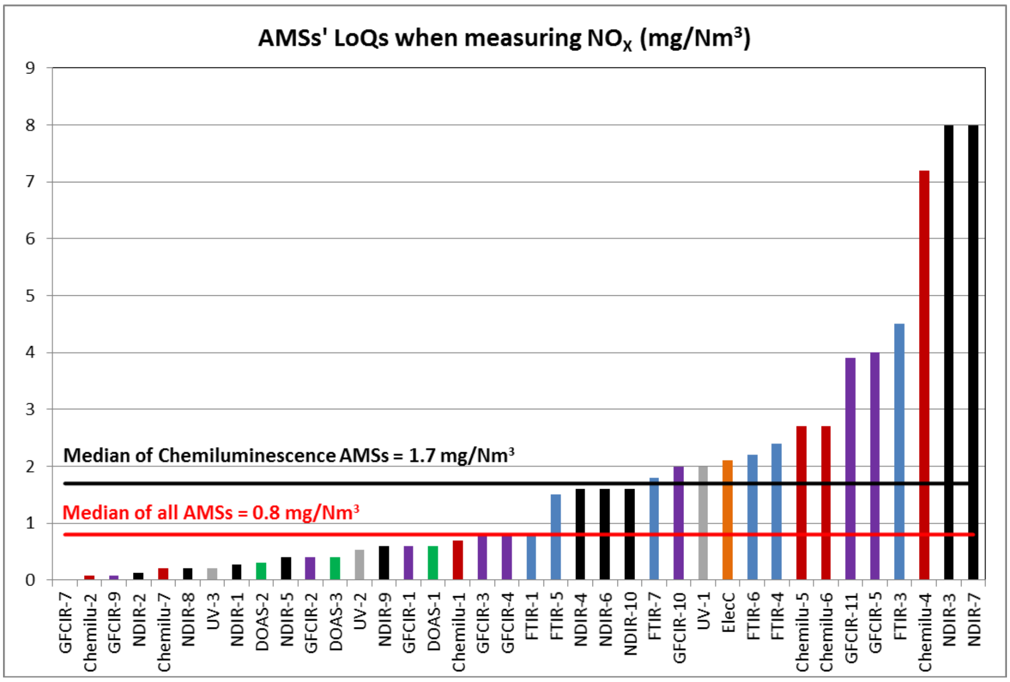


Figure 10: Certified AMSs' LoQs when measuring NO_x

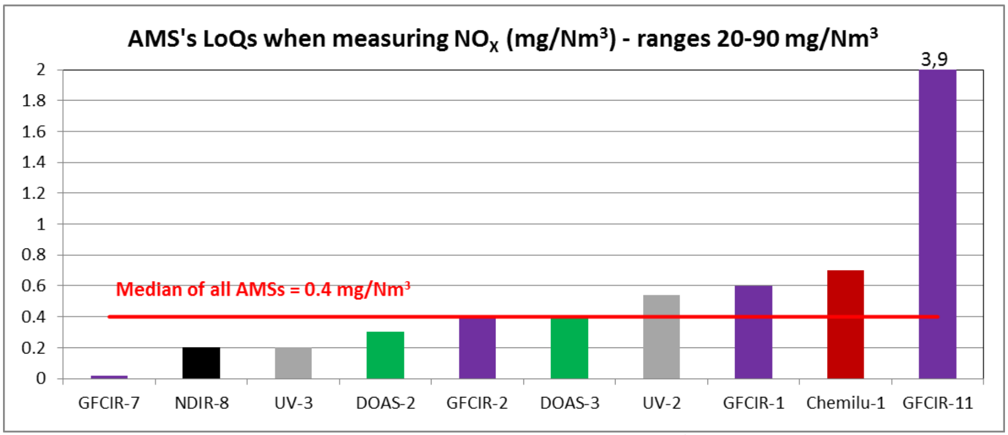


Figure 11: Certified AMSs' LoQs, on a 20 and 90 mg/Nm³ range, when measuring NO_x

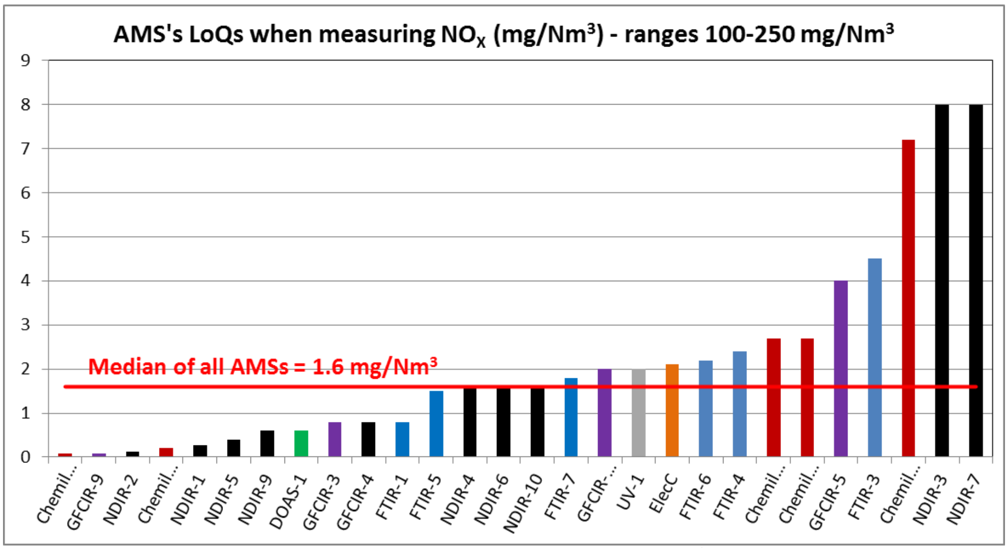


Figure 12: Certified AMSs' LoQs, on a 100 and 250 mg/Nm³ range, when measuring NO_x

.

Based on the ELV/LoQ = 5 ratio principle, for use as AMS, the median value of all AMSs' LoQs' (0.8 mg/Nm³) would lead to a minimum ELV of 4 mg/Nm³. And if we consider AMSs classified by certified range, ELV/LoQ = 5 would respectively lead to 2 and 8 mg/Nm³.

Analysing 10 QAL2 test reports however leads to minimum ELVs, enabling the fulfilment of the variability test, that are significantly higher than these values of 2 or even 8 mg/Nm³: they vary from 43 to 185 mg/Nm³. However, for 8 of these controls, the minimum ELV obtained by data reprocessing is quite maximised, given the site's concentration levels above 68 mg/Nm³, this hinders lowering the ELV because of a lack of sufficient data to make the test (cf. § 3.2.2.2). And when considering instead the minimum ELVs estimated by calculation, some are lower, but in other cases they remain very high, with a single value under 10 mg/Nm³ and an average value of 64 mg/Nm³.

The minimum values of 2 and 8 mg/Nm³, based on 5 times the median value of LoQs, hence appears low for instruments nowadays used on sites, given the QAL2 control results.

This is likely to be linked, as seen for CO, to the fact that the variability test is also impacted by the SRM's performances and not only by those of the AMS.

Measurement uncertainty:

The uncertainty required to use the SRM via an uncertainty budget is of 10% of the Daily ELV level. The IED mandating an uncertainty threshold of 20% for AMSs, the uncertainty budget should not exceed 15% of the Daily ELV set to 200 mg/Nm³ in the Directive.

The uncertainty ranges, obtained by certified AMSs according to the various measurement principles, are the following:

- Chemiluminescence: 6.1 to 19%; average: 9.9%
- NDIR: 5.1 to 14.7%; average: 10.2%
- GFCIR: 4.8 to 11.4%; average: 7.5 %
- FTIR: 6.5 to 9.8%; average: 8.3%
- UV Absorption: 4.6 to 12.1%; average: 9.3%
- DOAS: 4.5 to 11.8%; average: 9.3%
- Electrochemical cells: 12.7%

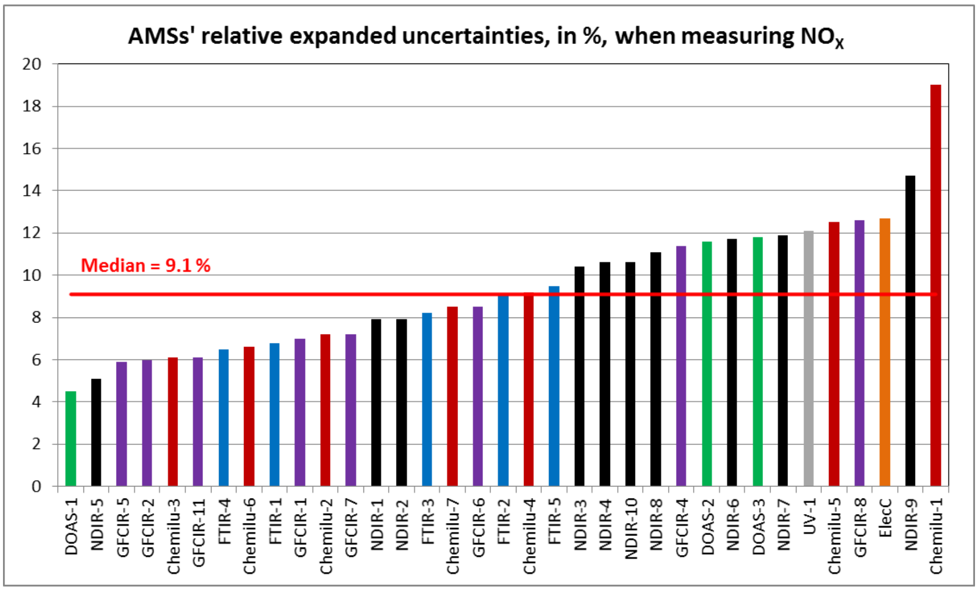


Figure 13: Certified AMSs' relative expanded uncertainties when measuring NO_x

Only one instrument has a relative expanded uncertainty above 15% and all instruments have a relative expanded uncertainty under 20%. However, the concentration level at which the relative uncertainty was calculated must be taken into account: it varies from 200 to 268 mg/Nm³, partly explaining the expanded uncertainties' differences between the instruments. For instance, for the instrument with the highest uncertainty level, the relative uncertainty was calculated at a level of 33 mg/Nm³; at a higher concentration, the uncertainty would be lower. Conversely, for analysers for which the uncertainty was calculated at 200 mg/Nm³ or more, the 15% threshold can quickly cease being fulfilled if the ELV is lowered. With the optimistic hypothesis that the uncertainty varies linearly with the concentration, the lowest ELV for which the best-performing certified instrument would cease to fulfil the 15% threshold is under 8 mg/Nm³, and the level at which 50% of the AMSs would cease fulfilling it is under 57 mg/Nm³.

For the Chemiluminescence method used as SRM, the relative expanded uncertainty threshold of 10% is reachable by 5 certified Chemiluminescence analysers out of 7. The choice may be done by selecting the analyser with the lowest LoQ. With the above hypothesis, the lowest ELV for which these instruments could fulfil the 10% threshold is comprised between 12 and 120 mg/Nm³.

The ILCs that aimed at evaluating the SRM's implementation performances showed that the 10% target uncertainty mandated by the European Standard is in fact only fulfilled on sites where concentrations are above 75 mgNO_2/Nm³, and if the ratio NO_2/NOx remains below 10%. The relative uncertainty increases when the concentration decreases (13% at 55 mg/Nm³ and 60% at 10 mg/Nm³), and the ILCs seem to show that the differences between measurements grows when the NO_2/NO_x ratio increases. Indeed, it was found during the ILCs that the insufficient capacity of sampling/conditioning systems not to lose NO_2 had a greater influence on the uncertainty when the ratio NO_2/NOx increases above 10 %. The treatment of all data from the INERIS ILCs, including trials with NO_2/NO_x ratio above 10%, shows that the target 10% uncertainty mandated by the European Standard is only fulfilled on sites for concentrations higher than 420 mg/Nm³ (See Figure 14). The “theoretical” calculation of a measurement with an uncertainty not exceeding 10% at 12 mg/Nm³ underestimates the inter-laboratory variability and the matrix effects contributions.

The $U_{max\ SRM} << U_{max\ AMS}$ condition that should be fulfilled for AMSs' calibration by SRMs cannot be fulfilled at concentration levels under 75 mg/Nm³ and this only if the ratio NO_2/NOx remains below 10% (generally true for waste incineration plants). The data from ILCs show that when NO_2/NO_x ratio > 10% the condition **$U_{max\ SRM} << U_{max\ AMS}$** is fulfilled for concentrations above 420 mg/Nm³

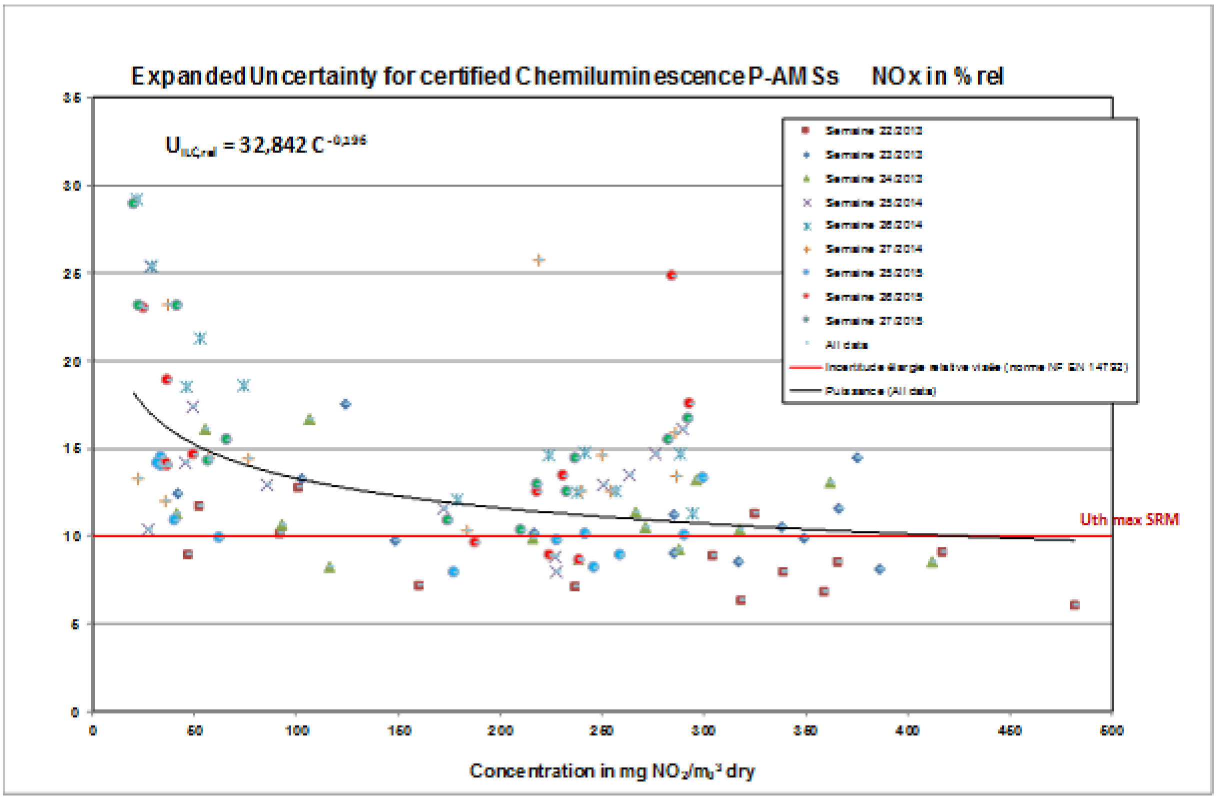


Figure 14: Estimation of actual uncertainty using ILC, when measuring NOx with NO_2/NO_x ratio > 10%

Comparison of the AMS / SRM measurements during QAL2 controls:

Analysing 28 QAL2 reports, corresponding to the control of 44 AMSs (cf. Annexes B and C), shows concentration levels between 30 and 380 mg/Nm³, with an average of 130 mg/Nm³. For 16 sites, the concentration level was under or equal to 75 mg/Nm³ (concentration level under which the ILCs show an uncertainty of SRM > 10%).

The concentrations measured by AMS and SRM are consistent and the calibration functions have a slope close to 1 for most tests. Significant differences between AMS and SRM measurements can be observed: for 7 controls, it is not possible to tell if the bias comes from the AMS or the SRM, and some calibration functions have slopes significantly different to 1 and/or with high intercept points. These “outlying” values are not all linked to concentration levels under 75 mg/Nm³.

It is difficult to tell up to which concentration levels the AMSs’ calibrations by SRM measurements would remain relevant, because the concentration levels found are rarely under 50 mg/Nm³.

Conclusion for NOx

The Chemiluminescence reference method has a good specificity and a low Limit of Quantification. All measurement methods considered, the certified AMSs also show good performances.

However, comparing instruments is difficult, given the variable certified ranges and the relative expanded uncertainty measurement calculation at concentration levels that can be very different.

Fulfilling the ELV/LoQ > 10 ratio mandated for the SRMs in France, leads to minimum ELVs of 17 mg/Nm³, by considering LoQ median value of chemiluminescence AMS.

And fulfilling the ELV/LoQ > 5 ratio considered for the AMSs, leads to minimum ELVs 2-8 mg/Nm^3 by considering LoQ median values respectively on a 20 and 90 mg/Nm^3 range, and 100 and 250 mg/Nm^3 range.

However, at these concentration levels, no AMS would respect the 15% uncertainty criteria for AMSs and the 10% one for SRMs. Also, the ILCs show that currently (for NO_2/NO_x ratio < 10%), the uncertainty required by the SRM is only fulfilled for concentrations above 75 mg/Nm^3.

The results' variability is among others linked to the NO_2 losses in the sampling lines and in the converter, these are not considered when certifying the instrument. Although the NO_2 proportion in most of combustion processes does not exceed 5%, specific NO and NO_2 measurements would be desirable in the future to lower the SRM's uncertainty level. The TDLAS-CRDS techniques have potential but no instrument is however currently certified for NO and NO_2.

Analysing the QAL2 test reports shows satisfactory results in terms of AMS and SRM measurement results comparability, up to concentration levels of 50 mg/Nm^3. However, as shown above, the $U_{max\ SRM} << U_{max\ AMS}$ condition that should be fulfilled for AMSs' calibration by SRMs is already not fulfilled. At lower concentration levels, the SRM measurement will be associated with a measurement uncertainty that are likely to lead to biased ELV compliance/incompliance declarations and to irrelevant AMS calibration in comparison with SRM measurements.

It is hence not advisable to lower the NO_x Daily ELV under 75 mg/Nm^3, to maintain an acceptable risk when declaring whether an AMS is compliant or non-compliant.

4.1.4 TOC

The comments below are based on the summary sheet found in Annex E.

The EN 12619 describes the SRM: TOC (often written as TVOC) measurement by Continuous Flame Ionisation Detector (FID) method.

Few AMSs are certified. In fact, from the 4 reports for which a QAL2 data reprocessing was made, on 2 sites, none of the the instruments have certification data. The certified instruments are mainly FID analysers, corresponding to the measurement technique for the SRM.

LoQ:

Half of the certified instruments have a LoQ under or equal to 0.04 mgC/Nm^3. Whether we take the FTIR analyser into account or not, the median value varies little, and the maximum value of 0.06 mgC/Nm^3 is low. Not all of these certified FIDs are necessarily portable and usable to implement an SRM, but it gives an estimate of the performance that can be reached by FID analysers. To fulfil the ELV/LoQ = 10 ratio recommended as a good practice for SRMs, this median value will lead to a minimum ELV of 0.4 mgC/Nm^3, and for use as an AMS, it would lead to a minimum ELV of 0.2 mgC/Nm^3, assuming an ELV/LoQ = 5 ratio. Both values are very low compared to the measurement uncertainty at such low concentration levels.

Analysing 10 QAL2 test reports leads to minimum ELVs, enabling the fulfilment of the variability test, that would already be higher: comprised between 0.8 and 4.6 mgC/Nm^3, with an average at 2.4 or 2.2 mgC/Nm^3, depending on if this ELV is estimated by data reprocessing or calculated based on the dispersion of differences between AMSs and SRMs. In any case, the resulting ELVs will still be higher than the minimum ELVs based on the LoQs. This is also likely to be linked, as seen with CO and NO_x, to the fact that the variability test is also impacted by the SRM's performances and not only those of the AMS.

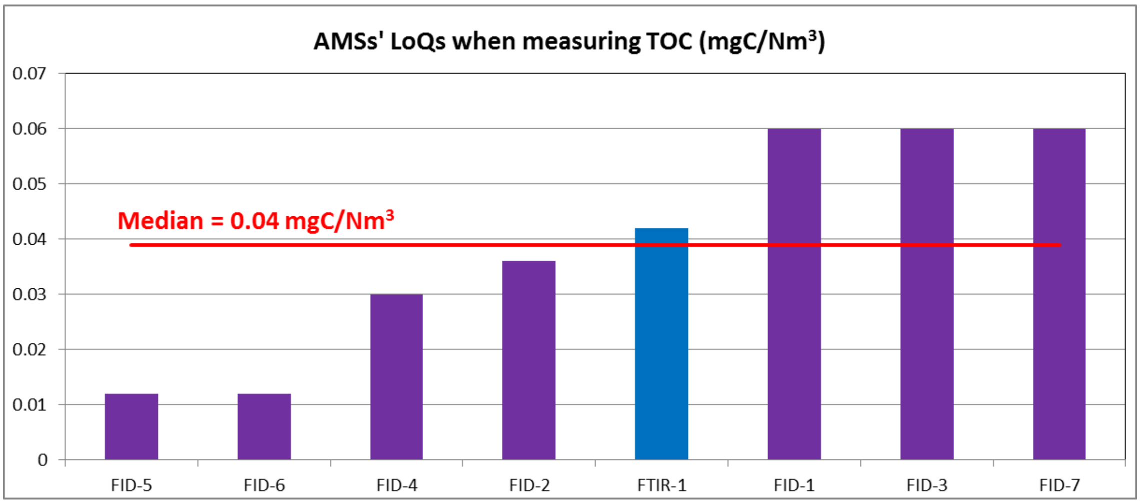


Figure 15: Certified AMSs' LoQs when measuring TOC (TVOC)

Measurement uncertainty:

To measure NMVOC (Non-Methane Volatile Organic Compounds – for some plants NMVOC is measured instead of TVOC, which is subject to an ELV), a French specific reference document was written: XP X 43-554. Only This reference document, is the only one to define an uncertainty level for the reference method at the Daily ELV level: 15%, being half of the uncertainty threshold measurement imposed to AMSs.

The uncertainty mandated via an uncertainty budget of 15% at the level of the Daily ELV of 10 mgC/Nm³ can be fulfilled by 5 certified FID analysers out of 7. The 7 certified instruments as well as the FTIR analyser fulfil the relative expanded uncertainty threshold of 23% (75% of the uncertainty threshold set at 30%) for use as AMS.

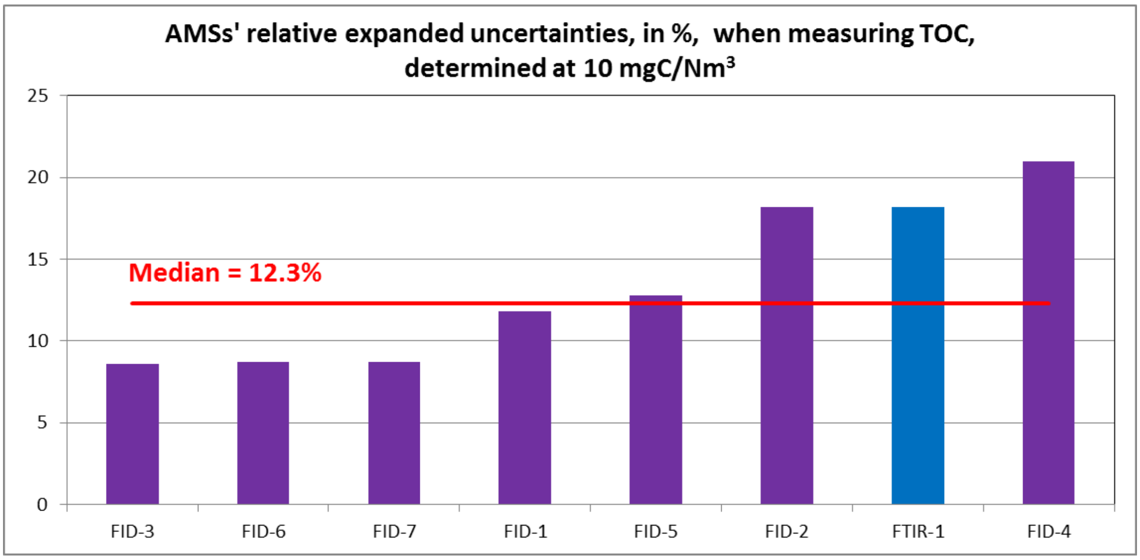


Figure 16: Certified AMSs' relative expanded uncertainties when measuring TOC (TVOC)

ILCs organised to evaluate the SRM's implementation show that the uncertainty increases when the concentration decreases, and that the 15% target set by the French norm is in fact only fulfilled on sites with concentrations above 50 mgC/Nm³.

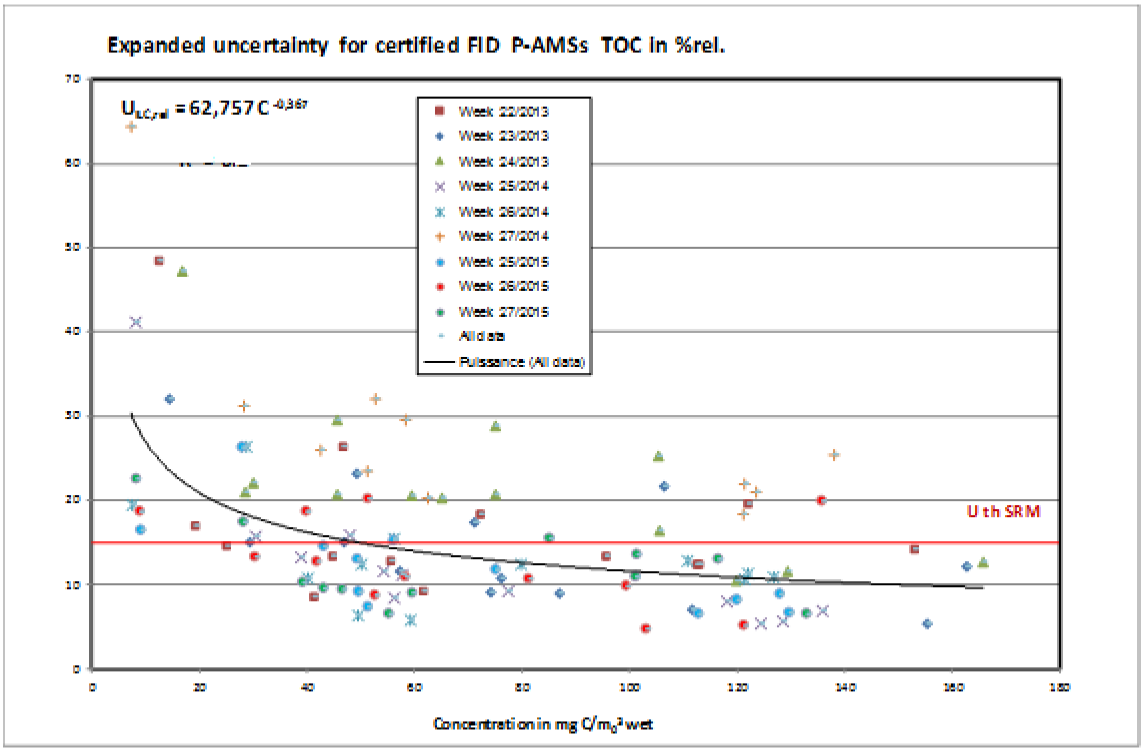


Figure 17: Estimation of actual uncertainty using ILC, when measuring TOC

The peculiarity of TOC measurement is that the detection by flame ionisation determines a TOC index without being able to quantify individually each volatile organic compound present in the matrix. However, the various instrument models do not all have the same response factors. The response factors for various families of compounds must be within ranges set by the EN 12619 Standard for the SRM and the EN 15267-3 Standard for AMSs, but this nevertheless induces a result variability linked to the use of different instruments during the ILCs, to which the implementation variability must be added. Any condensation point in the measurement line may hence cause a measurement bias. These elements contribute to higher uncertainty levels during ILCs than the estimation based on each instrument's performance characteristics.

For concentration levels of 10-20 mgC/Nm³, the measurement uncertainty is of 23% on average during the ILCs organised by INERIS, and of 20% for the comparisons organised to validate the Standard. These results are above the 15% target. And when decreasing to 10 mgC/Nm³, which is under the current Daily ELV, the uncertainty increases rapidly.

At the current Daily ELV level, the $U_{max\ SRM} \ll U_{max\ AMS}$ condition that should be fulfilled for AMSs' calibration by SRMs is already not fulfilled.

Setting ELVs by considering that the ELV/LoQ ratio must be above 10, or 5, meaning under 1 mgC/Nm³, would lead to measurements at the ELV level with very high uncertainty. This would affect the ELV compliance check both for periodic measurement and for self-monitoring, and would affect the accuracy of the AMSs' calibration function.

Comparison of the AMS / SRM measurements during QAL2 controls:

40 QAL2 test reports have been analysed. The measured average concentrations are comprised between 0.1 and 3 mgC/Nm³. For 80% of the controls, the differences between AMS and SRM were above 50% of the average AMS/SRM concentration. This can be linked to the fact that, at these concentration levels, measurements come with a significant uncertainty, as noticed during the ILCs for SRMs, and it is also likely to be the case for AMSs.

Besides, as previously mentioned, the response factors are neither exactly the same depending on the FID analyser model, nor identical between a FID and an infrared analyser. If the concentration increases, this can be linked to an increase of all the organic compounds present in the matrix, but this can also be linked to a variation in the specific TVOCs' spreading, leading to a different evolution of the FID index compared to the infrared index.

Conclusion for TOC

The FID reference method has good advantages: good sensitivity and linearity, large response dynamic, but also has numerous weaknesses: the method only provides a single index, the burner's geometry and its settings influence the measurement, the stability of air and hydrogen pressures and flows must be checked, and the instrument must work with a bottle of sufficient quality H_2 or H_2/He (without hydrocarbons). Any other method will have the disadvantage of giving an index with emissions factors that differ from chemical families. It is therefore difficult to calibrate an AMS with a different measurement principle than that of the SRM if the FID index evolves differently from that of the infrared index. For this reason, the United Kingdom enforces using a FID for self-monitoring.

Currently, the required uncertainty for the SRM is only reached for concentrations above 50 mgC/Nm³, and the measurement uncertainty exceeds 20% at the current Daily ELV level of 10 mgC/Nm³. The analysis of QAL2 test reports shows that for concentrations under the current Daily ELV, the average concentrations measured by AMS and SRM are rarely comparable (it is not possible to tell if the difference comes from one or the other measurement method).

A Daily ELV of 50 mg/Nm³ would enable a minimized risk when declaring whether an AMS is compliant or non-compliant. It is hence strongly recommended not to lower the Daily ELV under the current value of 50 mg/Nm³.

4.1.5 DUST

The comments below are based on the summary sheet found in Annex E.

The EN 13284-1 Standard describes the SRM: Manual gravimetric method with sampling using a filter.

LoQ:

The manual method has a **Limit of Quantification of about 3 mg/Nm³**, resulting from a weighting Limit of Quantification of about 1 mg for the filter and of 2 mg for the dry extract (coming from the sampling probe's rinsing, upstream of the filter), assuming a 1 hour sampling at a rate of about 1 m³/h. A minimum ELV calculation can be made from this LoQ, while fulfilling the good practice that the LoQ must be under 10% of the ELV, leading to a minimum Daily ELV of 30 mg/Nm³. For a compliant sampling on a plant with a Daily ELV of 10 mg/Nm³, a 3 hours and 20 minutes sampling would be necessary if the sampling flow is maintained at a rate of about 1 m³/h. A 1 hour and 40 minutes sampling is also possible by doubling the sampling flow to 2 m³/h. It is difficult to go beyond this flow, because of technical limitations linked with the site sampling conditions and the sampling pumps which are used.

The LoQs calculated for the AMSs using transmission or (retro)-diffusion opacity measurement techniques, or triboelectric techniques, are variable (0.00018 to 0.9 mg/Nm³), with a median value of 0.06 (mg/Nm³). Fulfilling the ELV/LoQ = 5 ratio leads to very low Daily ELVs: 0.3 mg/Nm³ for the median value, or even 0.07 mg/Nm³ for triboelectric probes that perform better here than opacity measurement.

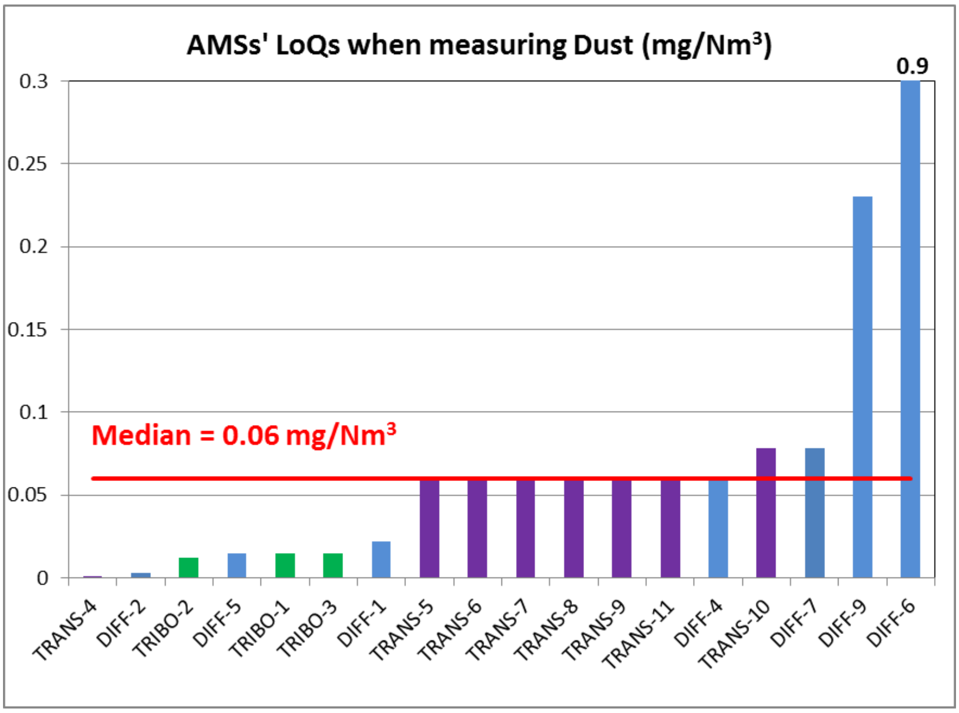


Figure 18: Certified AMSs' LoQs when measuring Dust

Analysing 12 QAL2 reports leads to minimum ELVs, enabling the fulfilment of the variability test, much higher than the 0.07 to 0.3 mg/Nm^3 values: 1.5 to 5.1 mg/Nm^3.

The minimum ELVs, based on 5 times the median value of LoQs, appear low for instruments nowadays used on sites, given the QAL2 control results. This is likely to be linked to the fact that the QAL2, and hence the variability test, is also impacted by the SRM's performances, and not only those of the AMS.

Measurement uncertainty:

The currently enforceable EN 13284-1 Standard does not foresee an uncertainty threshold. However, the revised text (expected for publication in 2017) mandates reaching a level of 20% at the Daily ELV, value that is very close to the level required for the AMSs, being 23%, and which does not fulfil the $U_{max\ SRM} << U_{max\ AMS}$ condition, necessary for a robust QAL2 calibration.

The ILCs made on industrial sites when validating the Standard show that the uncertainty is about 60% for average concentrations around 10 mg/Nm^3 and higher under this value. The target uncertainty of 20%, mandated for the SRM European Standard, is in fact only reached on sites with concentrations above 50 mg/Nm^3 for a half-hour sampling. Reaching a 20% level, at a level around 10 mg/Nm^3, would imply sampling for nearly 4 hours. Although such tests could be made for a QAL2, this would increase their cost for the plant operator, unless the number of admissible tests could be lowered (the EN 13284-2 Standard already allows calibrating with a limited number of 5, parallel, long-term measurements).

The uncertainty required for AMSs is 23%. The measurement relative expanded uncertainty varies according to the analysis principle:

- Opacity measurement / transmission: 5.2 to 13.4%; average: 7.2%
- Retro diffusion: 0.9 to 12.3%; average: 6.7%
- Triboelectric probe: 8.2% to 9.5%; average: 8.9%

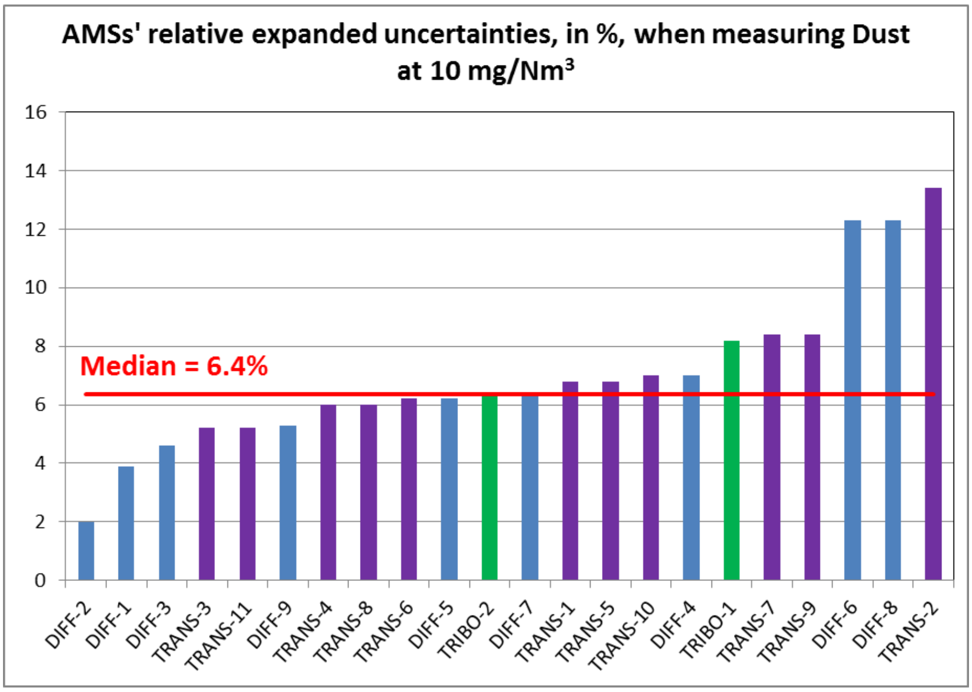


Figure 19: Certified AMSs' relative expanded uncertainties when measuring Dust

All the certified instruments respect the uncertainty criteria of 23% at the current Daily ELV level of 10 mg/Nm³. However, the relative uncertainty will increase if the Daily ELV is lowered; with the optimistic hypothesis that the uncertainty varies linearly with the concentration, the lowest ELV for which the best-performing certified instrument (DIFF-2) could comply with the 23% threshold would be 0.015 mg/Nm³. Considering an AMS near the median value, the lowest ELV for which the certified instrument could comply with the 23% threshold would be 2.8 mg/Nm³.

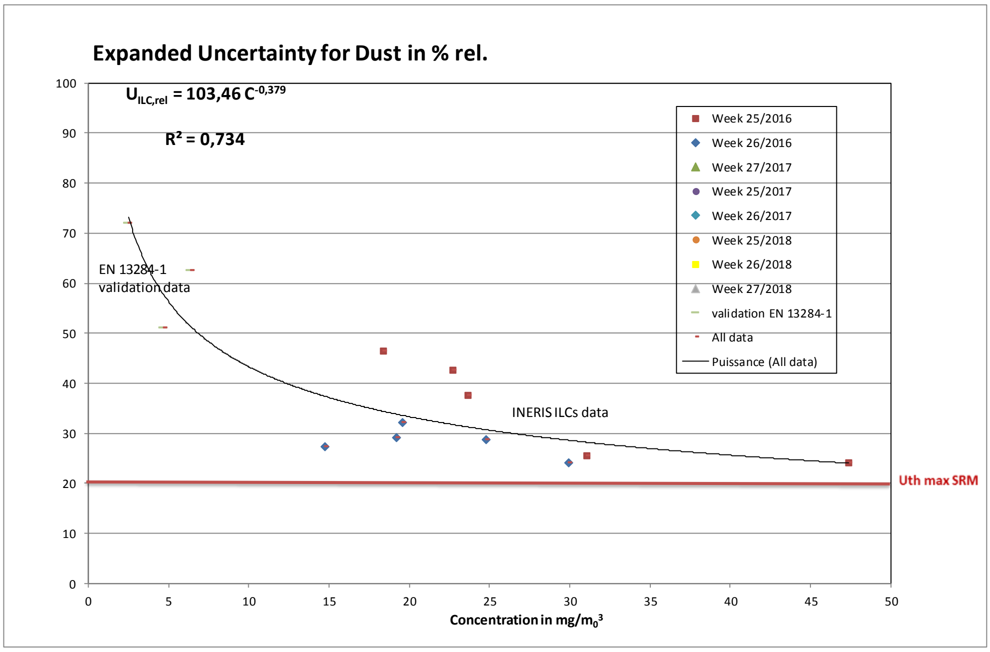


Figure 20: Estimation of actual uncertainty using ILC, when measuring dust

Analysing some QAL2 test reports shows that the lowest uncertainty levels, fulfilling the variability test, are 1 to 1.5 times those determined by the uncertainty budget. The lowest values are reached by 2 installations where the mean of the measured values is very low (0.12 mg/Nm³), but these values are suspicious because they are way under the SRM's LoQ.

If many AMSs could be tested in parallel and for concentration levels under 10 mg/Nm³, the relative expanded uncertainty would also be higher than that given in the certificates. However, the **$U_{max\ SRM} << U_{max\ AMS}$ condition that should be fulfilled for AMSs' calibration by SRMs is hence not fulfilled, this can affect the calibration function and therefore the accuracy of the results given by the AMS.**

Comparison of the AMS / SRM measurements during QAL2 controls:

Analysing QAL2 reports corresponding to the control of 39 AMSs (cf. Annexes B and C) shows that the average concentration levels during the tests vary from 0.12 to 9.2 mg/Nm³. The quality of the equations (R^2 value) increases with the concentration level. From very poor (0.15) at 0.25 mg/Nm³, it reaches 0.6 at a concentration of 9 mg/Nm³. On average, the calibration function is not relevant ($R^2 < 0.5$) under 5 mg/Nm³. The only surrogate that can be developed to have a realistic calibration function for such low concentration levels are:

- Using substitutes to the reference materials (for example, optical filters); there are very few substitutes proposed by AMS manufacturers. But their relevance must be checked during the certification test.
- Injecting dust in the duct. It must be mentioned that this technique is only valid if the injected dusts are of the same characteristics (dimension, colour) as those present in the duct in the case of optical AMSs. If it is not the case, it can induce a bias in establishing the calibration function.

Conclusion for Dust

The manual reference method has a high Limit of Quantification that can be lowered to 1 mg/Nm³ at the expense of longer samplings (2 to 4 hours), to respect the good practices (ELV/LoQ > 10).

The AMSs have generally low Limits of Quantification (0.3 mg/Nm³ as median value) which could enable quality measurements for Daily ELVs of 1.5 mg/Nm³. However, the analysis of QAL2 reports shows that the variability tests are only fulfilled for Daily ELVs above 1.5 to 5.1 mg/Nm³ depending on the case. This is mainly due to the SRM.

To respect an uncertainty level under 20%, the manual reference method, requires Daily ELVs equal to or above 50 mg/Nm³. At this concentration level, the AMSs have an uncertainty of about 7%. This uncertainty measurement could be a bit higher if, like for the ILCs, many instruments were simultaneously performing measurements on the same matrix.

The **$U_{max\ SRM} << U_{max\ AMS}$ condition that should be fulfilled for AMSs' calibration by SRMs is hence not fulfilled, this can affect the calibration function and therefore the accuracy of the results given by the AMS.**

Analysing QAL2 test reports confirms the impossibility of establishing a calibration function for concentrations under 5 mg/Nm³. For higher concentrations, the obtained calibration functions slopes are more reliable, without however confidence into the accuracy given due to the high uncertainty of the SRM.

Using the reference method is necessary to calibrate the AMSs, if the supplier does not propose reference material substitutes that are validated during the instrument's certification. **Nevertheless, its relatively poor performances may lead to poorly reliable calibration functions, which would lead to falsely declare an installation's compliance/non-compliance.**

A Daily ELV of 50 mg/Nm³ would provide a minimal risk when declaring whether an AMS is compliant or non-compliant. It is hence strongly recommended not to lower the Daily ELV under the current value of 10 mg/Nm³.

4.1.6 SO_2

The comments below are based on the summary sheet found in Annex E.

The EN 14791 describes the SRM: manual bubbling and ionic chromatography method.

LoQ:

The manual method has a Limit of Quantification of about 0.16 mg/Nm³, assuming a 1-hour sampling time. A minimum ELV calculation, based on this LoQ, while fulfilling the good practice that the LoQ must be under 10% of the ELV, leads to a minimum Daily ELV of 1.7 mg/Nm³.

The LoQs calculated for the AMSs using NDIR/GFCIR, FTIR, NDUV, GFCUV and DOAS techniques are variable (0.06 to 3.7 mg/Nm³), with a median value of 0.6 mg/Nm³, for a range of 75 mg/Nm³. Compliance with the ELV/LoQ = 5 ratio leads to very low Daily ELVs: 0.3 to 17.5 mg/Nm³ (3 mg/Nm³ as a median value). We note that no technique outperforms the others.

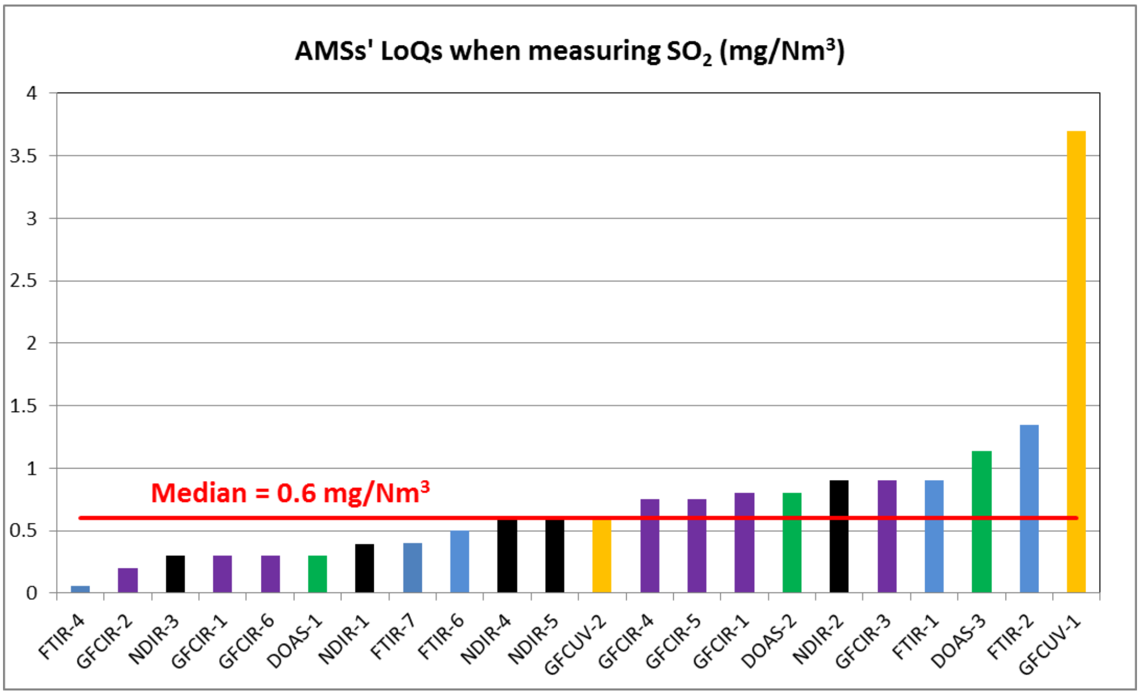


Figure 21: Certified AMSs' LoQs when measuring SO_2

Analysing 10 QAL2 test reports however leads to significantly higher minimum ELVs (7.1 to 27.6 mg/Nm³), enabling the fulfilment of the variability test, than these values of 0.3 to 17,5 mg/Nm³ (and 3 mg/Nm³ as median value): The minimum uncertainty values calculated are near what is stated in the certificates.

The minimum Daily ELVs based on 5 times the LoQs' median value appears low for instruments used on nowadays sites, given the QAL2 control results. This is likely to be linked to the fact that the QAL2, and hence the variability test, is also impacted by the SRM's performances, and not only those of the AMS.

Measurement uncertainty:

The currently enforceable EN 14791 Standard mandates reaching a level of 20% at the Daily ELV, a higher value than what is mandatory for AMSs, i.e. 15% when considering 75% of the legally-binding threshold, which is an important drawback and should lead to consider, in the near term, using an alternative automatic method (a Technical Specification describing an automatic method is being finalised by the CEN TC 264).

The ILCs led by INERIS to evaluate the SRM's implementation performances show that the 20% uncertainty is fulfilled for concentrations above 150 mg/Nm³.

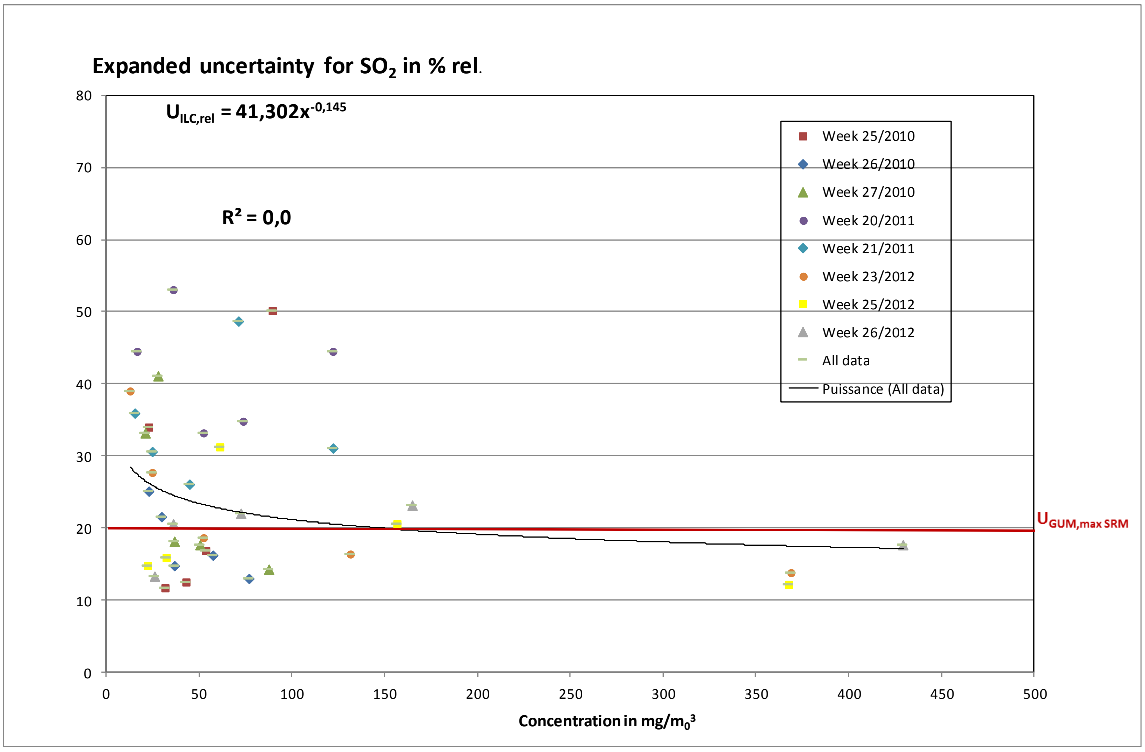


Figure 22: Estimation of actual uncertainty using ILC, when measuring SO_2

The mandatory uncertainty for AMSs, 15%, differs according to the analysis principle:

- NDIR: 7.6 to 15.3%; average: 10.4%
- GFCIR: 6.9 to 16.7%; average: 10.2%
- FTIR: 4.4 to 11.5%; average: 8.8%
- NDUV: 14%
- GFCUV: average: 11.2%
- DOAS: 5.2% to 13.6%; average: 10.7%

All the certified instruments, except 2 AMSs, respect the 15% uncertainty criteria for the current Daily ELV level of 50 mg/Nm³. However, the relative uncertainty will increase if the Daily ELV is lowered; with the optimistic hypothesis that the uncertainty varies linearly with the concentration, the lowest Daily ELV for which the certified best-performing instrument (GFCIR-6) could fulfil the 15% threshold would be 13.7 mg/Nm³. Considering an AMS near the median value, the lowest Daily ELV for which the certified instrument would fulfil the 15% threshold would be 33 mg/Nm³.

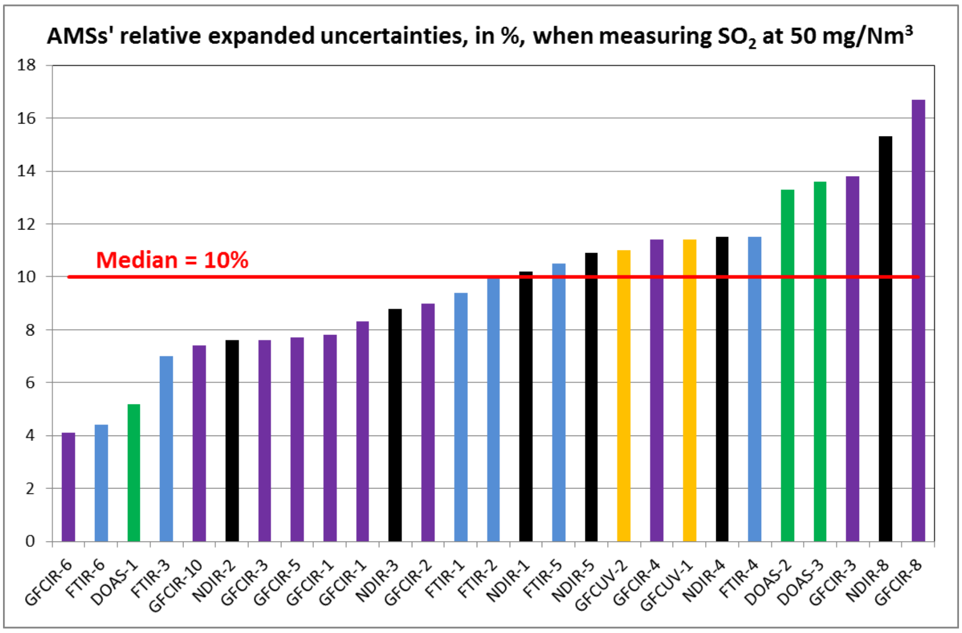


Figure 23: Certified AMSs' relative expanded uncertainties when measuring SO_2

Analysing some QAL2 reports shows that the lowest uncertainty levels, enabling the fulfilment of the variability test, are close to those determined by uncertainty budget.

If many AMSs could be tested in parallel and for concentration levels under 50 mg/Nm³, the relative expanded uncertainty would probably be higher than that given by the certificates.

Comparison of the AMS / SRM measurements during QAL2 controls:

Analysing QAL2 reports corresponding to the control of 41 AMSs (cf. Annexes B and C) shows that the average concentration levels during tests vary from 0.12 to 20 mg/Nm³. Many calibration functions result from AMS/SRM compared results to which zero measurements or span gases (for 14 calibration functions out of 41) were added. 5 of them are using effluent enrichment (spiking) to artificially modify the measured concentration levels. Adding up these measurements to determine the calibration function increases their quality, which often is satisfactory when referring to their R^2 value.

Nevertheless, 16 calibration functions out of 41 show slopes far from 1 or intercept points far from zero, thus showing that when only low-concentration data pairs are available, the calibration quality is uncertain. In this case, the AMSs must first be calibrated with a span gas. These results show that this is not applied everywhere in Europe and makes it difficult to interpret QAL2 results and the quality of the results given by the calibrated AMSs. This can also be caused by biased SRM measurements, which would explain that even if the AMS was calibrated, the slope could be very different from 1. Incompliance with t**he $U_{max\ SRM} \ll U_{max\ AMS}$ condition that should be fulfilled for AMSs' calibration by SRMs, brings doubt on the accuracy of the results given by the AMS.**

Conclusion for SO_2

The reference methods and the AMSs show satisfactory Limits of Quantification.

The manual SRM, however, gives results with an uncertainty above that of the measurements given by the AMSs.

The SRM fulfils an uncertainty level under 20% for Daily ELVs equal to or above 150 mg/Nm³, the AMSs' uncertainty being around 10% at 50 mg/Nm³. The **$U_{max\ SRM} \ll U_{max\ AMS}$ condition necessary for a robust QAL2 calibration at the level of the current Daily ELV of 50 mg/Nm³ for Waste Incineration is hence not fulfilled, this weakens the reliability of this calibration and therefore the accuracy of the results given by the AMS.**

Analysing QAL2 test reports for Waste Incineration plants shows that plant operators often use enriched (spiking) effluents or combine AMS/SRM comparison data with those from gas injection at zero or at span to artificially improve the calibration function.

In the current SRM implementation configuration, it is hence not desirable to lower the Daily ELV under 50 mg/Nm³ to maintain a minimal risk when declaring whether an AMS is compliant or non-compliant.

The possible improvement routes are the following:

- With the current SRM, reduce the number of parallel tests for QAL2 operations by significantly increasing the testing time.
- Use some certified GFCIR analysers as an alternative method to the SRM, which would enable fulfilling uncertainty levels under 8% at 50 mg/Nm³ and would approach about 13% at 30 mg/Nm³.

  The TDLAS-CRDS techniques also have potential. However, since no instrument are certified today for SO_2 the performance characteristics of these instruments are not available.

4.1.7 HCL

The comments below are based on the summary sheet found in Annex E.

The EN 1911 Standard describes the SRM: manual bubbling and ionic chromatography method. This method determines the chloride concentration. An EN TS 16429 specification technique was elaborated to automatically and specifically measure HCl (alone), but it is not yet enforceable.

LoQ:

The manual method (SRM) has a Limit of Quantification varying from 0.08 to 0.33 mg/Nm³ according to the analysis laboratories, assuming a 1 hour sampling. A minimum ELV calculation, based on this LoQ, while fulfilling the good practice that the LoQ must be under 10% of the ELV, leads to a minimum Daily ELV of 0.8 to 3.3 mg/Nm³, which is well under the current Daily ELV of 10 mg/Nm³.

The LoQs calculated for the AMSs using the GFCIR, FTIR, TDLAS and DOAS techniques are variable (0.008 to 1.08 mg/Nm³), with a median value at 0.18 mg/Nm³ for a certified range of 0-15 mg/Nm³. Fulfilling the ELV/LoQ = 5 ratio leads to very low Daily ELVs: 0,04 to 5,4 mg/Nm³, and 0.9 mg/Nm³ as median value. The laser diode technique outperforms the other techniques (LoQ = 0.06 mg/Nm³ - Minimum Daily ELV = 0.3 mg/Nm³).

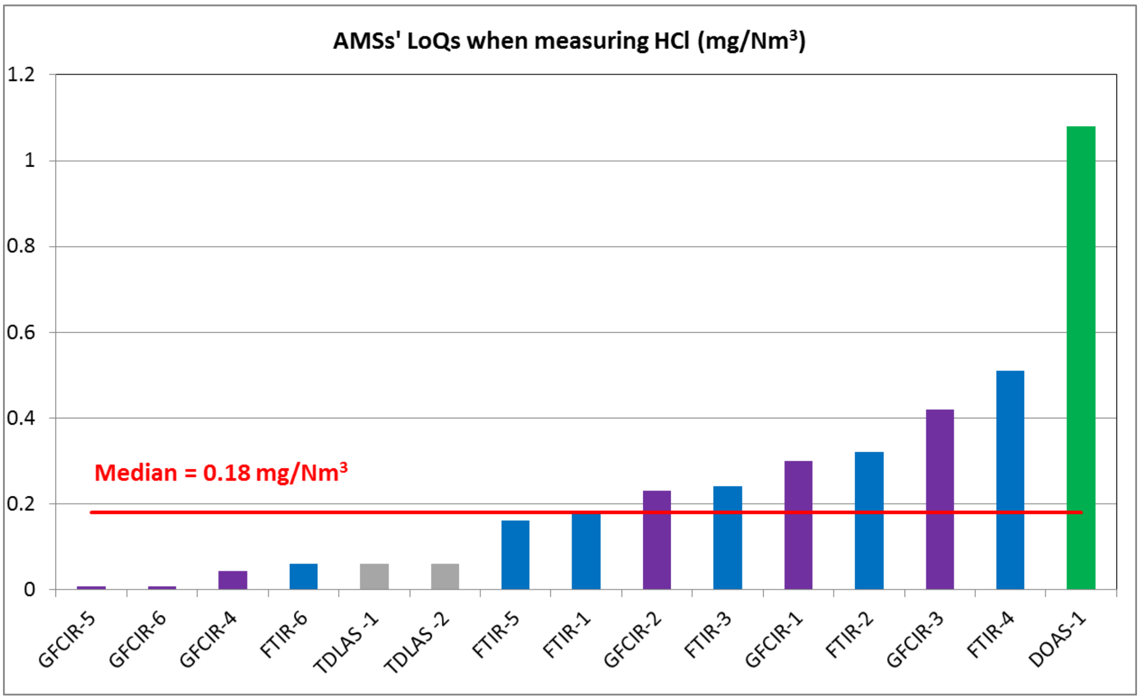


Figure 24: Certified AMSs' LoQs when measuring HCl

Analysing 10 QAL2 test reports however leads to much higher minimum ELVs (2.2 to 9.6 mg/Nm³) enabling the fulfilment of the variability test, than the values of 0.04 to 5.4 mg/Nm³: The calculated minimum uncertainty values are significantly lower than those stated in the certificates.

The minimum Daily ELVs, based on 5 times the LoQs' median value, appear low for the instruments nowadays used on sites, given the QAL2 control results. This is likely to be linked to the fact that the QAL2, and hence the variability test, is also impacted by the SRM's performances, and not only those of the AMS. No QAL2 calibration was available, for instruments using the TDLAS technique, to see if the minimum Daily ELVs can be significantly lowered.

Measurement uncertainty:

The EN 1911 Standard mandates a level of 20% at the Daily ELV level. This level cannot be improved given the method chosen.

The ILCs led by INERIS to evaluate the SRM's implementation performance show that at a concentration of 10 mg/Nm³, the uncertainty is very high (~70%). The target uncertainty of 20% mandated by the European Standard is in fact only fulfilled on sites for concentrations above 50 mg/Nm³. The results can be even poorer when the installation uses ammonia or urea to abate NO_x concentrations. In these conditions, an ammonium chloride aerosol is formed; it is gaseous above 180°C, but it can condensate in the sampling probe if cold points exist or it can be trapped on the filter if it is at a temperature colder than 180°C. In such cases, it was shown that towards 10 mg/Nm³, the uncertainty is not 70%, but exceeds 120%.

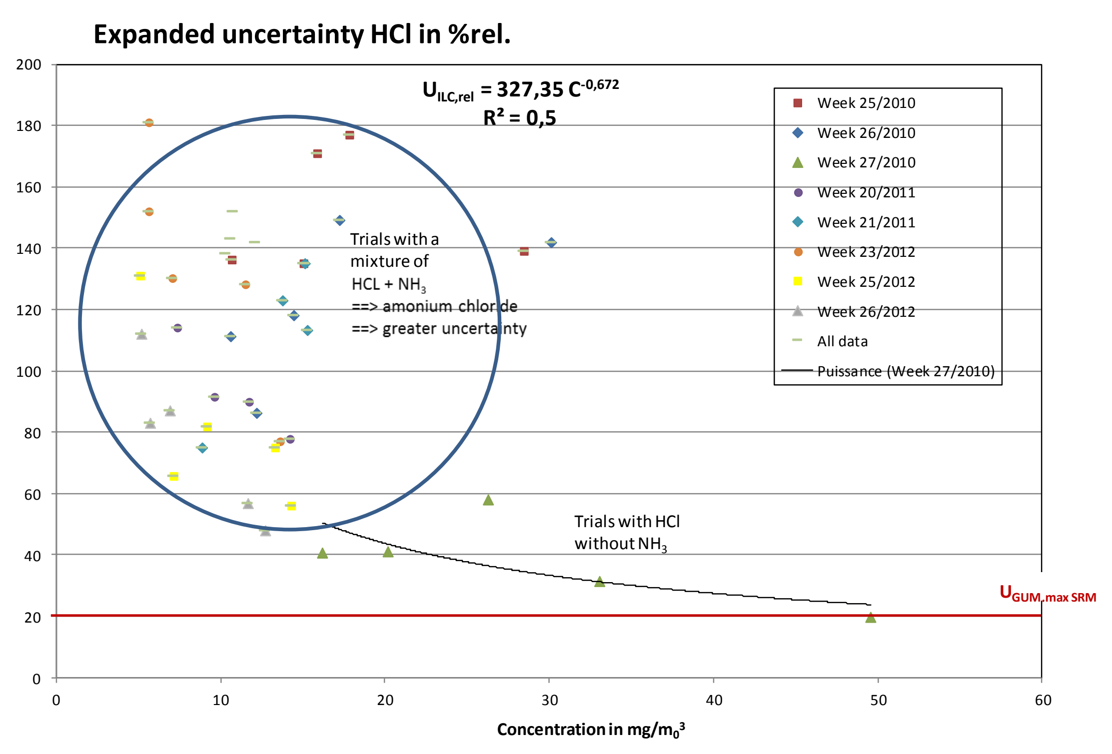


Figure 25: Estimation of actual uncertainty using ILC, when measuring HCl

75% of the legally-binding uncertainty for AMS is 30%. Expanded uncertainty varies according to the analysis principle:

- GFCIR: 7.9 to 12.8%; average: 10.6%
- FTIR: 8.1 to 12.2%; average: 10.6%
- TDLAS: 7.7 to 13.4%; average: 10.6%
- DOAS: 12.5%

All the certified instruments fulfil the 30% uncertainty threshold for the Daily ELV level of 10 mg/Nm³. However, the relative uncertainty will increase if the ELV is lowered; with the optimistic hypothesis that the uncertainty varies linearly with the concentration, the lowest Daily ELV for which the best-performing instrument (TDLAS-1) could fulfil the 30% threshold would be 2.6 mg/Nm³. Considering an AMS near the median value, the lowest Daily ELV for which the certified instrument would fulfil the 30% threshold would be 4 mg/Nm³.

Note that one of the 2 best-performing TDLASs in terms of LoQ also has the lowest uncertainty. The reverse result is obtained with the TDLAS-2.

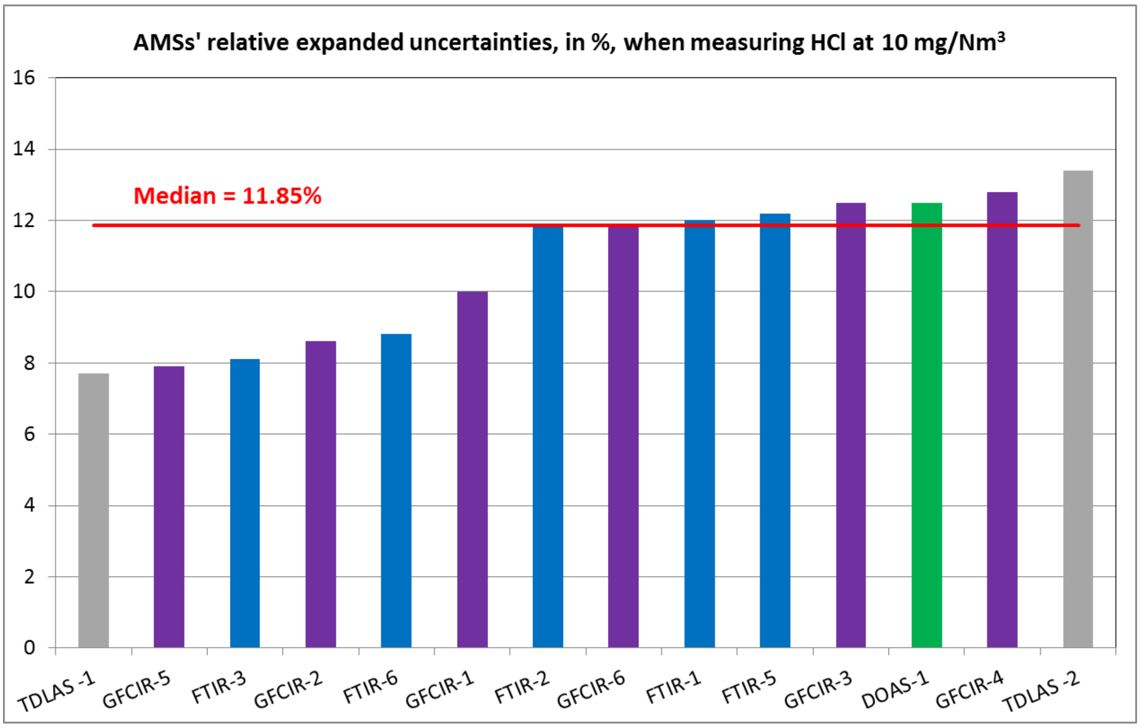


Figure 26: Certified AMSs' relative expanded uncertainties when measuring HCl

Analysing some QAL2 reports shows that the lowest uncertainty levels, enabling the fulfilment of the variability test, are 2 to 3 times lower than those determined by uncertainty budget.

If many AMSs could be tested in parallel and for concentration levels under 10 mg/Nm³, the relative expanded uncertainty would also be higher than that given in the certificates.

<u>Comparison of the AMS / SRM measurements during QAL2 controls:</u>

Analysing QAL2 reports corresponding to the control of 39 AMSs (cf. Annexes B and C) shows that the average concentration levels during the tests vary from 0.1 to 25.4 mg/Nm³. Many calibration functions result from AMS/SRM comparisons to which zero measurements (19 of them) or even span gas measurements (for 11 calibration functions), were added. 4 others also use effluent enrichment (spiking) to artificially modify the measured concentration levels. The quality of the calibration functions, despite the applied surrogates as described above, is satisfactory for only 12 of them ($R^2 > 0.9$), mostly for concentrations above 5 mg/Nm³. Under 5 mg/Nm³, only 2 R^2 values are above 0.9.

Incompliance with **the $U_{max\ SRM} \ll U_{max\ AMS}$ condition that should be fulfilled for AMSs' calibration by SRMs, sheds doubt on the accuracy of the results given by the AMS.**

Along with the fact that the SRM and AMS do not measure the same measurand and that the European Directive is focused on HCl alone, the only interest of a QAL2 for HCl is the potential detection of an AMS malfunction on the installation or of a problem in the probe positioning in the sampling point (unrepresentative point).

Conclusion for HCl

The reference methods and the AMS have satisfactory LoQs.

The manual SRM however gives results with uncertainties 5 to 10 times higher than the measurements given by the AMSs at the current Daily ELV for Waste Incineration (10 mg/Nm³), when referring to the instruments' certificates., For AMSs, if the variability between instruments considered, as during the ILCs' implementation, (implementation variability and variability linked with the instruments), the performances' difference between SRM and AMS in terms of uncertainty would likely to be less important, but still present.

The manual reference method fulfils an uncertainty level under 20% for Daily ELVs equal to or above 50 mg/Nm³, which is equal to 5 times the current Daily ELV for Waste Incineration. With the AMSs' uncertainty being around 10% at 50 mg/Nm³. The **$U_{max\ SRM}$ << $U_{max\ AMS}$ condition necessary for a reliable QAL2 calibration at the level of the current Daily ELV of 10 mg/Nm³ for Waste Incineration is hence not fulfilled, this weakens the reliability of this calibration and therefore the accuracy of the results given by the AMS.**

Analysing QAL2 test reports for Waste Incineration shows that control laboratories' often use enriched effluents or combine AMS/SRM comparison data with those from gas injection at zero or at span, to artificially improve the calibration function.

In the current SRM implementation configuration, a Daily ELV of 50 mg/Nm³ is necessary to declare whether an AMS is compliant or non-compliant. It would be desirable not to decrease ELV below 50 mg/Nm³.

The possible improvement routes are the following:

- With the current SRM, reduce the number of parallel tests for QAL2 operations by significantly increasing the testing time.
- Use certified FTIR, TDLAS or GFCIR analysers, fulfilling the EN TS 16429 "Stationary source emissions. Sampling and determination of hydrogen chloride content in ducts and stacks. Infrared analytical technique",as an alternative method to the SRM, which would enable fulfilling uncertainty levels under 8% at 10 mg/Nm³.

  While such automatic methods could enable lowering the measurement uncertainty, one of the difficulties with these methods is their calibration, which requires a specific injection device, long passive line periods and a significant gas consumption for calibration. Management of these aspects should be tested during validation tests which should terminate around June 2018.

4.1.8 HF

The comments below are based on the summary sheet found in Annex E.

The NF X 43-304 Standard describes the SRM (no European Standard available): Manual method by filtration and bubbling in soda and ionometry, spectrophotometry, or ion exchange chromatography analysis, after filter treatment. This method determines the fluoride ions' concentration.

LoQ:

The manual method has a Limit of Quantification varying between 0.08 and 0.17 mg/Nm³, depending on the analysis laboratory, assuming a 1-hour sampling time. A minimum ELV calculation, based on this LoQ, and fulfilling the good practice that the LoQ must be under 10% of the ELV, leads to a minimum Daily ELV of 0.8 to 1.7 mg/Nm³. To fulfil the ELV/LoQ > 10 ratio, it may be necessary to increase sampling time above 1 hour.

The LoQs calculated for the AMSs using the GFCIR, FTIR, TDLAS and DOAS techniques are variable (0.006 to 0.2 mg/Nm³), with a median value at 0.1 mg/Nm³ for a certified range of 3 or 5 mg/Nm³.

Fulfilling the ELV/LoQ = 5 ratio leads to the following Daily ELVs: 0.03 to 1 mg/Nm³ (0.5 mg/Nm³ for the median value, which is only half of the current daily ELV set at 1 mg/Nm³). Note that the FTIR-3 and the TDLAS-3 outperform the other techniques (LoQ = 0.006 or 0.008 mg/Nm³ - Minimum Daily ELV = 0.03 or 0.04 mg/Nm³).

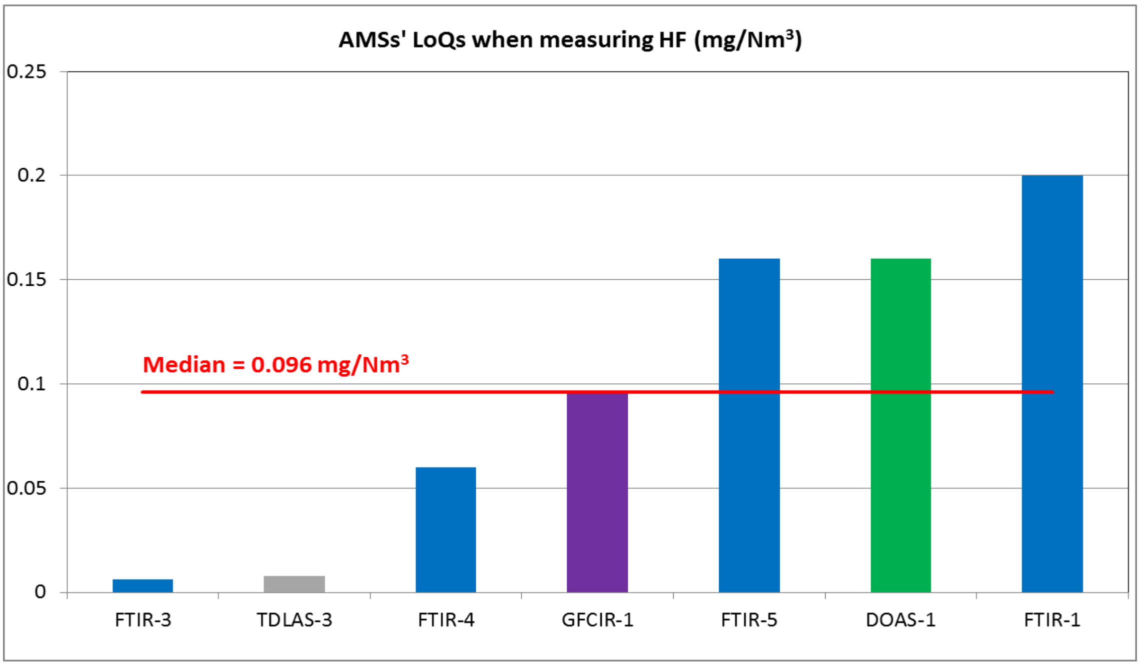


Figure 27: Certified AMSs' LoQs when measuring HF

Analysing 2 QAL2 test reports on a non-certified AMS however leads to minimum ELVs (0.1 and 0.2 mg/Nm³.) enabling the fulfilment of the variability test, that are lower than these values of 0.03 to 1 mg/Nm³: The calculated minimum uncertainty values are significantly lower than those stated by the certificates.

The minimum Daily ELVs, based on 5 times the LoQs' median value, appear suitable for the instruments nowadays used on sites, given the QAL2 control results.

Measurement uncertainty:

The NF X 43-304 Standard does not set a measurement uncertainty threshold, but it is desirable not to exceed a relative expanded uncertainty of 20%, corresponding to 50% of the threshold mandated for AMSs.

Too few results were obtained in ILCs to give reliable data on the estimation of the actual uncertainty of HF determination in the field.

The mandated uncertainty at 1 mg/Nm³ for AMSs is 30% (75% of the uncertainty threshold set to 40%). The uncertainty determined by uncertainty budget differs according to the analysis principle:

- GFCIR: 10.6%
- FTIR: average: 22%
- TDLAS: 10.8 to 37.9%; average: 21.7%
- DOAS: 18.4%

4 out of 10 of the certified instruments do not fulfil the 30% uncertainty criteria at the current Daily ELV level of 1 mg/Nm³.

The relative uncertainty will increase if the ELV is lowered; with the optimistic hypothesis that the uncertainty varies linearly with the concentration, the lowest ELV for which the best-performing (TDLAS-3) certified instrument will fulfil the 30% threshold is of 0.36 mg/Nm³.

Considering an AMS near the median value, the lowest ELV for which the certified instrument could fulfil the 30% threshold is 0.82 mg/Nm³.

Note that TDLAS-3, one of two best-performing AMS in terms of LoQ also has one of the two lowest uncertainties (10.8%).

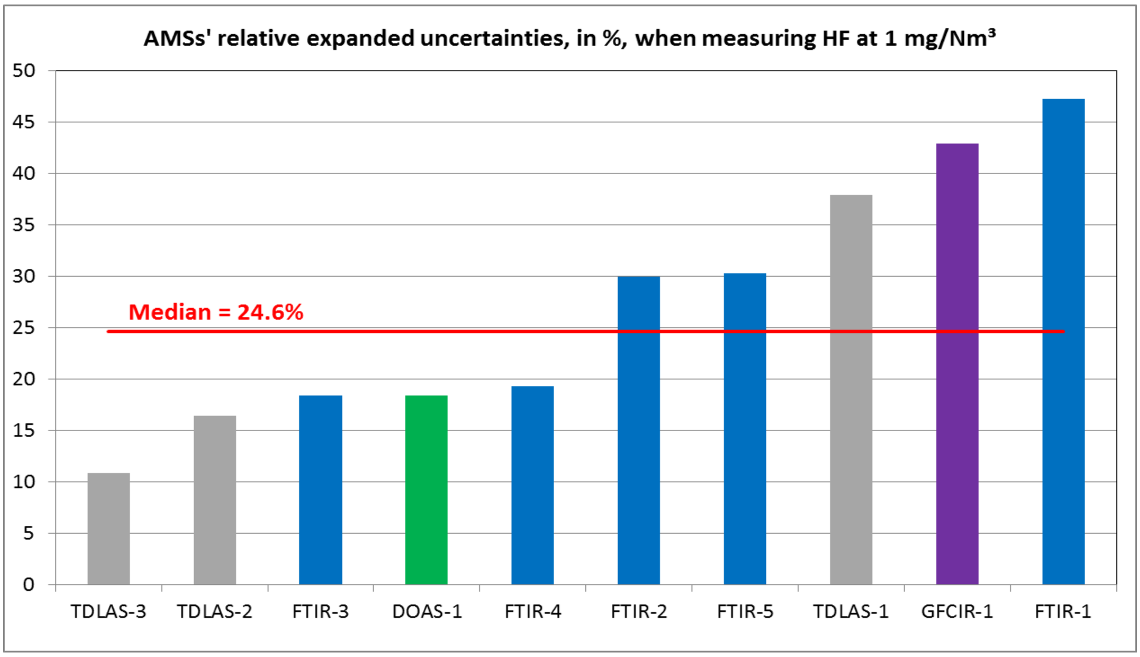


Figure 28 : Certified AMSs' relative expanded uncertainties when measuring HF

Note that the techniques proposed above for the AMSs only measure gaseous HF. Particulate fluor is not considered, while it is measured by the SRM. Also, it is possible that part of the gaseous fluor is absorbed on the particulates and the sampling system's materials, thus biasing the AMSs' measurements and increasing the difference between AMS and SRM.

Analysing some QAL2 test reports shows that the lowest uncertainty levels, enabling to fulfil the variability test, are much lower than those determined by uncertainty budget.

If many AMSs could be tested in parallel and for concentration levels under 1 mg/Nm³, the relative expanded uncertainty would probably also be higher than that given in the certificates.

Comparison of the AMS / SRM measurements during QAL2 controls:

Analysing QAL2 reports corresponding to the control of 11 AMSs (cf. Annexes B and C), shows that the average concentration levels during tests vary from 0.0 to 0.09 mg/Nm³.

9 calibration functions are based on results obtained by zero gas injection and in sensitivity, because the SRM results often are under the Limit of Quantification and cannot be used.

In practice, **because of the high SRM's LoQ and of the non-compliance with the $U_{max\ SRM} << U_{max\ AMS}$ condition to be fulfilled for AMSs' calibration by SRMs, the QAL2 calibration is inoperable at the current Daily ELV for Waste Incineration.**

Conclusion for HF

The reference method's sampling time must be adapted to fulfil the good practice that LoQ < 10% of the Daily ELV, for the Waste Incineration Daily ELV (currently: 1 mg/Nm³). The AMSs' LoQs are satisfactory.

The manual reference method fulfils an uncertainty level above 20% for Daily ELVs equal to or above 150 mg/Nm³, which is a Daily ELV 150 times the current Daily ELV for Waste Incineration, and the AMSs' uncertainty is about 25% at 1 mg/Nm³. **Given the incompliance with the $U_{max\ SRM} << U_{max\ AMS}$ condition to be fulfilled to calibrate AMSs with SRMs, the QAL2 calibration is inoperable at the current Daily ELV level for Waste Incineration for HF. A Daily ELV much higher than the current one will certainly be necessary to declare whether an AMS is compliant or non-compliant.**

The TDLAS technique has potential, but it does not measure particulate and gaseous fluor and can hence not be an alternative to the current manual SRM.

4.1.9 NH_3

The comments below are based on the summary sheet found in Annex E.

The NF X 43-303 Standard describes the SRM (no European Standard available): manual method by bubbling in a H_2SO_4 solution and ionic chromatography or molecular absorption spectrophotometry analysis. This method determines the ammonia concentration.

LoQ:

The manual method has a Limit of Quantification of about 0.08 mg/Nm³, assuming a 1 hour sampling time. A minimum ELV calculation, based on this LoQ, and fulfilling the good practice that the LoQ must be under 10% of the ELV, leads to a minimum Daily ELV of 0.8 mg/Nm³.

The LoQs calculated for the AMSs using the NDIR, GFCIR, FTIR, TDLAS and DOAS techniques are variable (0.012 to 0.88 mg/Nm³), with a median value of 0.21 mg/Nm³ for a range of 10, 15, 20 or 30 mg/Nm³. Fulfilling a ELV/LoQ = 5 ratio leads to the following Daily ELVs: 0.06 to 4.4 mg/Nm³ (1.05 mg/Nm³ for the median value). Note that the GFCIR and TDLAS-3 outperform the other techniques (LoQ ≤ 0.06 mg/Nm³ - Minimum Daily ELV ≤ 0.3 mg/Nm³).

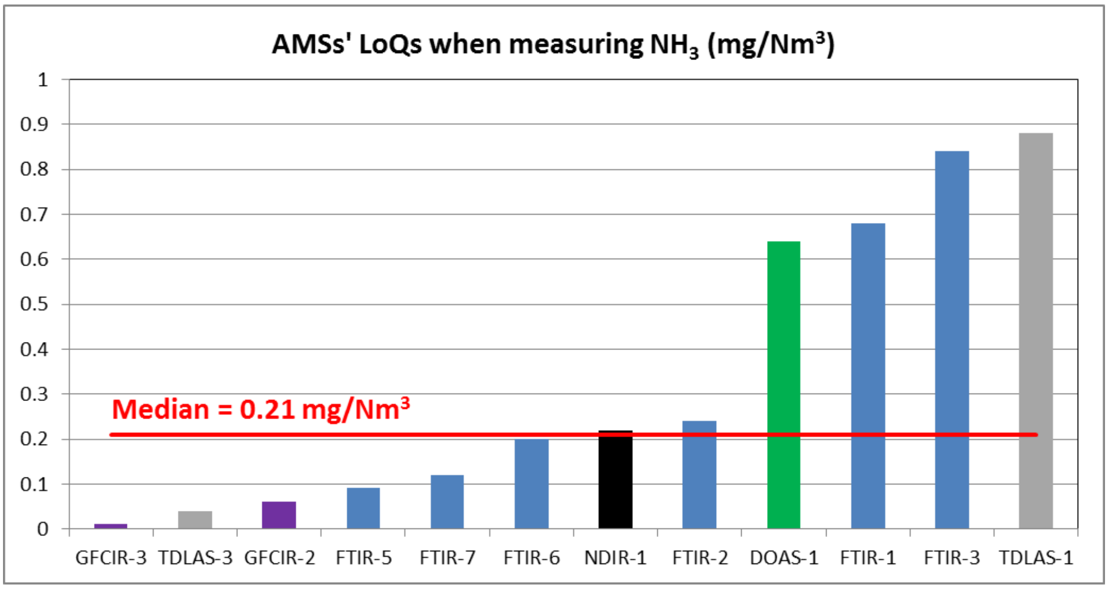


Figure 29: Certified AMSs' LoQs when measuring NH_3

Analysing 4 QAL2 test reports linked to 2 types of AMSs however leads to minimum ELVs, enabling the fulfilment of the variability test, that are higher than these values of 0.06 to 4.4 mg/Nm^3: 0.9 and 8.2 mg/Nm^3. The calculated minimum uncertainty values are significantly lower than those stated by the certificates for the NDIR-1 and about the same magnitude for the FTIR.

The minimum Daily ELVs, based on 5 times the LoQs' median value, would need to be increased for instruments nowadays used on sites, given the QAL2 control results. This is partly explained by the SRM's influence on the QAL2 calibration process.

Measurement uncertainty:

The NF X 43-303 Standard does not require an uncertainty level via an uncertainty budget.

No uncertainty data coming from ILCs are available for concentrations lower than 5 mg/Nm^3. Extrapolating based on the available data, the uncertainty at this concentration level is likely to be around 100%. Other results are available but they were obtained while presence HCl was in the matrix. Because of this, an ammonium chloride aerosol is formed; it is gaseous above 180°C, but it can condense in the sampling probe if cold points exist or it can be trapped on the filter if it is at a colder temperature than 180°C.

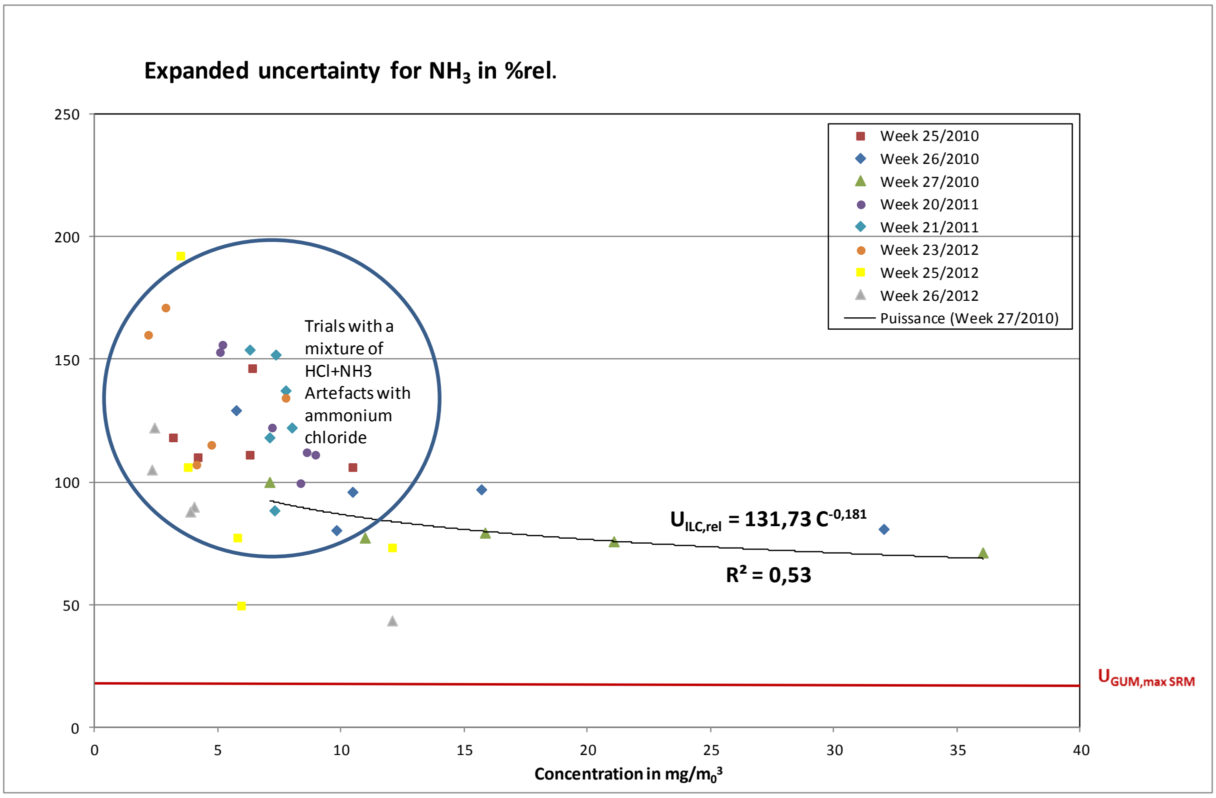


Figure 30: Estimation of actual uncertainty using ILC, when measuring NH_3

At 10 mg/Nm^3, the SRM's uncertainty is about 90%, while levels of 20% would be desirable if we set a target of 50% of the legally-binding threshold for NH_3 self-monitoring for certain Waste Incineration and Co-Incineration installations (cf. § 2.3.3). (In France, at national level, the Daily ELV, which applies since July First 2014 is at 30 mg/Nm^3)

The AMSs' measurement uncertainty, calculated at 10 mg/Nm^3, differs according to the analysis principle:

- NDIR: 12.4%
- GFCIR: 6.9 to 22.4%; average: 12.9%
- FTIR: 6.2 to 12.5%; average: 8.6%

- TDLAS: 5.4 to 19.7%; average: 10.2%
- DOAS: 5.5 to 24.5%; average: 15.0%

All the 16 certified instruments fulfil the 30% uncertainty criteria (75% of the uncertainty threshold mandated in France) for a concentration level of 10 mg/Nm³. However, the relative uncertainty will increase if the ELV is lowered; with the optimistic hypothesis considering that the uncertainty varies linearly with the concentration, the lowest ELV for which the best-performing certified instrument (TDLAS-2 and 3) would still fulfil the 30% threshold would be of 1.8 mg/Nm³. Considering an AMS near the median value, the lowest ELV for the certified instrument, fulfilling the 30% uncertainty, would be of 3.13 mg/Nm³.

Note that the TDLAS-3, which is one of the best performing in terms of LoQ, also has the lowest uncertainty (5.4%).

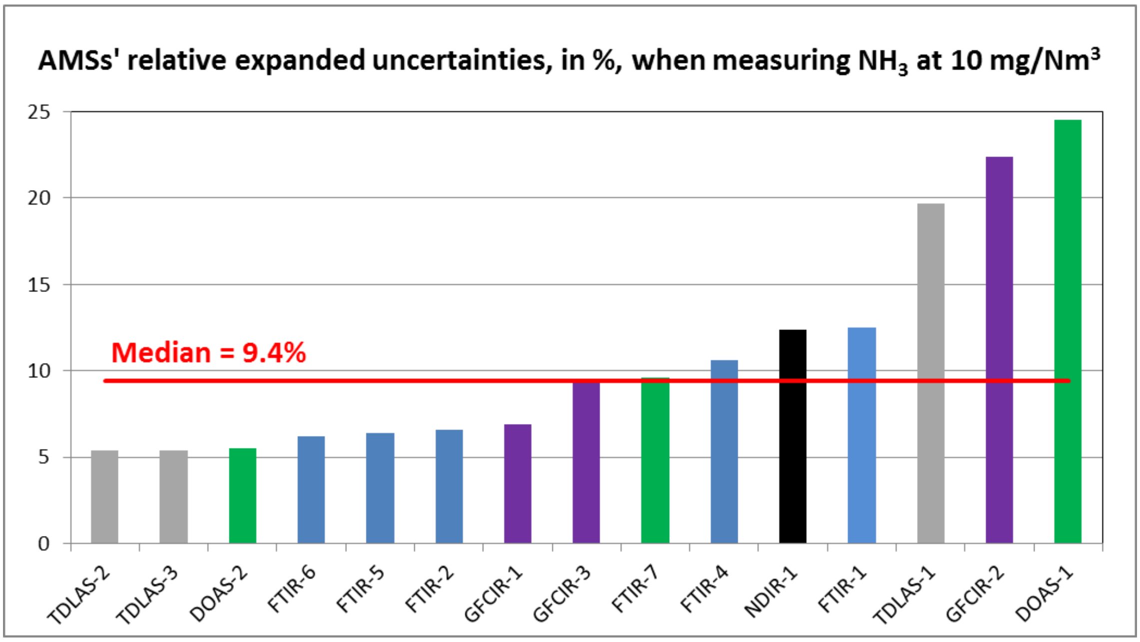


Figure 31: Certified AMSs' relative expanded uncertainties when measuring NH_3

Analysing some QAL2 test reports shows that the lowest uncertainty levels, enabling the fulfilment of the variability test, are 5 times lower than those determined by uncertainty budget for one of the instruments, but 5 times higher for the other instruments.

If many AMSs could be tested in parallel and for concentration levels under 10 mg/Nm³, the relative expanded uncertainty would probably be higher than that given in the certificates.

<u>Comparison of the AMS / SRM measurements during QAL2 controls:</u>

Analysing QAL2 reports corresponding to the control of 21 AMSs (cf. Annexes B and C) shows that the average concentration levels during tests varied from 0.06 to 9.9 mg/Nm³ on sites where the Daily ELV was between 4 and 30 mg/Nm³, most frequently 10 mg/Nm³. For a large number, of the 13 cases, the SRM measurements are under the LoQ, which shows that the manual SRM is unsuitable for QAL2 calibration for a Daily ELV of 10 mg/Nm³. Many calibration functions come from the AMS/SRM results comparison, to which some zero measurements (11 of them) or measurements with span gases (for 8 calibration functions), were added. The calibration functions' quality, despite the surrogates mentioned above and if we refer to the R² value, is satisfactory only for 6 of them (R² > 0.9). Note that some slopes are quite far from 1, showing that the French recommendation to calibrate the AMS with a span gas before calibration is not followed, which prevents detecting if the calibration result is outlying or not. This can also be due to biased SRM measurements, which would explain that even if the AMS has been calibrated, the slope can be very different from 1.

Incompliance with the $U_{max\ SRM} << U_{max\ AMS}$ condition, that should be fulfilled for AMSs' calibration by SRMs, weakens the accuracy of the results given by the AMS.

Conclusion for NH_3

The reference methods and the AMS show satisfactory Limits of Quantification.

The manual reference method gives results with an uncertainty at least 10 times above that of the measurements given by the AMSs at a concentration of 10 mg/Nm³, often set as a Daily ELV.

The $U_{max\ SRM} << U_{max\ AMS}$ condition, necessary for a reliable QAL2 calibration at the level of 10 mg/Nm³ is hence not fulfilled, this weakens the reliability of this calibration and therefore the accuracy of the results given by the AMS.

In many QAL2 calibration cases, an important number of SRM measurements are under the LoQ, showing that the **manual SRM is not suitable for QAL2 calibration at 10 mg/Nm³**. Many calibration functions come from AMS/SRM comparison results, to which zero measurements and, in some cases, measurements with span gases, have been added. The calibration functions' quality, despite the surrogates used and described above, is satisfactory only for 30% of calibrations ($R^2 > 0.9$). **A Daily ELV higher than the current one in France (30 mg/Nm³) will certainly be necessary to declare with a minimal risk whether an AMS is compliant or non-compliant."**

The TDLAS techniques have potential. Some certified instruments have a low Limit of Quantification and a calculated uncertainty of 5.4%. This technique could be an alternative to the current reference method. The QAL2 calibrations made by this technique at a level of 10 mg/Nm³ would ensure that the calibrated AMSs' results are more reliable. It would be useful to have a Standard describing this alternative method, describing the calibration process with a calibration gas or an alternative instrument.

4.1.10 HG

The comments below are based on the summary sheet found in Annex E

The EN 13211 Standard describes the SRM: Manual method of determination of the concentration of total mercury by filtration and bubbling in an acid solution and atomic absorption spectrophotometry after filter treatment. This method determines the mercury concentration as Hg^0 (elementary mercury) and Hg^{2+} (ionic mercury).

LoQ:

The manual method has a Limit of Quantification varying from 0.024 to 0.048 µg/Nm³ depending on the analysis laboratory to which the trapping devices are given, assuming a 1 hour sampling time. A calculation of the minimum ELV, based on this LoQ, and fulfilling the good practice that LoQ must be under 10% of the ELV, leads to a minimum Daily ELV of 0.24 to 0.48 µg/Nm³.

The LoQs calculated for the AMSs using the Zeeman Effect Atomic Absorption, UV CVAAS Cold Vapour Atomic Absorption Catalytic Reduction and UV DOAS Catalytic Reduction techniques are variable (0.024 to 0.72 µg/Nm³), with a median value of 0.14 µg/Nm³ for a range of 10 to 45 µg/Nm³ depending on the AMSs. Fulfilling the ELV/LoQ = 5 ratio leads to very low Daily ELVs: 0.12 to 3.6 µg/Nm³ (0.7 µg/Nm³ as a median value).

Measurement uncertainty:

The EN 13211 Standard does not set an uncertainty level mandated via an uncertainty budget for the SRM, and the legislation does not set a threshold for self-monitoring either.

The ILCs led by CEN to validate EN 13211 have shown a relative expanded uncertainty of 42% in the range 4-10 µg/m³ and 26 % for the range 40-100 µg/m³.

The uncertainty determined by uncertainty budget for certified AMSs differs according to the analysis principle:

- Zeeman Effect Atomic Absorption: 2.3% at 30 µg/Nm^3
- UV CVAAS Cold Vapour Atomic Absorption Catalytic Reduction: about 10 % at 30 µg/Nm^3
- UV DOAS Catalytic Reduction: average: 10.7% at 30 µg/Nm^3

If many AMSs could be tested in parallel and for concentration levels under 50 µg/Nm³, the relative expanded uncertainty would probably be higher than that given in the certificates.

Note that the techniques proposed above only measure gaseous Hg while the SRM also considers the particulate fraction, which contributes to increase the measurement uncertainty compared to AMS measurements. However, the particulate fraction is generally low (< 1% of the total Hg) and the difference between the AMS and SRM measurements, is hence limited.

Analysing QAL2 reports corresponding to the control of 2 AMSs (cf. Annexes B and C) shows that the average concentration levels during tests were under the Limit of Quantification for one of them and below 20 µg/Nm³ for the others. In this second case, the calibration function has a high intercept point.

Incompliance with the $U_{max\ SRM} << U_{max\ AMS}$ condition, that should be fulfilled for AMSs' calibration by SRMs, weakens the accuracy of the results given by the AMS.

Alternative methods to the SRM were tested in Germany, based on mercury adsorption on solid adsorbing traps composed of activated or iodised carbon. The combination of KCl traps or Dowex ® ion exchange with activated carbon traps also enables differentiating oxidised from elementary mercury in the gas stack. Handling the traps is generally very easy and the sampling can easily be automated, enabling longer sampling times by hours, days or weeks, which is not possible with the reference bubbling method. Comparisons were made on industrial sites and have shown equivalence with the SRM (project financed by VGB and associating GDF SUEZ, Enel and E.ON with the Magdeburg University http://www.bmua.de/pdfs/Quecksilberkonzentrationen.pdf).

Conclusion for Hg

The reference methods and the AMSs have satisfactory Limits of Quantification.

The manual reference method however gives results for which the uncertainty is at least 3 times higher (30%) than those given by AMSs at the level of the current Daily ELV for Waste Incineration (50 µg/Nm³).

The **$U_{max\ SRM} << U_{max\ AMS}$ condition necessary for a reliable QAL2 calibration at the level of the current Daily ELV of 50 µg/Nm³ for Hg for Waste Incineration is hence not fulfilled, this weakens the reliability of this calibration and therefore the accuracy of the results given by the AMS.**

Some of the AMSs have interesting performance characteristics, for instance the MERCEM 300Z from SICK Maihak, but it is not usable as an alternative method to the SRM.

With the SRM, a Daily ELV above 50 µg/Nm³ would be necessary to declare with a minimal risk whether an AMS is compliant or non-compliant.

Alternative methods to the SRM were tested in Germany, based on mercury adsorption on solid adsorbing traps enabling to differentiate oxidised and elementary mercury in the gas stack. The possibility of increasing the sampling time, by hours, days or weeks, enables much more reliable QAL2 calibrations than the current SRM.

4.1.11 PAH

The NF X 43 329 Standard describes the SRM (no European Standard available): the sample is taken in an isokinetic manner; the particulate fraction is collected on a filter whose material must be chosen according to the sampled gases' temperature and physical-chemical nature; the gaseous fraction is trapped by condensation and adsorption on XAD2 resin.

Liquid and solid samples are taken to a laboratory and are extracted/prepared to enable a High-Performance Liquid Phase Chromatography (HPLC) or a gaseous phase chromatography coupled with mass spectrometry (GC/MS).

ILCs on SRM implementation during the validation of the standard, limited to 5 laboratories, were performed in 2001 and gave the following results, giving the absolute expanded uncertainty (noted U), according to the concentration (noted C):

Fluoranthene
range: 30 – 1050 µg/Nm^3 $U = 0.0006C^2 - 0.1266C + 56.678$
Indeno (1,2,3-c,d) pyrene
range: 5 – 150 µg/Nm^3 $U = 0.006C^2 + 0.4966C + 5.4468$
Benzo (g,h,i) perylene
range: 5 – 100 µg/Nm^3 $U = 0.0048C^2 + 0.7150C + 0.7014$
Dibenzo (a,h) anthracene
range: 1 – 25 µg/Nm^3 $U = 0.4076C + 4.2936$
Benzo (a) pyrene
range: 5 – 300 µg/Nm^3 $U = 0.2908C + 23.45$
Benzo (k) fluoranthene
range: 3 – 250 µg/Nm^3 $U = 0.0082C^2 + 0.8554C + 30.948$
Benzo (b) fluoranthene
range: 5 – 800 µg/Nm^3 $U = 0.0004C^2 + 0.9582C - 7.566$
Benzo (a) anthracene
range: 10 – 250 µg/Nm^3 $U = 0.0018C^2 + 0.2772C + 13.691$

Conclusion for PAH:

Given the limited number of ILCs organised for PAHs and with only 5 laboratories making parallel trials, the given uncertainty levels must be considered as indicative.

It is difficult to assess the SRM results' reliability and to make recommendations in terms of limit concentration levels under which the uncertainty would not be acceptable to declare (in)compliance.

4.2 PERSPECTIVES FOR NEW, BETTER-PERFORMING METHODS

The techniques described below, except the TDLAS technique for which some AMSs are already certified, are still at experimental stages or are used for ambient air characterisation where there are less sampling difficulties than for emissions sampling (hot, wet and corrosive gases).

4.2.1 TUNABLE DIODE LASER ABSORPTION SPECTROSCOPY (TDLAS)

Classic analysers are limited because they use white light and filters. The available power for a given wavelength is relatively weak.

With the TDLAS method, the light sources and the filters are replaced by a material (like silicon) that emits light at a nearly-fixed wavelength. The bandwidth is around 10^{-4} cm. Interferences with other gases are very limited.

Laser diodes are probably the most widely used tunable lasers. They present the advantage of virtually covering all the light spectrum, from near-ultraviolet to mid-infrared. For a given material, the reading bandwidth is of a few tens of nanometers in the near-infrared and up to several micrometres in the mid-infrared (quantum cascade laser).

Many methods exist to tune diode lasers' wavelengths.

A diode laser's tunability may be obtained by modifying its voltage or its temperature.

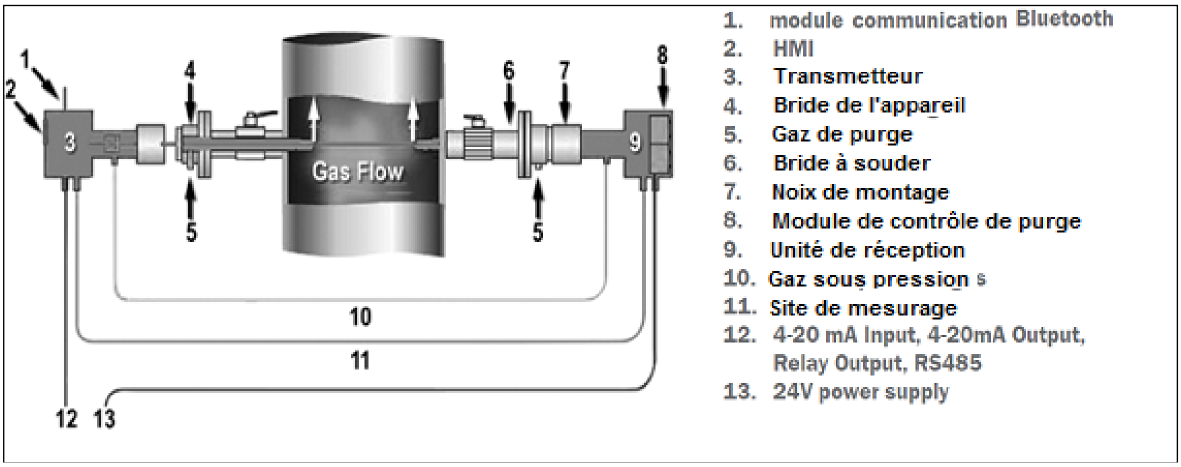


Figure 32: LGA-4000 Process Laser Gas Analysis System Scheme (figure from Teledyne)

Advantages

- The diode laser emits at a precise wavelength, giving it a very good selectivity,
- No gas treatment for on-site version,
- No temperature influence,
- Short response time (2 to 10 sec),
- Many measurable gases: HCl, HF, H_2S, NH_3, O_2, H_2O, CO, CO_2, NO, NO_2, N_2O, HCN, C_2H_2, C_3H_6, CH_3I, CH_3OH…

Weaknesses

The diode laser can be impacted by minor modulations which may create problems on the measured substance.

4.2.2 CAVITY RING DOWN SPECTROSCOPY (CRDS) – ABSORPTION TECHNIQUE

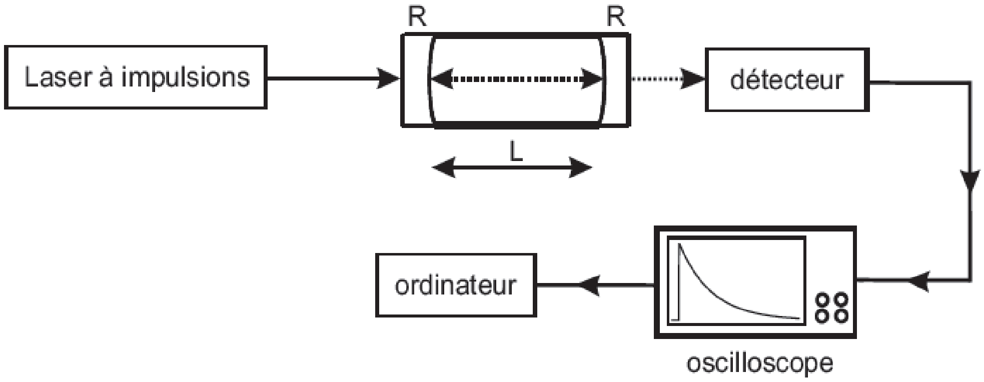
Traditional infrared spectroscopy, such as the FTIR Fourier transform, uses a measurement cavity containing reflecting mirrors to lengthen the light's path (the distance crossed by the infrared beam in the sample) up to a few tens of meters. As the light path intervenes proportionally in the measurements' sensitiveness, the FTIR spectroscopy's is hence limited. The very high sensitiveness of the Cavity Ring Down Spectroscopy (CRDS) absorption spectroscopy is hence one of its advantages. Highly-reflecting mirrors contain the light beam in the cavity, making it resonate (called an optically-resonating cavity). When injecting a laser impulsion in the cavity, it will take 10,000 paths until the light impulse is totally extinguished. The light paths hence obtained with an extended cavity are multiplied by a 1,000-factor compared to a traditional spectroscopy, thus increasing equally the sensitivity.

Advantages

- Very sensitive technique because of the great mirrors' reflectivity, producing very long light paths and giving a very good sensitiveness,
- Good time and space resolution,
- Avoids source fluctuations.

Disadvantage

No experimental feedback for emissions because the technique is mostly used for ambient air measurement.



4.3 R coefficient de réflexion des miroirs de la cavité de haute finesse de longueur L

Figure 33: CRDS instrument with an impulsion laser

4.3.1 OPTICAL FEEDBACK CAVITY ENHANCED ABSORPTION SPECTROSCOPY (OFCEAS)

OFCEAS uses the extended cavity principle, enabling the system to analyse long light paths (1 to 10 km) and hence have very low Limits of Detection. The laser source is a continuous one (non-impulsed), giving the system a great stability. The main novelty of the OFCEAS is its "feedback" principle: part of the emitted beam is sent back from the cavity to the laser. This feedback enables tuning the laser and the cavity to create a resonating phenomenon. This phenomenon's immediate consequence is the particularly strong intensity and very narrow bandwidth of the wavelengths, giving a great sensitivity.

Advantages

- Very high spectrum resolution measurement.
- Gas sampling is made by a low-pressure probe carrying the sample from the sampling point to the analyser avoiding substances' absorption / desorption, condensation or the need to carry via a heated tube. The sample is hence complete. The very low suction rate enables very low response times and minimum fouling.
- The analyser should show very low zero drifts and sensitiveness, a low detection limit (ppb) and a limited maintenance (10 years life expectancy for infrared laser sources), a good reliability and low operation costs.

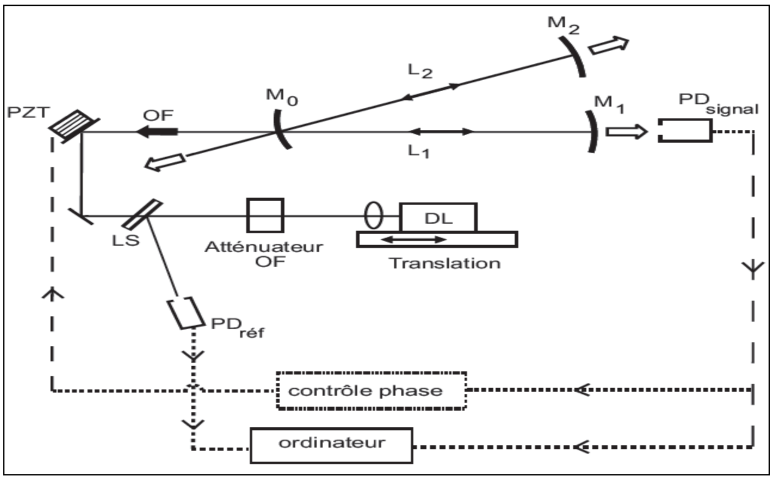


Figure 34: Experimental OFCEAS Scheme (AP2e Document)

4.3.2 INTERFERENTIAL SPECTROMETRY THROUGH SELECTIVE MODULATION (ISSM)

IR or UV absorption bands' fine structures are separated by a nearly-constant difference in wavelengths. It is hence possible, by using a suitable optical device, to create optical interference fringes between these spectrum lines.

Such a method is nearly-totally specific, because each substance is found, on one hand, by the absorption band's wavelength, and on the other hand, by the difference between the spectrum lines on the same band.

This principle enables creating multi-substances analysers (SO_2, NO, HCl...).

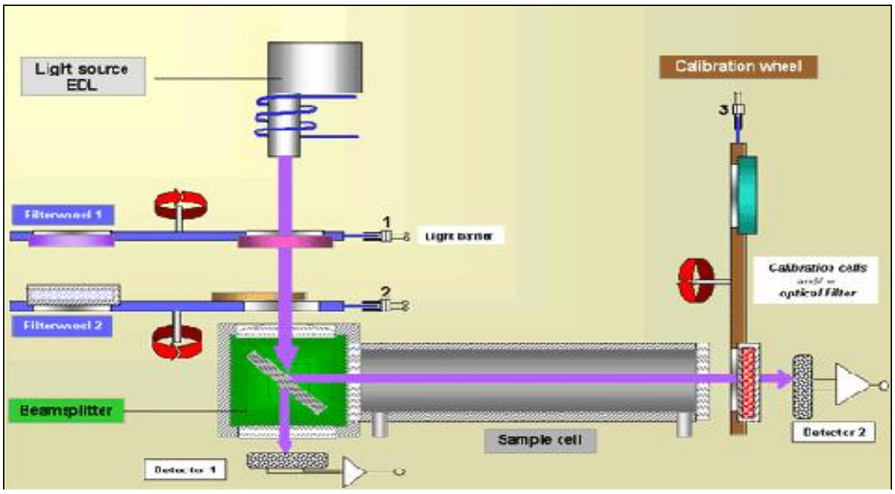


Figure 35: Interferential Spectrometry through Selective Modulation (ISSM) measurement principle

5. LIST OF ANNEXES

Annex	Title	Number of pages
Annex A	QAL2 test reports analysis: Minimum ELV and relative expanded uncertainty fulfilling the variability test	5
Annex B	QAL2 test reports analysis: Comparison of average concentrations measured by AMSs and SRMs – Calibration functions	11
Annex C	QAL2 test reports analysis: Graph representation of measurements [AMS;SRM] and calibration function	11
Annex D	Calculation of the uncertainty associated with a concentration expressed on dry gas and at an oxygen reference concentration	4
Annex E	Summary sheets showing SRM and AMS performances	11

ANNEX A

QAL2 test reports analysis:

Minimum ELV and relative expanded uncertainty fulfilling the variability test

QAL2 of AMSs measuring CO

Rapport d'essais	Marque	Modèle	Principe	Uc,rel requise (%)	* Cmoy mesurée par SRM	** Nombre de mesures AMS/SRM	* VLE du site	* S_D	Nombre couples de valeurs pour test	Incertitude minimale pour test de variabilité conforme (%)	* VLE min avec retraitement des données	* $S_{D,min}$ pour VLEmin	nbre couples pour test	* VLE min calculée avec S_D	* VLE min calculée avec $S_{D,min}$	Commentaires
S01	Environnement SA	MIR FT	FTIR	10	5,9	6	30	0,31	6	2,2	6,8	idem	idem	6,1		
				10	5,9	6	30	0,18	6	1,2	6,0	0,24	3	3,5	4,7	
S02	Sick	MCS 100 EHW P	IR	10	24,7	17	50	0,73	17	2,9	23,6	0,39	3	14,4	7,7	VLE ne peut être testée plus bas car plus que 3 couples de valeurs
				10	24,7	18	50	0,69	18	2,8	23,5	0,64	3	13,5	12,6	VLE ne peut être testée plus bas car plus que 3 couples de valeurs
S05	ABB	ABB ACF	FTIR	10	8,8	18	50	1,45	16	5,8	29,2	idem	idem	28,4		
				10	8,8	15	50	1,10	14	4,4	20,1	0,99	13	21,5	19,5	
S08	Environnement SA	MIR 9000	IR	10	21,7	15	50	1,29	15	5,2	18,6	1,15	3	25,2	22,5	VLE ne peut être testée plus bas car plus que 3 couples de valeurs
				10	25,6	16	50	1,15	15	4,6	17,7	0,60	3	22,5	11,8	VLE ne peut être testée plus bas car plus que 3 couples de valeurs
				10	51,6	18	50	18,25	Test de variabilité ne passe pas							
				10	48,2	17	50	0,87	12	3,5	16,0	0,41	3	17,1	8,0	VLE ne peut être testée plus bas car plus que 3 couples de valeurs

* : en (mg/m $_0^3$ sec 11 % O_2) ** : pour déterminer la fonction d'étalonnage VLE min calculéeavec S_D= S_Dx1,96x100/Uc,rel VLE min calculée avec $S_{D,min}$= $S_{D,min}$x1,96x100/Uc,rel

QAL2 of AMSs measuring NO_x

Rapport d'essais	Marque	Modèle	Principe	Uc,rel requise (%)	* Cmoy mesurée par SRM	** Nombre de mesures AMS/SRM	* VLE du site	* S_D	Nombre couples de valeurs pour test	Incertitude minimale pour test de variabilité conforme (%)	* VLE min avec retraitement des données	* $S_{D,min}$ pour VLEmin	nbre couples pour test	* VLE min calculée avec S_D	* VLE min calculée avec $S_{D,min}$	Commentaires
S01	Environnement SA	MIR FT	FTIR	20	78,2	17	70	1,29	3	4,3				12,6		impossible de tester à une concentration plus faible car à 69 mg/m$_0^3$ il ne resterait que 2 couples pour test de variabilité
				20	78,2	18	70	0,54	4	1,7				5,3		impossible de tester à une concentration plus faible car à 69 mg/m$_0^3$ il ne resterait que 2 couples pour test de variabilité
S02	Sick	MCS 100 EHW P	IR	20	74,1	18	80	2,68	9	6,9	43,0	3,06	3	26,3	29,9	VLE ne peut être testée plus bas car plus que 3 couples de valeurs
				20	74,1	18	80	1,38	9	3,5	44,3	1,80	3	13,5	17,7	VLE ne peut être testée plus bas car plus que 3 couples de valeurs
S05	ABB	ABB ACF	FTIR	20	67,8	17	80	3,13	10	8,0	67,9	1,37	3	30,7	13,5	VLE ne peut être testée plus bas car plus que 3 couples de valeurs
				20	67,8	15	80	7,76	12	19,6	69	6,56	7	76,1	64,3	
S08	Environnement SA	MIR 9000	IR	20	166,9	18	200	6,57	18	6,6	141,9	9,55	3	64,4	93,6	VLE ne peut être testée plus bas car plus que 3 couples de valeurs
				20	168,4	17	200	7,94	17	7,9	144	10,31	3	77,8	101,0	VLE ne peut être testée plus bas car plus que 3 couples de valeurs
				20	187,1	18	200	14,16	11	14,4	184,8	16,72	6	138,7	163,8	
				20	187,1	18	200	4,75	12	4,8	152,1	0,29	3	46,6	2,8	VLE ne peut être testée plus bas car plus que 3 couples de valeurs

* : en (mg/m $_0^3$ sec 11 % O_2) ** : pour déterminer la fonction d'étalonnage VLE min calculéeavec S_D= S_Dx1,96x100/Uc,rel VLE min calculée avec $S_{D,min}$= $S_{D,min}$x1,96x100/Uc,rel

QAL2 of AMSs measuring TOCs

Rapport d'essais	Marque	Modèle	Principe	Uc,rel requise (%)	* Cmoy mesurée par SRM	Nombre de mesures AMS/SRM	* VLE du site	* S_D	Nombre couples de valeurs pour test	Incertitude minimale pour test de variabilité conforme (%)	* VLE min avec retraitement des données	* $S_{D,min}$ pour VLEmin	nbre couples pour test	* VLE min calculée avec S_D	* VLE min calculée avec $S_{D,min}$	Commentaires
S01	Environnement SA	MIR FT	FTIR	30	0,8	6	10	0,09	6	1,9	0,8	0,05	3	0,6	0,3	il ne peut pas être testé une VLE plus basse car plus que 3 couples de données
				30	0,8	6	10	0,12	6	2,5	0,8	0,001	3	0,8	0,01	il ne peut pas être testé une VLE plus basse car plus que 3 couples de données
S02	SICK MAIHAK	EUROFID	FID	30	1,6	15	10	0,517	15	10,4	3,5	idem	idem	3,4		
				30	1,6	15	10	0,509	15	10,2	3,2	0,48	14	3,3	3,1	
S05	ABB	Multi FID	FID	30	1,2	13	10	0,680	13	13,7	4,6	idem	idem	4,4		
				30	1,2	17	10	ne passe pas								
S08	Environnement SA	Graphite 52 M	FID	30	0,94	18	10	0,246	15	4,9	1,7	idem	idem	1,6	-	
				30	0,91	18	10	0,613	15	12,3	4,2	idem	idem	4,0	-	
				30	0,91	18	10	0,378	15	7,6	1,3	0,22	13	2,5	1,4	
				30	0,91	18	10	0,551	15	11,1	1,7	0,24	14	3,6	1,57	

* : en (mg/m $_0^3$ sec 11 % O_2)   ** : pour déterminer la fonction d'étalonnage   VLE min calculéeavec S_D= S_Dx1,96x100/Uc,rel   VLE min calculée avec $S_{D,min}$= $S_{D,min}$x1,96x100/Uc,rel

QAL2 of AMSs measuring SO₂

Rapport d'essais	Marque	Modèle	Principe	Uc,rel requise (%)	* Cmoy mesurée par SRM	** Nombre de mesures AMS/SRM	* VLE du site	* S_D	Nombre couples de valeurs pour test	Incertitude minimale pour test de variabilité conforme (%)	* VLE min avec retraitement des données	* $S_{D,min}$ pour VLEmin	nbre couples pour test	* VLE min calculée avec S_D	* VLE min calculée avec $S_{D,min}$	Commentaires
S01	Environnement SA	MIR FT	FTIR	20	7,7	6	35	1,04	6	6,2	10,2	0,95	5	10,2	9,3	
				20	7,7	6	35	0,94	6	5,6	10,7	0,99	5	9,2	9,7	
S02	Sick	MCS 100 EHW P	IR	20	20,2	18	50	1,294	18	5,2	15,2	0,41	3	12,68	4,0	VLE ne peut être testée plus bas car plus que 3 couples de valeurs
				20	20,2	17	50	1,099	17	4,4	14	0,95	3	10,77	9,3	VLE ne peut être testée plus bas car plus que 3 couples de valeurs
S05	ABB	ABB ACF	FTIR	20	7,2	19	50	2,296	19	9,2	20,6	2,08	17	22,5	20,4	
				20	7,2	19	50	2,67	19	10,7	27,6	2,76	17	26,2	27,0	
S08	Environnement SA	MIR 9000	IR	20	9,99	16	50	2,553	16	10,2	25,1	2,48	13	25,0	24,3	
				20	10,9	18	50	1,273	18	5,1	7,1	0,70	11	12,5	6,9	
				20	10,9	18	50	5,145	Ne passe pas le test de variabilité					-	-	
				20	10,9	18	50	1,68	18	6,7	18,0	1,78	14	16,5	17,5	

* : en (mg/m $_0^3$ sec 11 % O_2)   ** : pour déterminer la fonction d'étalonnage   VLE min calculéeavec S_D= S_Dx1,96x100/Uc,rel   VLE min calculée avec $S_{D,min}$= $S_{D,min}$x1,96x100/Uc,rel

QAL2 of AMSs measuring Dust

Rapport d'essais	Marque	Modèle	Principe	Uc,rel requise (%)	* Cmoy mesurée par SRM	Nombre de mesures AMS/SRM	* VLE du site	* S_D	Nombre couples de valeurs pour test	Incertitude minimale pour test de variabilité conforme (%)	* VLE min avec retraitement des données	* $S_{D,min}$ pour VLEmin	nbre couples pour test	* VLE min calculée avec S_D	* VLE min calculée avec $S_{D,min}$	Commentaires
S01	Durag	D-R-300 b	Opacimétrie	30	0,12	16	5	0,21	16	8,4	1,5	idem	idem	1,4		droite : y=0,33 x
				30	0,12	16	5	0,21	16	8,4	1,5	idem	idem	1,4		droite : y=0,22 x
S02	SICK MAIHAK	FWE 200	lumière diffusée extractive	30	3,6	17	10	0,559	17	11,2	3,1	0,16	3	3,7	1,1	VLE ne peut être testée plus bas car plus que 3
				30	3,6	17	10	0,571	17	11,4	3,1	0,16	3	3,7	1,1	VLE ne peut être testée plus bas car plus que 3 couples de valeurs
				30	3,6	17	10	0,550	17	11,0	3,1	0,29	4	3,6	1,9	VLE ne peut être testée plus bas car plus que 3 couples de valeurs
				30	3,6	17	10	0,551	17	11,0	3,1	0,29	4	3,6	1,9	VLE ne peut être testée plus bas car plus que 3 couples de valeurs
S05	OLDHAM	EP1000	Rétrodiffusion	30	9,2	19	10	1,293	10	26,3	8,8	idem	idem	8,45		
				30	9,2	19	10	1,387	11	28,1	8,6	idem	idem	9,06		
S08	Durag	D-RX 250	Opacimétrie	30	4,30	16	10	0,680	15	13,7	2,7	0,35	5	4,4	2,3	
				30	4,30	16	10	0,616	15	12,4	3,4	0,49	9	4,0	3,2	
				30	6,57	7	10	0,741	5	15,9	4,0	idem	idem	4,8	-	C_{moy} > VLE site car dopage pour 2 essais
				30	6,57	7	10	0,935	5	20,0	5,1	idem	idem	6,1		C_{moy} > VLE site car dopage pour 2 essais

* : en (mg/m $_0^3$ sec 11 % O_2)   ** : pour déterminer la fonction d'étalonnage   VLE min calculéeavec S_D= S_Dx1,96x100/Uc,rel   VLE min calculée avec $S_{D,min}$= $S_{D,min}$x1,96x100/Uc,rel

QAL2 of AMSs measuring HCl

Rapport d'essais	Marque	Modèle	Principe	Uc,rel requise (%)	* Cmoy mesurée par SRM	** Nombre de mesures AMS/SRM	* VLE du site	* S_D	Nombre couples de valeurs pour test	Incertitude minimale pour test de variabilité conforme (%)	* VLE min avec retraitement des données	* $S_{D,min}$ pour VLEmin	nbre couples pour test	* VLE min calculée avec S_D	* VLE min calculée avec $S_{D,min}$	Commentaires
S01	Environnement SA	MIR FT	FTIR	40	1,3	16	8	0,97	16	24,3	4,9	idem	idem	4,8	-	
				40	1,3	16	8	0,96	16	24,1	4,9	idem	idem	4,7	-	
S02	Sick	MCS 100 EHW P	IR	40	2,3	16	10	0,35	16	7,0	2,4	0,46	7	1,7	2,2	
				40	2,3	17	10	0,27	17	5,5	2,2	0,38	4	1,3	1,9	
S05	ABB	ABB ACF	FTIR	40	1,3	19	10	1,01	19	20,2	3,8	0,76	18	5,0	3,7	
				40	1,3	19	10	0,87	19	17,4	3,7	0,74	18	4,3	3,6	
S08	Environnement SA	MIR 9000	IR	40	8,99	17	10	0,90	13	18,2	5,2	0,97	8	4,4	4,8	dopage pour 3 essais
				40	20,4	17	10	1,04	13	20,9	5,2	0,97	6	5,1	4,8	C_{moy} > VLE site car dopage pour 4 essais
				40	12,09	18	10	1,36	9	27,7	6,8	1,30	7	6,6	6,4	C_{moy} > VLE site car dopage pour 4 essais
				40	11,23	17	10	1,87	10	38,1	9,6	idem	idem	9,2	-	C_{moy} > VLE site car dopage pour 4 essais

* : en (mg/m $_0^3$ sec 11 % O_2)   ** : pour déterminer la fonction d'étalonnage   VLE min calculéeavec S_D= S_Dx1,96x100/Uc,rel   VLE min calculée avec $S_{D,min}$= $S_{D,min}$x1,96x100/Uc,rel

QAL2 of AMSs measuring HF

Rapport d'essais	Marque	Modèle	Principe	Uc,rel requise (%)	* Cmoy mesurée par SRM	** Nombre de mesures AMS/SRM	* VLE du site	* S_D	Nombre couples de valeurs pour test	Incertitude minimale pour test de variabilité conforme (%)	* VLE min avec retraitement des données	* $S_{D,min}$ pour VLEmin	nbre couples pour test	* VLE min calculée avec S_D	* VLE min calculée avec $S_{D,min}$	Commentaires
S01	Environnement SA	MIR FT	FTIR	40	0,1	6	1	0,004	6	0,8	0,2	idem	idem	0,02	-	droite : y=x-0,22 - "bonne" régression du fait de l'injection de gaz de point d'échelle - en dessous de 0,2 mg/m_0^3 plus qu'un point pour test variabilité car ttes les valeurs de SRM sont à 0,09 mg/m_0^3
				40	0,1	6	1	0,001	6	0,2	0,1	idem	idem	0,005	-	droite : y=0,995 x -0,077 - "bonne" régression du fait de l'inj de gaz de point d'échelle - en dessous de 0,1 mg/m_0^3, plus de point pour test variabilité car toutes les valeurs SRM sont à 0,1 mg/m_0^3
S05	ABB	ABB ACF	FTIR	40	aucune mesure AMS ni SRM supérieure à 0									0,00	0,0	

* : en (mg/m $_0^3$ sec 11 % O_2) ** : pour déterminer la fonction d'étalonnage VLE min calculéeavec S_D= S_Dx1,96x100/Uc,rel VLE min calculée avec $S_{D,min}$= $S_{D,min}$x1,96x100/Uc,rel

QAL2 of AMSs measuring NH_3

Rapport d'essais	Marque	Modèle	Principe	Uc,rel requise (%)	* Cmoy mesurée par SRM	** Nombre de mesures AMS/SRM	* VLE du site	* S_D	Nombre couples de valeurs pour test	Incertitude minimale pour test de variabilité conforme (%)	* VLE min avec retraitement des données	* $S_{D,min}$ pour VLEmin	nbre couples pour test	* VLE min calculée avec S_D	* VLE min calculée avec $S_{D,min}$
S01	Environnement SA	MIR FT	FTIR	40	9,9	18	10	1,54	9	31,5	8,2	1,42	6	7,5	7,0
				40	9,9	18	10	1,53	8	31,5	8,2	1,47	6	7,5	7,2
S02	Sick	MCS 100 EHW P	IR	40	0,7	18	30	0,4	18	2,7	0,8	0,15	16	2,0	0,7
				40	0,7	18	30	0,337	18	2,2	1	0,18	16	1,7	0,9

* : en (mg/m $_0^3$ sec 11 % O_2) ** : pour déterminer la fonction d'étalonnage VLE min calculéeavec S_D= S_Dx1,96x100/Uc,rel VLE min calculée avec $S_{D,min}$= $S_{D,min}$x1,96x100/Uc,re

ANNEX B

QAL2 test reports analysis:

Comparison of average concentrations measured by AMSs and SRMs – Calibration functions

QAL2 test reports of AMSs measuring CO

Réf. Rapport	Point de mesure	VLE (mg/m$_0^3$ sec, O$_2$ref)	Plage de concentration mesurée par SRM hors injections gaz pour étalonnage (mg/m$_0^3$ sec, O$_2$ref)	Cmoyenne mesurée (mg/m$_0^3$ sec, O$_2$ref)			Equation de la fonction d'étalonnage	R^2	Injection gaz pour étalonnage pour déterminer la fonction		Commentaire
				Par SRM	Par AMS (mesure non étalonnée)	Par AMS (valeur étalonnée)			zéro	point d'échelle	
S01	Ligne 1 titulaire	30	4,9 - 6,8	5,89	2,88	4,78	AMSétal=AMS x 0,978 + 2,138	0,999		94 mg/m$_0^3$	qualité apparente de la droite liée au mesures avec gaz de point d'échelle
S01	Ligne 1 redondant	30	4,9 - 6,8	5,89	1,17	4,31	AMSétal=AMS x 0,976 + 3,419	0,997		94 mg/m$_0^3$	qualité apparente de la droite liée au mesures avec gaz de point d'échelle
S01	Ligne 2 titulaire	30	4,9 - 7,9	5,70	2,53	4,20	AMSétal=AMS x 0,980 + 2,095	0,998		94 mg/m$_0^3$	qualité apparente de la droite liée au mesures avec gaz de point d'échelle
S01	Ligne 2 redondant	30	4,9 - 7,9	5,70	0,51	2,62	AMSétal=AMS x 0,984 + 2,364	0,998		94 mg/m$_0^3$	qualité apparente de la droite liée au mesures avec gaz de point d'échelle
S02	Titulaire	50	15,9 - 27,8	25,4	24,15	25,3	AMSétal=AMS x 1,051 - 0,050	0,997	x		
S02	Redondant	50	15,9 - 27,8	25,4	23,16	25,5	AMSétal=AMS x 1,079 + 0,382	0,971			
S05	Titulaire	50	1,2 - 60,4	7,52	8,45	9,35	AMSétal=AMS x 0,97 + 0,93	0,97			
S05	Redondant	50	1,2 - 60,4	8,81	13,09	9,52	AMSétal=AMS x 0,78 - 0,55	0,99			
S04	Titulaire	50	9,4 - 13,2	11,0	10,4	10,8	AMSétal=AMS x 1,00 + 0,31	1,00	x	75 mg/m$_0^3$	qualité de la fonction améliorée par mesures avec gaz pour étalonnage
S04	Redondant	50	9,4 - 13,2	11,0	7,59	9,,58	AMSétal=AMS x 1,03 + 1,77	1,00	x	75 mg/m$_0^3$	qualité de la fonction améliorée par mesures avec gaz pour étalonnage
S08	Ligne 1 titulaire	50	14 - 31	45,6	47,1	45,4	AMSétal=AMS x 0,969 - 0,106	0,990	x		
S08	Ligne 2 titulaire	50	15 - 236	51,7	29,9	51,5	AMSétal=AMS x 5,664 - 120,216	0,644			Ne passe pas le test de variabilité
S03	Ligne 1 titulaire	50	10,0 - 20,2	15,5	16,0	15,6	AMSétal=AMS x 1,004 - 0,459	1,000	x	97 mg/m$_0^3$	
S03	Ligne 1 redondant	50	10,0 - 20,2	15,5	15,4		AMSétal=AMS x 1,000 + 0,054	1,000		97 mg/m$_0^3$	
S06	Titulaire	50	6,3 - 31	14,9	12,4	14,6	AMSétal=AMS x 1,02 + 1,33	0,93	x		
S06	Redondant	50	6,3 - 31	14,9	14	13,7	AMSétal=AMS x 0,99 + 0,54	0,95	x		
T01	Titulaire	50	3,2 - 3,7	3,44	1,81	2,88	AMSétal=AMS x 0,99 + 0,9	1	x	161 mg/m$_0^3$	fonction d'étalonnage avec pente à 1 liée aux mesures avec le gaz pour étalonnage ; concentation élevée par rapport à la VLE
T01	Redondant	50	3,2 - 3,7	3,44	1,42	2,68	AMSétal=AMS x 1,01 + 0,9	1	x	161 mg/m$_0^3$	fonction d'étalonnage avec pente à 1 liée aux mesures avec le gaz pour étalonnage ; concentation élevée par rapport à la VLE
T02	Titulaire	50	0,3 - 0,6	0,46	1,92	1,14	AMSétal=AMS x 1,00 - 0,80	1,00	x	160 mg/m$_0^3$	fonction d'étalonnage avec pente à 1 liée aux mesures avec le gaz pour étalonnage ; concentation élevée par rapport à la VLE
T02	Redondant	50	0,3 - 0,6	0,46	1,60	0,92	AMSétal=AMS x 1,01 - 0,71	1,00	x	160 mg/m$_0^3$	fonction d'étalonnage avec pente à 1 liée aux mesures avec le gaz pour étalonnage ; concentation élevée par rapport à la VLE
V01	Titulaire	50	4,18 - 5,6	4,77	3,65	4,60	AMSétal=AMS x 0,992 - 0,757	1,000	x	97 mg/m$_0^3$	
V01	Redondant	50	4,18 - 5,6	4,77	1,69	4,30	AMSétal=AMS x 1,004 + 2,012	0,999	x	97 mg/m$_0^3$	fonction d'étalonnage avec pente à 1 liée aux mesures avec le gaz pour étalonnage
I01		30	3,2 - 13,2	4,19	2,72	4,23	AMSétal=AMS x 0,71 + 2,42	-			
E01	Ligne 3	50	2,7 - 55,9	16,1	14,6	17,7	AMSétal=AMS x 0,95 + 1,17	-			
E02	Ligne 4	50	4,0 - 27,8	12,5	11,6	12,5	AMSétal=AMS x 1,02 - 1,7	-			
E03		100	1,5 - 17,7	6,44	7,07	5,89	AMSétal=AMS x 1,0 - 1,74	0,980		629 mg/m$_0^3$	concentration gaz pour étalonnage utilisé élevée par rapport à la VLE jour pour déterminer la
E06		100	16 - 46	26,1	9,98	29,6	AMSétal=AMS x 0,96 + 28,27	0,990		629 mg/m$_0^3$	concentration gaz pour étalonnage utilisé élevée par rapport à la VLE jour pour déterminer la
U01		50	3,1 - 40	5,43	8,55	9,28	AMSétal=AMS x 1,0258 - 3,9275	0,960	x		ordonnée à l'origine élevée au vu du niveau de concentration ; pente proche de 1 liée à un pic de concentration à 40 mg/m$_0^3$
U02	Ligne 1	50	toutes valeurs de SRM et d'AMS négatives !				AMSétal=AMS x 0,9821 + 0,17	1,00	x		toutes valeurs de SRM et d'AMS négatives ! Fonction d'téalonnage obtenue avec des gaz pour étalonnage
U02	Ligne 2	50	3,5 - 10,3	5,63	8,04	5,55	AMSétal=AMS x 0,6901	0,815	x		fonction d'étalonnage fournie en conclusion différente : obtenue avec des gaz pour étalonnage
U03	Ligne 1	50	0 - 25	4,84	13 7	4,66	AMSétal=AMS x 0,344 - 0,03	0,127	x		fonction d'étalonnage fournie en conclusion différente : obtenue avec des gaz pour étalonnage
U03	Ligne 2	50	1,4 - 27	8,39	16,1	7,82	AMSétal=AMS x 0,1045 + 4,58	0,017	x		fonction d'étalonnage fournie en conclusion différente : obtenue avec des gaz pour étalonnage
w01		50	5,3 - 78,9	32,0	24,7	32,2	AMSétal=AMS x 1,0777 + 6,3325	0,9982			
w02		50	-3,4 - 1,5	-1,26	-1,81	-1,29	AMSétal=AMS x 0,7238	0,5692			toutes valeurs de SRM et d'AMS négatives !
w03		50	-2,2 - 10,2	1,26	0,38	1,26	AMSétal=AMS x 1,8841 + 0,7109	0,7788			
N03		30	0,9 - 4,2	2,7	2,4	2,9	AMSétal=AMS x 1,207	-			
N04		50	0,8 - 1,7	1,35	1,62	1,40	AMSétal=AMS x 0,864	-			
N05		50	0,1 - 1,7	0,83	1,86	0,86	AMSétal=AMS x 0,463	-			
N06		50	2,1 - 4,3	3,02	2,97	3,10	AMSétal=AMS x 1,044	-			
G01	Ligne 2	50	0 - 51,3	3,7	4,3	3,6	AMSétal=AMS x 1,0048 - 0,37	-			
G02	Ligne 4	50	0,1 - 2,2	0,9	6,3	0,8	AMSétal=AMS x 1,2053 - 6,97	-		49 mg/m$_0^3$	ordonnée à l'origine élevée au regard du niveau de concentration
B01		100	6,8-12,5	9,3	10,8	9,3	AMSétal=AMS x 1,02 - 0,071	-	x	260 mg/m$_0^3$	

QAL2 test reports of AMSs measuring NOx

Réf. Rapport	Point de mesure	VLE (mg/m$_0^3$ sec, O$_2$ref)	Plage de concentration mesurée par SRM hors injections gaz pour étalonnage (mg/m$_0^3$ sec, O$_2$ref)	Cmoyenne mesurée (mg/m$_0^3$ sec, O$_2$ref)			Equation de la fonction d'étalonnage	R²	Injection gaz pour étalonnage pour déterminer la fonction		Commentaire
				Par SRM	Par AMS (mesure non étalonnée)	Par AMS (valeur étalonnée)			zéro	point d'échelle	
S01	Ligne 1 titulaire	70	64 - 96	78,2	70,1	78,4	AMSétal=AMS x 1,127 - 0,063	0,998	x	201 mg/m$_0^3$	
S01	Ligne 1 redondant	70	64 - 96	78,2	77,8	77,9	AMSétal=AMS x 1,014 - 0,854	0,997	x	201 mg/m$_0^3$	
S01	Ligne 2 titulaire	70	89 - 158	125,4	98,7	125,6	AMSétal=AMS x 1,285 - 1,040	0,996	x	199 mg/m$_0^3$	
S01	Ligne 2 redondant	70	89 - 158	125,4	115,3	122,3	AMSétal=AMS x 1,086 - 2,768	0,991	x	199 mg/m$_0^3$	
S02	Titulaire	80	0 - 127	74,1	83,1	73,9	AMSétal=AMS x 1,102 - 14,087	0,985			
S02	Redondant	80	0 - 127	74,1	73,1	74,0	AMSétal=AMS x 1,066 - 5,682	0,959			
S05	Titulaire	80	50 - 106	67,5	86,8	78,2	AMSétal=AMS x 1,01 - 7,74	0,74	x		
S05	Redondant	80	54 - 106	67,5	80,4	74,0	AMSétal=AMS x 0,99 - 4,48	0,95	x		
S04	Titulaire	80	57 - 82	69,6	72,0	69,6	AMSétal=AMS x 0,97 - 0,05	1,00	x		
S04	Redondant	80	57 - 82	69,6	69,9	69,6	AMSétal=AMS x 0,99 + 0,15	1,00	x		
S08	Ligne 1 titulaire	200	122 - 197	166,9	122,7	167,2	AMSétal=AMS x 0,954 + 51,753	0,95			
S08	Ligne 2 titulaire	200	132 - 232	187,1	154,6	187,0	AMSétal=AMS x 0,914 + 46,454	0,888			
S03	Ligne 1 titulaire	200	116 - 180	166,2	156,1	165,6	AMSétal=AMS x 1,043 + 2,463	0,991			
S03	Ligne 1 redondant	200	116 - 180	166,2	171,3		AMSétal=AMS x 1,028 + 4,511	0,986			
S06	Titulaire	200	165 - 218	191,9	211,6	191,9	AMSétal=AMS x 0,88 + 0,07	0,99	x		
S06	Redondant	200	165 - 218	191,9	216	191,9	AMSétal=AMS x 0,88 - 0,55	0,99	x		
T01	Titulaire	400	361 - 420	382	393	383	AMSétal=AMS x 0,99 - 0,1	1,00	x		
T01	Redondant	400	361 - 420	382	mêmes valeurs d'AMS - erreur de copier/coller ?				x		
T02	Titulaire	400	270 - 320	293,2	219,5	293,6	AMSétal=AMS x 0,91 - 0,17	1,00	x		
T02	Redondant	400	270 - 320	293,2	250,7	288,4	AMSétal=AMS x 0,99 - 11,0	0,80			mesures au zéro non ajoutées
V01	Titulaire	80	45 - 87	72,3	85,6	72,3	AMSétal=AMS x 0,959 - 4,527	0,918			
V01	Redondant	80	45 - 87	72,3	78,0	72,3	AMSétal=AMS x 1,019 - 3,902	0,894			
I01		100	57 - 101	82,8	103,0	non calculée	AMSétal=AMS x 0,82 - 1,32	-			
E01	Ligne 3	200	31 - 251	93,6	85,7	94,5	AMSétal=AMS x 0,98 + 0,9	-			
E02	Ligne 4	200	8,3 - 40,1	29,3	32,9	29,3	AMSétal=AMS x 0,78 - 1,5	-			
E03		200	38 - 79	64,5	54,6	58,7	AMSétal=AMS x 1,0 + 5,66	0,975	x	702 mg/m$_0^3$	gaz pour étalonnage utilisé pas du tout approprié par rapport à la VLE jour pour déterminer la fonction d'étalonnage
E06		200	80 - 95	87	69,6	72,9	AMSétal=AMS x 1,05	0,992	x	702 mg/m$_0^3$	gaz pour étalonnage utilisé pas du tout approprié par rapport à la VLE jour pour déterminer la fonction d'étalonnage
E07											
E08											
U01		200	167 - 259	215	194	221	AMSétal=AMS x 1,1417 - 0,6438	0,9951	x		
U02	Ligne 1	200	167 - 203	184	230	191	AMSétal=AMS x 0,8202 + 1,64	0,98	x		
U02	Ligne 2	200	173 - 189	178	177	175	AMSétal=AMS x 0,9352	0,986	x		
U03	Ligne 1	200	204 - 265	241	218	240	AMSétal=AMS x 1,1022 - 1,02	0,979	x		
U03	Ligne 2	200	167 - 215	199	224	207	AMSétal=AMS x 0,9187 + 0,87	0,982	x		
w01		200	54 - 114	83,9	49,3	84,6	AMSétal=AMS x 1,687 + 1,959	0,987			
w02		200	38 - 149	86,1	67,1	89,3	AMSétal=AMS x 1,177 + 16,875	0,979			
w03		200	37 - 95	68,9	48,5	69,7	AMSétal=AMS x 1,3820 + 1,4565	0,9979			
N03		180	55,5 - 96,3	52,3	56,3	54,8	AMSétal=AMS x 0,975	-			
N04		200	24 - 105	52,7	52,1	54,5	AMSétal=AMS x 0,967 + 3,767	-			
N05		200	27 - 88	52,1	50,5	55,6	AMSétal=AMS x 1,037 + 2,736	-			
N06		200	30 - 121	69,9	57,5	72,3	AMSétal=AMS x 1,085 + 9,20	-			
G01	Ligne 2	100	35 - 297	109	111	109	AMSétal=AMS x 0,9355 + 3,610	-			
G02	Ligne 4	100	55 - 69	59,0	63,2	59,3	AMSétal=AMS x 0,9376 + 0,004	-			
B01		400	73 - 163	128	127	130	AMSétal=AMS x 1 + 1,105	-			

QAL2 test reports of AMSs measuring TOC

Réf. Rapport	Point de mesure	VLE (mg/m$_0^3$ sec, O_2ref)	Plage de concentration mesurée par SRM hors injections gaz pour étalonnage (mg/m$_0^3$ sec, O_2ref)	Cmoyenne mesurée (mg/m$_0^3$ sec, O_2ref)			Equation de la fonction d'étalonnage	R²	Injection gaz pour étalonnage pour déterminer la fonction		Commentaire
				Par SRM	Par AMS (mesure non étalonnée)	Par AMS (valeur étalonnée)			zéro	point d'échelle	
S01	Ligne 1 titulaire	10	0,7 - 1,0	0,83	0,09	0,58	AMSétal=AMS x 0,928 + 0,510	0,988		8 mg/m$_0^3$	ordonnée à l'origine élevée par rapport aux concentrations mesurées ; qualité de la droite liée aux mesures avec le gaz de point d'échelle
S01	Ligne 1 redondant	10	0,7 - 1,0	0,83	0,28	0,64	AMSétal=AMS x 0,950 + 0,351	0,989		8 mg/m$_0^3$	ordonnée à l'origine élevée par rapport aux concentrations mesurées ; qualité de la droite liée aux mesures avec le gaz de point d'échelle
S01	Ligne 2 titulaire	10	0,6 - 0,8	0,58	0,18	0,4	AMSétal=AMS x 0,950 + 0,352	0,993		8 mg/m$_0^3$	ordonnée à l'origine élevée par rapport aux concentrations mesurées ; qualité de la droite liée aux mesures avec le gaz de point d'échelle
S01	Ligne 2 redondant	10	0,6 - 0,8	0,58	0,20	0,42	AMSétal=AMS x 0,964 + 0,191	0,991		8 mg/m$_0^3$	qualité de la droite liée aux mesures avec le gaz pour étalonnage de point d'échelle
S02	Titulaire	10	1,1 - 2,9	1,57	0,35	1,24	AMSétal=AMS x 1,003 + 0,735	0,997	x	34 mg/m$_0^3$	qualité de la droite liée aux mesures avec le gaz pour étalonnage de point d'échelle
S02	Redondant	10	1,1 - 2,9	1,57	1,71	1,35	AMSétal=AMS x 1,004 - 0,284	0,998	x	34 mg/m$_0^3$	qualité de la droite liée aux mesures avec le gaz pour étalonnage de point d'échelle
S05	Titulaire	10	0 - 2,1	0,7	1,1	0,79	AMSétal=AMS x 0,45 + 0,25	0,13			
S05	Redondant	10	0 - 2,1	1,22	0,29	1,36	AMSétal=AMS x 1,17 + 0,84	0,02			
S04	Titulaire	10	0 - 3,1	1,64	0,59	1,32	AMSétal=AMS x 0,98 + 0,44	1,00	x	20 mg/m$_0^3$	qualité de la droite liée aux mesures avec le gaz pour étalonnage de point d'échelle
S04	Redondant	10	0 - 3,1	1,64	0,1	1,1	AMSétal=AMS x 0,96 + 0,75	0,99	x	20 mg/m$_0^3$	5 mesures AMS sur 5 égales à 0,1 ; fonction d'étalonnage avec pente de 1 liée aux mesures avec le gaz pour étalonnage de point d'échelle
S08	Ligne 1 titulaire	10	0,6 - 1,2	0,91	0,48	0,84	AMSétal=AMS x 0,964 + 0,390	0,994	x	11 mg/m$_0^3$	qualité de la droite améliorée avec les mesures lors de l'injection de gaz pour étalonnage à 0 et au point d'échelle
S08	Ligne 2 titulaire	10	0,4 - 2,6	0,91	0,50	0,84	AMSétal=AMS x 0,963 + 0,308	0,987	x	11 mg/m$_0^3$	qualité de la droite améliorée avec les mesures lors de l'injection de gaz pour étalonnage à 0 et au point d'échelle
S03	Ligne 1 titulaire	10	0,6 - 0,7	0,67	0,02	0,45	AMSétal=AMS x 1,064 + 0,356	0,997	x	11 mg/m$_0^3$	5 mesures AMS sur 6 égales à 0 ; fonction d'étalonnage avec pente de 1 liée aux mesures avec le gaz pour étalonnage de point d'échelle
S03	Ligne 1 redondant	10	0,6 - 0,7	0,67	0,08	0,48	AMSétal=AMS x 0,966 + 0,395	0,997	x	11 mg/m$_0^3$	fonction d'étalonnage avec pente proche de 1 liée aux mesures avec le gaz pour étalonnage de point d'échelle
S06	Titulaire	10	1,2 - 2,0	1,56	0,78	1,26	AMSétal=AMS x 0,95 + 0,43	0,99	x	10,5 mg/m$_0^3$	fonction d'étalonnage avec pente proche de 1 liée aux mesures avec le gaz pour étalonnage de point d'échelle
S06	Redondant	10	1,2 - 2,0	1,56	0,55	1,1	AMSétal=AMS x 0,90 + 0,53	0,99	x	10,5 mg/m$_0^3$	fonction d'étalonnage avec pente proche de 1 liée aux mesures avec le gaz pour étalonnage de point d'échelle
T01	Titulaire	10	1 - 1,1	1,04	-0,98	0,28	AMSétal=AMS x 0,98 + 0,9	1	x	41,5 mg/m$_0^3$	valeurs de l'AMS égales à -0,6 ou -0,7 mg/m^3 humide ; fonction d'étalonnage avec pente proche de 1 liée aux mesures avec le gaz pour étalonnage de point d'échelle
T01	Redondant	10	1 - 1,1	1,04	0,87	0,94	AMSétal=AMS x 1 + 0	1	x	41,5 mg/m$_0^3$	fonction d'étalonnage avec pente proche de 1 liée aux mesures avec le gaz pour étalonnage de point d'échelle
T02	Titulaire	10	0,3 - 0,7	1,24	-0,65	0,56	AMSétal=AMS x 0,99 + 1,01	1,00	x	32 mg/m$_0^3$	valeurs de l'AMS comprises entre -0,7 et -0,4 mg/m^3 humide ; fonction d'étalonnage avec pente proche de 1 liée aux mesures avec le gaz pour étalonnage de point d'échelle
T02	Redondant	10	0,3 - 0,7	1,24	0		AMSétal=AMS x 0,99 + 0,75		x	32 mg/m$_0^3$	les 5 valeurs de l'AMS sont nulles ; fonction d'étalonnage avec pente proche de 1 liée aux mesures avec le gaz pour étalonnage de point d'échelle

Réf. Rapport	Point de mesure	VLE (mg/m_0^3 sec, O_2ref)	Plage de concentration mesurée par SRM hors injections gaz pour étalonnage (mg/m_0^3 sec, O_2ref)	Cmoyenne mesurée (mg/m_0^3 sec, O_2ref)			Equation de la fonction d'étalonnage	R²	Injection gaz pour étalonnage pour déterminer la fonction		**Commentaire**
				Par SRM	Par AMS (mesure non étalonnée)	Par AMS (valeur étalonnée)			zéro	point d'échelle	
V01	Titulaire	10	0,19 - 0,22	0,2	0		AMSétal=AMS x 1,036 - 0,103	0,996	x	11 mg/m_0^3	les 5 valeurs de l'AMS sont nulles ; fonction d'étalonnage avec pente proche de 1 liée aux mesures avec les gaz pour étalonnage à 0 et à 11 mg/m^3
V01	Redondant	10	0,19-0,22	0,2	0		AMSétal=AMS x 1,007 + 0,189	0,999	x	11 mg/m_0^3	les 5 valeurs de l'AMS sont nulles ; fonction d'étalonnage avec pente proche de 1 liée aux mesures avec les gaz pour étalonnage à 0 et à 11 mg/m^3
I01		10	toutes valeurs SRM à 0,8 mg/m03	0,8	0,45	non calculée	AMSétal=AMS x 1,77	-			
E01	Ligne 3	10	0,7 - 1,3	0,91	0,14	0,90	AMSétal=AMS x 0,93 + 0,7	-		9,8 mg/m_0^3	pente proche de 1 liée aux mesures avec injection de gaz pour étalonnage
E02	Ligne 4	10	0,1 - 0,5	0,17	0,23	0,18	AMSétal=AMS x 1,02 - 0,1	-		9,8 mg/m_0^3	l'application de gaz pour étalonnage améliore la détermination de la fonction d'étalonnage
E03		10	0,2 - 1,7	0,68	0,80	0,81	AMSétal=AMS x 1,22 + 0,46	0,999		16 mg/m_0^3	
E06		10	0,5 - 6,6	2,37	1,72	2,15	AMSétal=AMS x 1,25 - 0,06	0,996		16 mg/m_0^3	
U01		10	0,3 - 5,4	0,46	0,27	0,45	AMSétal=AMS x 0,6544 + 0,2979	0,5709	x		
U02	Ligne 1	10	0,9 - 5,0	2,97	0,27	3,08	AMSétal=AMS x 2,7894 + 1,5	0,605	x		fonction d'étalonnage fournie en conclusion différente : obtenue avec des gaz pour étalonnage
U02	Ligne 2	10	0,9 - 3,7	2,15	0,21	2,04	AMSétal=AMS x 2,3431 + 1,37	0,562	x		fonction d'étalonnage fournie en conclusion différente : obtenue avec des gaz pour étalonnage
U03	Ligne 1	10	0,2 - 1,5	0,85	1,88	0,79	AMSétal=AMS x 0,425	0,479	x		fonction d'étalonnage fournie en conclusion différente : obtenue avec des gaz pour étalonnage
U03	Ligne 2	10	0,2 - 0,4	0,27	1,32	0,27	AMSétal=AMS x 0,206	0,147			fonction d'étalonnage fournie en conclusion différente : obtenue avec des gaz pour étalonnage
N02		10	0,4	0,40	0,25	0,40	AMSétal=AMS x 1,624	-			
N04		10	0,7 - 2,3	1,60	1,21	1,70	AMSétal=AMS x 1,408	-			
N05		10	1,5 - 2,6	1,79	0,57	1,74	AMSétal=AMS x 3,004 + 0,01	-			
N06		10	0,7 - 1,8	0,97	0,63	0,91	AMSétal=AMS x 1,458	-			
G01		10	0 - 0,4	0	0,3	0	AMSétal=AMS x 1,040 - 0,323	-		10,2 mg/m_0^3	5 mesures SRM égales à -0,1 mg/m_0^3 et 6 égales à 0 sur 16 ; fonction d'étalonnage établie avec la mesure liée à l'injection de gaz pour étalonnage
G02		10	0,5 - 1,5	1,1	0,1	1,1	AMSétal=AMS x 0,9613 + 0,946	-		12,8 mg/m_0^3	ordonnée à l'origine relativement élevée au regard du niveau de concentration émis ; pente proche de 1 liée à la mesure avec injection de gaz pour étalonnage
B01		20	0 - 0,6	0,25	1,3	0,16	AMSétal=AMS x 0,965 - 0,939		x	40 mg/m_0^3	pente proche de 1 liée à la mesure avec injection de gaz pour étalonnage

QAL2 test reports of AMSs measuring Dust

Réf. Rapport	Point de mesure	VLE (mg/m_0^3 sec, O_2ref)	Plage de concentration mesurée par SRM hors injections gaz pour étalonnage (mg/m_0^3 sec, O_2ref)	Cmoyenne mesurée (mg/m_0^3 sec, O_2ref)			Equation de la fonction d'étalonnage	R²	Commentaire
				Par SRM	Par AMS (mesure non étalonnée)	Par AMS (valeur étalonnée)			
S01	Ligne 1 titulaire	5	0 - 0,7	0,12	0,57	0,13	AMSétal=AMS x 0,233		peu de mesures SRM > 0 ; pente montrant un décalage significatif ; lié à la SRM ou à l'AMS ?
S01	Ligne 1 redondant	5	0 - 0,7	0,12	0,36	0,12	AMSétal=AMS x 0,300		peu de mesures SRM > 0 ; pente montrant un décalage significatif ; lié à la SRM ou à l'AMS ?
S01	Ligne 2 titulaire	5	1,5 - 2,1	1,76	0,43	1,82	AMSétal=AMS x 2,434		
S01	Ligne 2 redondant	5	1,5 - 2,1	1,76	0,27	1,8	AMSétal=AMS x 3,675		
S02	Titulaire A	10	2,4 - 6,1	3,57	12,72	3,59	AMSétal=AMS x 0,129 + 1,566	0,72	
S02	Titulaire B	10	2,4 - 6,1	3,57	13,77	3,59	AMSétal=AMS x 0,123 + 1,518	0,712	
S02	Redondant A	10	2,4 - 6,1	3,57	15,92	3,59	AMSétal=AMS x 0,102 + 1,583	0,72	
S02	Redondant B	10	2,4 - 6,1	3,57	63,61	3,59	AMSétal=AMS x 0,025 + 1,590	0,72	
S05	Titulaire	10	0,4 - 389	9,21	9,91	10,7	AMSétal=AMS x 2,21 - 9,26	0,81	
S05	Redondant	10	0,4 - 38,9	9,21	14,28	11,06	AMSétal=AMS x 0,89 -1,41	0,441	
S04	Titulaire	10	0,7 - 4,4	2,75	6,03	2,76	AMSétal=AMS x -0,07 + 2,47	0,01	
S04	Redondant	10	0,7 - 4,4	2,75	5,2	2,76	AMSétal=AMS x -0,09 + 2,51	0,14	
S08	Ligne 1 titulaire	10	1,7 - 19,0	4,3	5,79	4,32	AMSétal=AMS x 0,605 + 0,712	0,972	dopage 6 essais sur 18 ; concentration = 1,9 mg/m_0^3 sans dopage
S08	Ligne 2 titulaire	10	1,7 - 23,3	6,57	4,03	6,62	AMSétal=AMS x 2,381 - 2,656	0,967	dopage 2 essais sur 7 ; concentration = 0,7 mg/m_0^3 sans dopage
S03	Ligne 1 titulaire	10	0,3 - 15,8	6,64	6,5	6,63	AMSétal=AMS x 0,778 + 1,245	0,904	dopage sur 3 essais ; concentration = 3,2 mg/m_0^3 sans dopage
S03	Ligne 1 redondant	10	0,3 - 15,8	6,01	4,96	5,98	AMSétal=AMS x 1,100 + 0,410	0,902	dopage sur 3 essais ; concentration = 3,2 mg/m_0^3 sans dopage
S06	Titulaire	10	0,4 - 5,1	3,3	1,14	3,2	AMSétal=AMS x 1,80 + 0,05	0,395	
S06	Redondant	10	0,4 - 5,1	3,3	0				toutes les valeurs de l'AMS sont égales à 0
T01	Titulaire	10	0,2 - 0,6	0,25	0,32	0,25	AMSétal=AMS x 0,50	0,11	
T01	Redondant	10	0,2 - 0,6	0,25	0,45	0,25	AMSétal=AMS x 0,39	0,18	
T02	Titulaire	10	0,4 - 0,6	0,45	0,63	0,47	AMSétal=AMS x 0,40		
T02	Redondant	10	0,4 - 0,5	0,42	0,80	0,42	AMSétal=AMS x 0,30		
V01	Titulaire	10	0,3 - 7,6	1,35	0,17	1,36	AMSétal=AMS x 4,683 + 0,015	0,987	dopage sur 3 essais ; concentration = 0,44 mg/m_0^3 sans dopage
V01	Redondant	10	0,3 - 7,6	1,35	0,33	1,35	AMSétal=AMS x 3,192 + 0,239	0,983	dopage sur 3 essais ; concentration = 0,44 mg/m_0^3 sans dopage
I01		5	0,4 - 0,8	0,55	0,30	non calculée	AMSétal=AMS x 1,96	-	toutes les mesures AMS sont égales à 0,3 mg/m_0^3
E01	Ligne 3	10	0,6 - 1,9	1,12	0,35	1,10	AMSétal=AMS x 2,62		4 mesures sur 5 SRM sont < LQ
E02	Ligne 4	10	1,03 - 1,5	1,36	1,45	1,40	AMSétal=AMS x 0,79		6 mesures sur 7 SRM sont < LQ
E03		10	0,5 - 0,8	0,61	0,14	0,11	AMSétal=AMS x 1,04	0,989	pente de la fonction proche de 1 liée à un dopage ou utilisation d'un substitut à 80 mg/m_0^3
E06		10	1,2 - 1,8	1,59	0,49	0,53	AMSétal=AMS x 1,075	0,985	pente de la fonction proche de 1 liée à un dopage ou utilisation d'un substitut à 80 mg/m_0^3
U01		10	0,12 - 0,27	0,19	0,38	0,20	AMSétal=AMS x 0,7764 - 0,645	1	
w01		10	0,4 - 7,0	3,75	5,05	3,88	AMSétal=AMS x 0,3173 + 0,5414	0,7295	
w02		10	0,6 - 5,9	3,47	5,55	3,49	AMSétal=AMS x 0,041 + 2,0997	0,0617	
w03		10	0,2 - 7,1	3,59	4,25	3,68	AMSétal=AMS x 0,4204 + 0,0927	0,9036	
N03		10	0,4 - 0,5	< 0,4	< 0,1	0,4	AMSétal=AMS x 4,925	-	
N04		5	0,1 - 0,7	0,37	0,68	0,45	AMSétal=AMS x 0,666	-	8 mesures SRM sur 18 notées < 0,5 mg/m^3
N05		5	0,3 - 0,6	0,39	0,34	0,43	AMSétal=AMS x 0,116 + 0,47	-	12 mesures AMS sur 18 notées < 0,3 mg/m^3 ;10 mesures SRM sur 18 notées < 0,5 mg/m^3
N06		5	0,2 - 1,0	0,40	0,29	0,47	AMSétal=AMS x 0,429 + 0,43	-	12 mesures AMS sur 17 notées < 0,3 mg/m^3
G01	Ligne 2	5	0 - 8,2	1,4	0,8	1,4	AMSétal=AMS x 1,089 + 0,305	-	
G02	Ligne 4	5	0 - 1,3	0,2	0,14	0,2	AMSétal=AMS x 1,213 - 0,001 ?	-	mesures de la SRM sont égales à 0,1 mg/m^3 ; comment a été déterminée la fonction d'étalonnage fournie ?
B01		30	0,7 - 3	1,6	0,5	1,6	AMSétal=AMS x 1,923		

QAL2 test reports of AMSs measuring SO_2

Réf. Rapport	Point de mesure	VLE (mg/m$_0^3$ sec, O_2ref)	Plage de concentration mesurée par SRM hors injections gaz pour étalonnage (mg/m$_0^3$ sec, O_2ref)	Cmoyenne mesurée (mg/m$_0^3$ sec, O_2ref)			Equation de la fonction d'étalonnage	R^2	Injection gaz pour étalonnage pour déterminer la fonction		Commentaire
				Par SRM	Par AMS (mesure non étalonnée)	Par AMS (valeur étalonnée)			zéro	point d'échelle	
S01	Ligne 1 titulaire	35	5,6 - 11,0	7,74	7,61	7,63	AMSétal=AMS x 0,999 + 0,006	0,999	x	57,2 mg/m$_0^3$	
S01	Ligne 1 redondant	35	5,6 - 11,0	7,74	6,78	7,06	AMSétal=AMS x 0,948 + 0,655	0,998	x	57,2 mg/m$_0^3$	
S01	Ligne 2 titulaire	35	4,8 - 6,9	5,73	5,88	6,08	AMSétal=AMS x 1,000 - 0,787	0,999	x	57,2 mg/m$_0^3$	
S01	Ligne 2 redondant	35	4,8 - 6,9	5,73	6,49	6,25	AMSétal=AMS x 0,978 - 1,283	0,999	x	57,2 mg/m$_0^3$	
S02	Titulaire	50	4,6 - 34,4	20,2	23,1	20,4	AMSétal=AMS x 0,892 - 0,0174	0,984	x		
S02	Redondant	50	4,6 - 34,4	20,2	19,9	20,4	AMSétal=AMS x 1,018 + 0,207	0,991	x		
S05	Titulaire	50	0 - 29	7,15	6,14	7,5	AMSétal=AMS x 1,13 + 0,46	0,96			
S05	Redondant	50	0 - 29	7,15	5,54	7,52	AMSétal=AMS x 1,15 + 0,97	0,92			
S04	Titulaire	50	2,1 - 12,7	8,24	22,3	15,4	AMSétal=AMS x 1,04 - 7,56	0,91	x	57,5 mg/m$_0^3$	pente proche de 1 liée aux mesures avec gaz pour étalonnage
S04	Redondant	50	2,1 - 12,7	8,24	20,7	14,5	AMSétal=AMS x 1,05 - 7,17	0,92	x	57,5 mg/m$_0^3$	pente proche de 1 liée aux mesures avec gaz pour étalonnage
S08	Ligne 1 titulaire	50	1,0 - 33	9,99	0,88	9,99	AMSétal=AMS x 7,463 + 3,513	0,937			dopage pour 4 essais jusqu'à 20 mg/m$_0^3$; 4,4 mg/m$_0^3$ sans dopage
S08	Ligne 2 titulaire	50	1,0 - 33	10,9	5,50	10,6	AMSétal=AMS x 1,487 + 2,468	0,701			dopage pour 6 essais sur 18 jusqu'à 30 mg/m$_0^3$; 5,8 mg/m$_0^3$ sans dopage
S03	Ligne 1 titulaire	50	0,6 - 20	7,35	23,2	7,34	AMSétal=AMS x 1,286 - 18,733	0,948			dopage sur 3 essais jusqu'à 20 mg/m$_0^3$; 3,4 mg/m$_0^3$ sans dopage ; sans ces dopages, valeurs AMS < 0,8 mg/m$_0^3$
S03	Ligne 1 redondant	50	0,6 - 20	7,35	14,97	7,31	AMSétal=AMS x 1,430 - 12,895	0,976			
S06	Titulaire	50	8,6 - 27,7	16,3	13,7	15,6	AMSétal=AMS x 0,89 + 2,70	0,90	x		ajout de 3 mesures à 0
S06	Redondant	50	8,6 - 27,7	16,3	15,8	15,0	AMSétal=AMS x 0,56 + 5,24	0,51	x		ajout de 3 mesures à 0
T01	Titulaire	50	0,4 - 2,1	1,12	2,81	1,70	AMSétal=AMS x 1 - 0,7	1	x	158 mg/m$_0^3$	fonction d'étalonnage essentiellement déterminée par l'ajout de 3 mesures à 0 et de 3 mesures avec gaz pour étalonnage ; Sans ces points la pente aurait été de 0,5 mg/m$_0^3$; l'utilisation de gaz proche de la VLE aurait été plus appropriée
T01	Redondant	50	0,4 - 2,1	1,12	mêmes valeurs d'AMS - erreur de copier/coller ?				x	158 mg/m$_0^3$	
T02	Titulaire	50	0,1 - 0,6	0,30	0,98	0,70	AMSétal=AMS x 1,00 - 0,55	1,00	x	160 mg/m$_0^3$	fonction d'étalonnage essentiellement déterminée par l'ajout de 3 mesures à 0 et de 3 mesures avec gaz pour étalonnage ; Sans ces points la pente aurait été de 0,5 mg/m$_0^3$; l'utilisation de gaz proche de la VLE aurait été plus appropriée
T02	Redondant	50	0,1 - 0,6	0,30	0,17	0,24	AMSétal=AMS x 0,99 - 0,03	1,00	x	160 mg/m$_0^3$	fonction d'étalonnage essentiellement déterminée par l'ajout des mesures liées aux injections de gaz pour étalonnage ; l'utilisation de gaz proche de la VLE aurait été plus appropriée
V01	Titulaire	50	4,9 - 33	14,0	12,9	14,0	AMSétal=AMS x 1,042 + 0,175	0,933			dopage sur 3 essais jusqu'à 20 mg/m$_0^3$; 11,5 mg/m$_0^3$ sans dopage
V01	Redondant	50	4,9 - 33	14,0	15,2	14,0	AMSétal=AMS x 1,015 - 0,501	0,895			dopage sur 3 essais jusqu'à 20 mg/m$_0^3$; 11,5 mg/m$_0^3$ sans dopage
I01		40	0,5 - 3,8	1,49	3,46	non calculée	AMSétal=AMS x 0,42				
E01	Ligne 3	50	0,6 - 4,3	1,43	1,60	1,39	AMSétal=AMS x 1,00 - 0,5	-		60 mg/m$_0^3$	toutes les valeurs SRM étaient < LQ
E02	Ligne 4	50	2,4 - 45,7	6,26	8,73	6,29	AMSétal=AMS x 1,62 - 10,8	-			
E03		50	0,08 - 0,15	0,12	2,20	1,03	AMSétal=AMS x 1,06 - 1,88	0,916	x	577 mg/m$_0^3$	gaz pour étalonnage utilisé pas du tout approprié par rapport à la VLE jour pour déterminer la fonction d'étalonnage
E06		50	0,1 - 0,2	0,14	3,26	1,36	AMSétal=AMS x 1,06 - 2,96	0,975	x	577 mg/m$_0^3$	gaz pour étalonnage utilisé pas du tout approprié par rapport à la VLE jour pour déterminer la fonction d'étalonnage
E07											
E08											
U01		50	3,3 - 51	7,90	8,00	8,10	AMSétal=AMS x 1,0278 - 0,2264	0,9394	x		
U02	Ligne 1	50	4,1 - 21	15,5	15,4	16,0	AMSétal=AMS x 0,9485 + 0,87	0,5819	x		
U02	Ligne 2	50	1,9 - 21	7,28	14,10	6,27	AMSétal=AMS x 0,0854 + 4,47	0,03	x		fonction d'étalonnage fournie en conclusion différente : obtenue avec des gaz pour étalonnage
U03	Ligne 1	50	0 - 38	10,8	10,9	10,4	AMSétal=AMS x 0,7181 + 2,24	0,064	x		valeurs très disperceses même si les moyennes sont comparables, d'où le R^2 très faible - fonction d'étalonnage fournie en conclusion différente : obtenue avec des gaz pour étalonnage
U03	Ligne 2	50	0 - 10	3,81	12,9	3,80	AMSétal=AMS x -0,0384 + 3,22	0,004	x		fonction d'étalonnage fournie en conclusion différente : obtenue avec des gaz pour étalonnage
N03		40	0,1 - 10,4	1,1	1,2	1,10	AMSétal=AMS x 1,052 - 0,16	-			15 mesures AMS sur 18 notées < 0,6 mg/m$_0^3$
N04		50	0,1 - 0,8	0,46	< 1,6	0,48	AMSétal=AMS x 0,296	-			toutes les mesures AMS sont notées < 1,5 mg/m$_0^3$
N05		50	0,1 - 0,6	0,30	1,74	0,33	AMSétal=AMS x 0,191	-			toutes les mesures AMS sont notées < 1,5 mg/m$_0^3$
N06		50	0,17 - 0,6	0,36	4,48	0,38	AMSétal=AMS x 0,085	-			
G01		50	0,3 - 66	9,5	9,9	9,4	AMSétal=AMS x 1,0112 - 0,43				
G02		50	0,2 - 0,6	0,2	5,9	0,1	AMSétal=AMS x 1,0112 - 0,44			68 mg/m$_0^3$	pente proche de 1 liée à la mesure avec le gaz pour étaonnage
B01		200	1,4 - 12	5,6	6,1	5,7	AMSétal=AMS x 1,0112 - 0,45		x	516 mg/m$_0^3$	pente proche de 1 liée à la mesure avec le gaz pour étaonnage

QAL2 test reports of AMSs measuring HCl

Réf. Rapport	Point de mesure	VLE (mg/m_0^3 sec, O_2ref)	Plage de concentration mesurée par SRM hors injections gaz pour étalonnage (mg/m_0^3 sec, O_2ref)	Cmoyenne mesurée (mg/m_0^3 sec, O_2ref)			Equation de la fonction d'étalonnage	R^2	Injection gaz pour étalonnage pour déterminer la fonction		Commentaire
				Par SRM	Par AMS (mesure non étalonnée)	Par AMS (valeur étalonnée)			zéro	point d'échelle	
S01	Ligne 1 titulaire	8	0,4 - 3,7	1,25	6,91	1,35	AMSétal=AMS x 0,105 + 0,625	0,120	x	16,2 mg/m_0^3	
S01	Ligne 1 redondant	8	0,4 - 3,7	1,25	5,59	1,24	AMSétal=AMS x 0,127 + 0,580	0,117	x	16,2 mg/m_0^3	
S01	Ligne 2 titulaire	8	2,3 - 5,3	3,66	7,30	3,68	AMSétal=AMS x 0,493 + 0,047	0,686	x	16,5 mg/m_0^3	
S01	Ligne 2 redondant	8	2,3 - 5,3	3,86	8,45	3,78	AMSétal=AMS x 0,408 + 0,371	0,508	x	16,5 mg/m_0^3	
S02	Titulaire	10	1,4 - 2,8	2,27	3,01	2,23	AMSétal=AMS x 0,523 + 0,520	0,862	x		
S02	Redondant	10	1,4 - 2,8	2,27	3,54	2,27	AMSétal=AMS x 0,618 + 0,068	0,920	x		
S05	Titulaire	10	0 - 5,8	1,33	1,08	1,45	AMSétal=AMS x 1,80 - 0,41	0,46			
S05	Redondant	10	0 - 5,8	1,33	4,57	1,36	AMSétal=AMS x 0,30 - 0,03	0,60			
S04	Titulaire	10	0,1 - 1,3	0,82	1,52	0,84	AMSétal=AMS x 1,04 - 0,67	1,0	x	16,8 mg/m_0^3	
S04	Redondant	10	0,1 - 1,3	0,82	1,95	1,18	AMSétal=AMS x 1,15 - 1,25	0,99	x	16,8 mg/m_0^3	
S08	Ligne 1 titulaire	10	0,1 - 35	8,99	5,51	9,03	AMSétal=AMS x 1,601 + +0,212	0,972			dopage pour 3 essais sur 17 ; 4,8 mg/$m_0$3 sans dopage
S08	Ligne 2 titulaire	10	0,3 - 49	25,4	25,6	25,6	AMSétal=AMS x 1,168 - 2,105	0,928			dopage pour 4 essais sur 18 ; 13,8 mg/m_0^3 sans dopage
S03	Ligne 1 titulaire	10	3,5 - 18,4	7,31	5,60	7,29	AMSétal=AMS x 1,072 + 1,167	0,981			dopage sur 2 essais ; 5,3 mg/m_0^3 sans dopage
S03	Ligne 1 redondant	10	3,5 - 18,4	7,31	7,13	7,27	AMSétal=AMS x 0,957 + 0,410	0,967			dopage sur 2 essais ; 5,3 mg/m_0^3 sans dopage
S06	Titulaire	10	1,8 - 4,7	3,02	8,28	3,05	AMSétal=AMS x 0,38 - 0,17	0,79	x		
S06	Redondant	10	1,8 - 4,7	3,12	4,90	2,94	AMSétal=AMS x 0,33 + 1,11	0,42	x		
T01	Titulaire	10	5,0 - 19,6	10,4	10,6	10,0	AMSétal=AMS x 0,81 + 1,2	0,93			Ajout des mesures par injection de gaz à zéro
T01	Redondant	10	5,0 - 19,6	10,4	9,97	10,0	AMSétal=AMS x 0,85 + 1,2	0,93			Ajout des mesures par injection de gaz à zéro
T02	Titulaire	10	3,2 - 8,4	5,19	2,86	5,02	AMSétal=AMS x 1,27 + 0,21	0,92	x		
T02	Redondant	10	3,2 - 8,4	5,26	2,79	5,05	AMSétal=AMS x 1,29 + 0,24	0,87	x		
V01	Titulaire	10	2,0 - 23,0	10,2	12,8	10,2	AMSétal=AMS x 0,879 - 0,843	0,871			
V01	Redondant	10	2,0 - 17,0	9,4	11,3	9,4	AMSétal=AMS x 0,904 - 0,469	0,924			
I01		8	4,1 - 9,7	5,57	5,88	non calculée	AMSétal=AMS x 1,15 - 1,83	-			
E01	Ligne 3	10	1,5 - 3,1	2,37	3,33	2,34	AMSétal=AMS x 1,14 - 1,8	-		12 mg/m_0^3	pente proche de 1 du fait de la mesure avec le gaz pour étalonnage
E02	Ligne 4	10	0,8 - 3,2	1,70	0,01	1,61	AMSétal=AMS x 0,88 - 0,1	-		12 mg/m_0^3	valeurs AMS comprises entre -0,1 et 0,2 mg/m_0^3 ; valeurs SRM toutes > LC
E03		10	0,6 - 1,2	0,93	1,24	0,90	AMSétal=AMS x 1,04 - 0,56	0,829	x	12 mg/m_0^3	
E06		10	0,4 - 0,8	0,56	1,78	0,90	AMSétal=AMS x 1,10 - 1,55	0,871	x	12 mg/m_0^3	pente proche de 1 du fait de la mesure avec le gaz pour étalonnage
U01		10	2,4 - 18,4	7,22	7,91	7,39	AMSétal=AMS x 0,9318 + 0,164	0,9462	x		
U02	Ligne 1	10	1,3 - 4,2	2,63	4,08	2,66	AMSétal=AMS x 0,4547 + 0,52	0,501	x		fonction d'étalonnage fournie en conclusion différente : obtenue avec des gaz pour étalonnage
U02	Ligne 2	10	2,5 - 7,2	3,53	1,82	3,15	AMSétal=AMS x 0,8305 + 1,45	0,271	x		fonction d'étalonnage fournie en conclusion différente : obtenue avec des gaz pour étalonnage
U03	Ligne 1	10	8,5 - 13,8	11,6	11,3	11,5	AMSétal=AMS x 0,9953 + 0,3	0,867	x		
U03	Ligne 2	10	8,2 - 14	11,5	10,3	10,0	AMSétal=AMS x 1,0795 + 0,51	0,881	x		
N03		8	0,1 - 0,3	0,1	0,37	0,1	AMSétal=AMS x 0,250	-			toutes les mesures de la SRM sont égales à 0,1 mg/m_0^3
N04		10	0 - 0,2	0,13	< 0,33	0,13	AMSétal=AMS x 0,469	-			toutes mesures AMS notées < 0,3 mg/m_0^3 ; 12 mesures SRM sur 18 notées < 0,1 mg/m_0^3
N05		10	0,1 - 0,5	0,19	0,40	0,19	AMSétal=AMS x 0,393	-			12 mesures AMS sur 18 notées < 0,3 mg/m_0^3 ; 2 mesures SRM sur 18 notées < 0,1 mg/m_0^3
N06		10	0,10 - 0,11	0,10	0,32	0,11	AMSétal=AMS x 0,333	-			toutes mesures AMS notées < 0,3 mg/m_0^3 ; toutes mesures SRM notées < 0,1 mg/m_0^3
G01		10	0,2 - 41,8	3,5	3,4	3,5	AMSétal=AMS x 0,9216 + 0,237	-			
G02		10	0,2 - 0,9	0,3	-0,04	0,3	AMSétal=AMS x 1,068 + 0,284	-		13 mg/m_0^3	toutes mesures AMS < 0 ; fonction d'étalonnage établie avec mesures liées à l'injection de gaz de point d'échelle
B01		10	0,,7 - 3	1,6	9,3	1,6	AMSétal=AMS x 0,316 - 1,116				

QAL2 test reports of AMSs measuring HF

Réf. Rapport	Point de mesure	VLE (mg/m$_0^3$ sec, O$_2$ref)	Plage de concentration mesurée par SRM hors injections gaz pour étalonnage (mg/m$_0^3$ sec, O$_2$ref)	Cmoyenne mesurée (mg/m$_0^3$ sec, O$_2$ref)			Equation de la fonction d'étalonnage	R²	Injection gaz pour étalonnage pour déterminer la fonction		Commentaire
				Par SRM	Par AMS (mesure non étalonnée)	Par AMS (valeur étalonnée)			zéro	point d'échelle	
S01	Ligne 1 titulaire	1	0,06 - 0,10	0,09	0,09	0,02	AMSétal=AMS x 0,997 - 0,108	0,998	x	18,5 mg/m$_0^3$	qualité de la droite liée à l'injection de gaz de point d'échelle ; concentation élevée par rapport aux concentrations du site
S01	Ligne 1 redondant	1	0,06 - 0,10	0,09	0,17	-0,03	AMSétal=AMS x 0,998 - 0,221	0,999	x	18,5 mg/m$_0^3$	qualité de la droite liée à l'injection de gaz de point d'échelle alors que valeurs étalonnées sont négatives dans le bas de droite
S01	Ligne 2 titulaire	1	0,1 - 0,2	0,12	0,25	0,02	AMSétal=AMS x 0,981 - 0,242	0,998	x	18,5 mg/m$_0^3$	qualité de la droite liée à l'injection de gaz de point d'échelle , concentation en outre très élevée par rapport aux concentrations du site
S01	Ligne 2 redondant	1	0,1 - 0,2	0,12	0,26	0,05	AMSétal=AMS x 1,169 - 0,269	1,000	x	18,5 mg/m$_0^3$	qualité de la droite liée à l'injection de gaz de point d'échelle ; concentation très élevée par rapport aux concentrations du site
S05	Titulaire	1		0	0		AMSétal=AMS x 0,98 - 0,01		x	3,2 et 7,3 mg/m$_0^3$	aucune mesure SRM, ni AMS > 0 ; droite issue d'injections de gaz pour étalonnage à 0 et à 2 points d'échelle
S05	Redondant	1		0	0		AMSétal=AMS x 1,169 - 0,271		x	3,2 et 7,3 mg/m$_0^3$	aucune mesure SRM, ni AMS > 0 ; droite issue d'injections de gaz pour étalonnage à 0 et à 2 points d'échelle
S04	Titulaire	1	0 - 0,1	0,02	0		AMSétal=AMS x 1,00 + 0,02	1,00	x	17,8 mg/m$_0^3$	1 mesure sur 5 > 0 pour SRM et 0 pour AMS ; fonction étalonnage déterminée par les injections de gaz pour étalonnage
S04	Redondant	1	0 - 0,1	0,02	0,30	0,10	AMSétal=AMS x 1,00 - 0,07	1,00	x	17,8 mg/m$_0^3$	1 mesure sur 5 > 0 pour SRM et 0 pour AMS ; fonction étalonnage déterminée par injection de gaz pour étalonnage
V01	Titulaire	1	0,04 - 0,06	0,05	0,05	0,05	AMSétal=AMS x 1,000 - 0,001	1,000	x	17 mg/m$_0^3$	
V01	Redondant	1	0,04 - 0,06	0,05	0,002	0,002	AMSétal=AMS x 0,242		x	17 mg/m$_0^3$	16 valeurs de l'AMS sur 18 égales à 0 ; fonction d'étalonnage déterminée par mesures avec injection de gaz pour étalonnage à 16 mg/m03
E01	Ligne 3				-0,02		non déterminée car C trop basses				toutes les valeurs AMS sont négatives
E02	Ligne 4	1	0,30 - 0,60	0,07	0,013	0,10	AMSétal=AMS x 2,90	-			

QAL2 test reports of AMSs measuring NH$_3$

Réf. Rapport	Point de mesure	VLE (mg/m$_0^3$ sec, O$_2$ref)	Plage de concentration mesurée par SRM hors injections gaz pour étalonnage (mg/m$_0^3$ sec, O$_2$ref)	Cmoyenne mesurée (mg/m$_0^3$ sec, O$_2$ref)			Equation de la fonction d'étalonnage	R²	Injection gaz pour étalonnage pour déterminer la fonction		**Commentaire**
				Par SRM	Par AMS (mesure non étalonnée)	Par AMS (valeur étalonnée)			zéro	point d'échelle	
S01	Ligne 1 titulaire	10	4,2 - 9,1	9,89	10,62	9,94	AMSétal=AMS x 0,964 - 0,303	0,780	x	11,3 mg/m$_0^3$	
S01	Ligne 1 redondant	10	4,2 - 9,1	9,89	11,84	9,95	AMSétal=AMS x 0,873 - 0,412	0,770	x	11,3 mg/m$_0^3$	
S01	Ligne 2 titulaire	10	3,5 - 10,5	7,84	9,05	7,70	AMSétal=AMS x 0,757 + 0,989	0,709	x	11,3 mg/m$_0^3$	
S01	Ligne 2 redondant	10	3,5 - 10,5	7,84	10,75	7,75	AMSétal=AMS x 0,686 + 0,417	0,809	x	11,3 mg/m$_0^3$	16 mesures SRM sur 18 égales à 0
S02	Titulaire	30	0 - 8,9	0,69	0,77	0,68	AMSétal=AMS x 1,034 - 0,456	0,973			2 mesures 18 sont données différentes de 0 pour la SRM
S02	Redondant	30	0 - 8,9	0,69	0,98	0,69	AMSétal=AMS x 1,540 - 0,644	0,977			2 mesures 18 sont données différentes de 0 pour la SRM ; ordonnée à l'origine élevée par rapport au niveau de
S04	Titulaire	4	0 - 0,2	0,06	0,17	-0,02	AMSétal=AMS x 1,02 - 0,21	1,00	x	11,4 mg/m$_0^3$	2 mesures SRM sur 5 > 0 ; pente proche de 1 liée à l'injection de gaz pour étalonnage de point d'échelle
S04	Redondant	4	0 - 0,2	0,06	0,10	-0,10	AMSétal=AMS x 1,01 - 0,16	1,00	x	11,4 mg/m$_0^3$	2 mesures SRM sur 5 > 0 ; pente proche de 1 liée à l'injection de gaz pour étalonnage de point d'échelle
S03	Ligne 1 titulaire	30	2,2 - 3,3	3,27	3,21	2,16	AMSétal=AMS x 0,674				points très dispersés autour de la droite
V01	Titulaire	30	0,10 - 0,14	0,11	0	0,10	AMSétal=AMS x 0,996 + 0,122	1,000	x	12 mg/m$_0^3$	18 valeurs AMS égales à 0 ; fonction d'étalonnage liée à l'injection de gaz pour étalonnage de point d'échelle
V01	Redondant	30	0,10 - 0,14	0,11	0		AMSétal=AMS x 0,999 + 0,105	1,000	x	12 mg/m$_0^3$	18 valeurs AMS égales à 0 ; fonction d'étalonnage liée à l'injection de gaz pour étalonnage de point d'échelle
I01		10	2,5 - 6,1	4,5	2,46	non calculée	AMSétal=AMS x 1,21 + 1,48	-			
U02	Ligne 1	10 en l'absence de VLE	0 - 2,3	0,98 (0,84 aberrant exclus)	0,90	0,84	AMSétal=AMS x 0,6673 + 0,17	0,42	x		fonction d'étalonnage fournie en conclusion différente : obtenue avec des gaz pour étalonnage
U02	Ligne 2	10 en l'absence de VLE	0 - 1,3	0,51	0,03	1,42	AMSétal=AMS x -43,0	0,206	x		fonction d'étalonnage fournie en conclusion différente : obtenue avec des gaz pour étalonnage
U03	Ligne 1	10 en l'absence de VLE	0 - 0,9	0,07	0,20	0,04	AMSétal=AMS x 0,2202	0,019	x		6 mesures SRM sur 18 > 0 - fonction d'étalonnage fournie en conclusion différente : obtenue avec des gaz pour étalonnage
U03	Ligne 2	10 en l'absence de VLE	0 - 0,01	< 0	2,4	-	-	-			toutes valeurs SRM < 0,01 mg/m$_0^3$
N03		10	0,2 - 0,7	0,5	1,29	0,5	AMSétal=AMS x 0,410	-			
N04		10	0,05 - 0,11	0,11	0,49	0,11	AMSétal=AMS x 0,222	-			toutes mesures SRM notées < 0,1 mg/m$_0^3$
N05		10	0,10 - 0,12	0,11	0,46	0,12	AMSétal=AMS x 0,260	-			toutes mesures AMS notées < 0,4 mg/m$_0^3$; 12 mesures SRM sur 18 notées < 0,1 mg/m$_0^3$
N06		10	0,10 - 0,11	0,10	0,43	0,11	AMSétal=AMS x 0,251	-			toutes mesures AMS notées < 0,4 mg/m$_0^3$; 12 mesures SRM sur 17 notées < 0,1 mg/m$_0^3$
G01		10	0 - 14,2	1,0	1,2	1,0	AMSétal=AMS x 0,9184 - 0,086	-			11 mesures SRM sur 15 égales à 0 ; pente proche de 1 liée à une mesure de 14 mg/m$_0^3$

QAL2 test reports of AMSs measuring Hg

Réf. Rapport	VLE (mg/m_0^3 sec, O_2ref)	Plage de concentration mesurée par SRM hors injections gaz pour étalonnage (mg/m_0^3 sec, O_2ref)	Cmoyenne mesurée (mg/m_0^3 sec, O_2ref)			Equation de la fonction d'étalonnage	R²	Injection gaz pour étalonnage pour déterminer la fonction		**Commentaire**
			Par SRM	Par AMS (mesure non étalonnée)	Par AMS (valeur étalonnée)			zéro	point d'échelle	
E10	0,05	0,0016 - 0,0068	0,0027	0,0022	0,0025	AMSétal=AMS x 1,205	-			
G01	0,03	0,0002 - 0,982	0,0198	0,0198	0,0197	AMSétal=AMS x 1,009 - 0,240	-			ordonnée à l'origine élevée par rapport au niveau de concentration du site et à la VLE
G02	0,03	0	0	0		AMSétal=AMS x 1,003 + 0,202	-		0,0498	toutes mesures AMS et SRM nulles ; fonction déterminée grace à l'injection d'un gaz pour étalonnage mais ordonnée à l'origine élevée par rapport à la VLE

ANNEX C

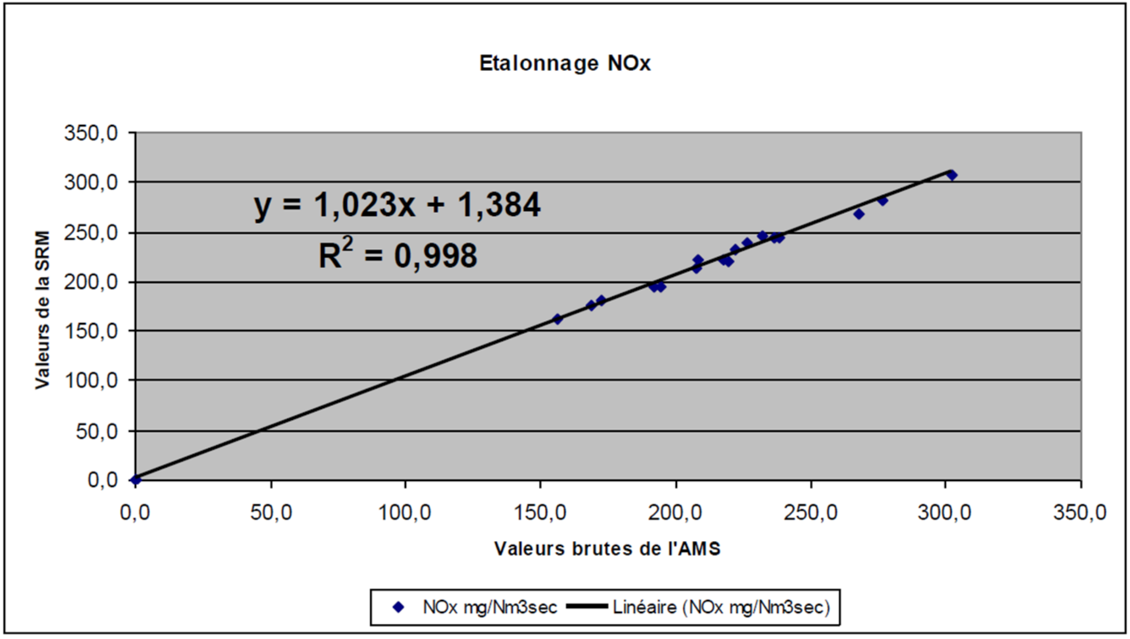
QAL2 test reports Analysis:
Graph representation of measurements [AMS;SRM] and calibration function

Selection of graphs showing the difficulties which can be encountered with calibration tests found valid according to the relevant standards criteria when the emission concentration levels are significantly lower than the ones given in Annex VI of the Industrial Emission Directive

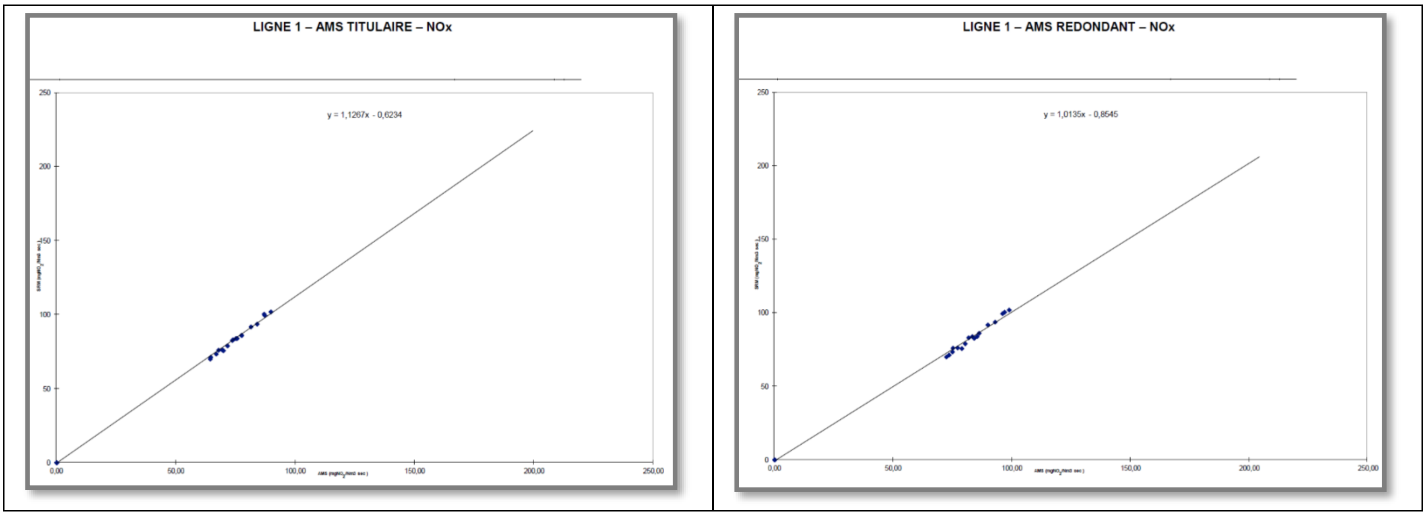
NO_x

The calibration functions are near equation y = x, with a determination factor near 1. These functions' "quality" is among others linked to measures covering a wide range: 0-320 mg/Nm³ for the first plant, 0-100 mg/Nm³ for the second one.

Example 1 (Plant S03 – line 1)



Example 2 (Plant S01 – line 1 - duty and standby)

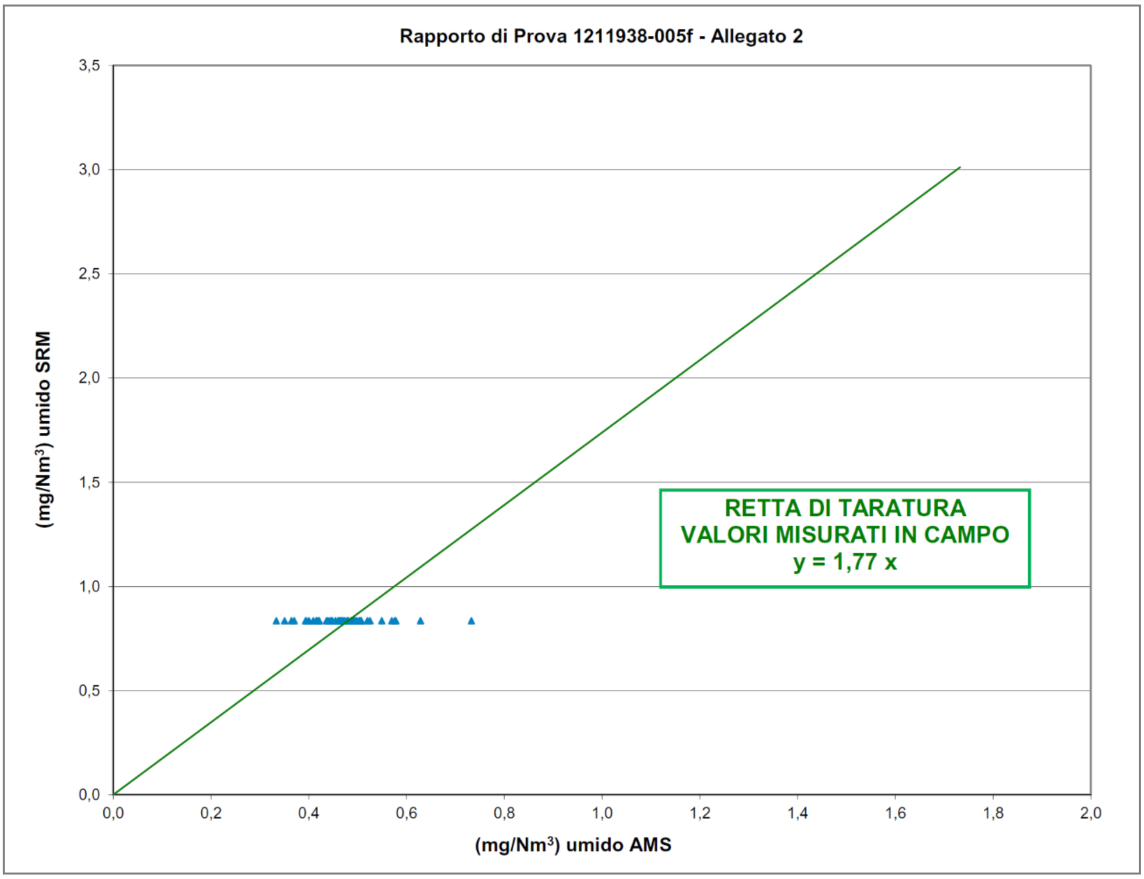


TOC

Example 1: The SRM's measurement are constant. For the AMS as for the SRM, the concentrations likely are near, or below, their LoQs.

It is thanks to a zero measurement that the slope is not zero. However, with a 1.77 slope, there can be doubts on the measurements that would be given at the current Daily ELV of 10 mg/Nm³, applying this function, if a malfunction of the installation or of the Flue Gas Cleaning led to an emissions peak. Doubts can also be expressed on the possibility to check the AMS's compliance if the ELV was lowered to the level of the measured values.

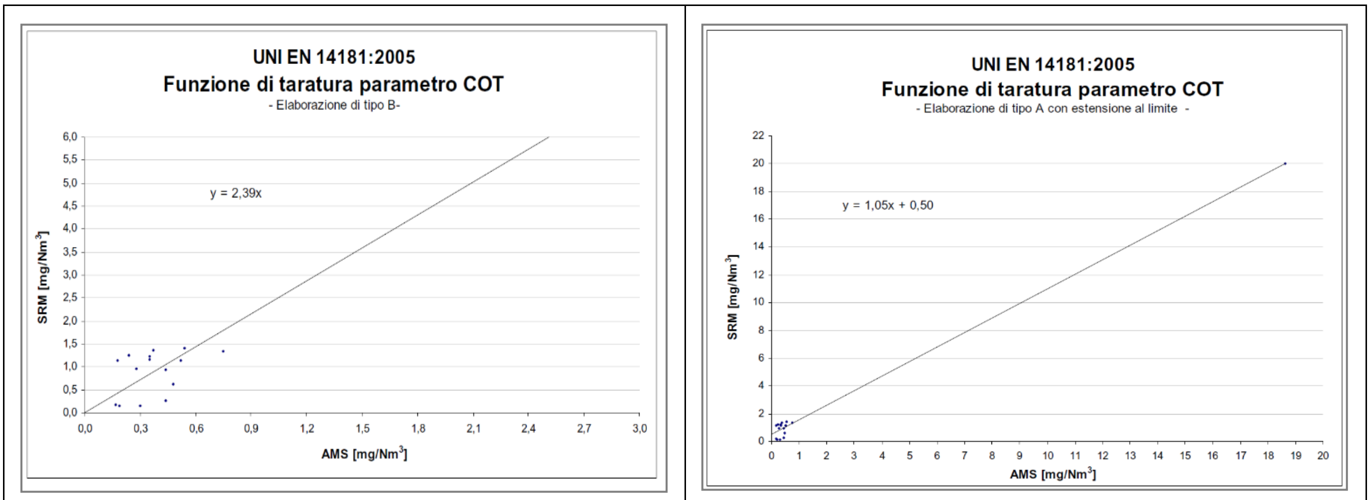
Example 1 (Plant I01 – line 1)



Example 2: The narrow concentration range covered during the measurements also is at a relatively low concentration level (< 1.5 mg/Nm³), leads to a calibration function with a slope very different from 1. This is likely linked to measurements close to the LoQ and hence associated to high uncertainties.

Adding measurements coming from span gas injection to about 20 mg/Nm³ "improves" the calibration function, whose slope is then close to 1. At the current Daily ELV, the AMS will be able to give consistent data, but at lower concentration levels, this calibration function will lead to a discrepancy between the SRM and the AMS and to the impossibility of checking compliance with the Daily ELV if it is lowered to the level of the values measured during the QAL2 control.

Example 2 (Plant I03 – line 4)



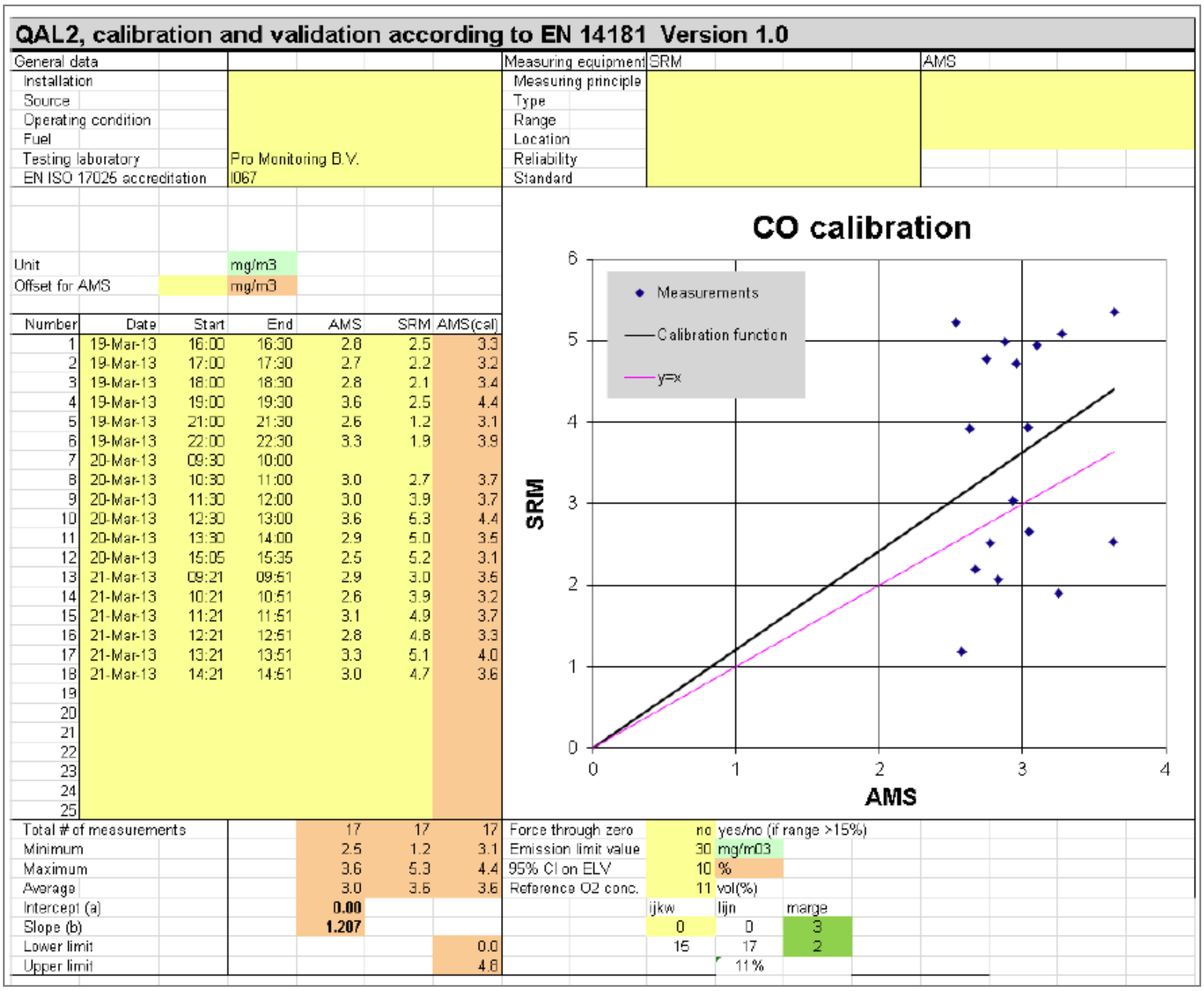
Without Span Gas

With Span Gas

CO

The narrow concentration range covered during the measurements, from 1 to 5 mg/Nm³, also is at a relatively low concentration level, leading to a cloud of points. It is thanks to a zero measurement that the slope is at 1.2. The spread of the values obtained at the concentration level measured during the QAL2 control raises doubts on the values that would be given by the AMS by applying this function at that level. Lowering the Daily ELV to these concentration levels would raise serious doubts on the compliance/incompliance declaration.

Example 1 (Plant N03)



QAL2, calibration and validation according to EN 14181 Version 1.0

General data		Measuring equipment	SRM	AMS
Installation		Measuring principle		
Source		Type		
Operating condition		Range		
Fuel		Location		
Testing laboratory	Pro Monitoring B.V.	Reliability		
EN ISO 17025 accreditation	l067	Standard		

Unit		mg/m3
Offset for AMS		mg/m3

Number	Date	Start	End	AMS	SRM	AMS(cal)
1	19-Mar-13	16:00	16:30	2.8	2.5	3.3
2	19-Mar-13	17:00	17:30	2.7	2.2	3.2
3	19-Mar-13	18:00	18:30	2.8	2.1	3.4
4	19-Mar-13	19:00	19:30	3.6	2.5	4.4
5	19-Mar-13	21:00	21:30	2.6	1.2	3.1
6	19-Mar-13	22:00	22:30	3.3	1.9	3.9
7	20-Mar-13	09:30	10:00			
8	20-Mar-13	10:30	11:00	3.0	2.7	3.7
9	20-Mar-13	11:30	12:00	3.0	3.9	3.7
10	20-Mar-13	12:30	13:00	3.6	5.3	4.4
11	20-Mar-13	13:30	14:00	2.9	5.0	3.5
12	20-Mar-13	15:05	15:35	2.5	5.2	3.1
13	21-Mar-13	09:21	09:51	2.9	3.0	3.5
14	21-Mar-13	10:21	10:51	2.6	3.9	3.2
15	21-Mar-13	11:21	11:51	3.1	4.9	3.7
16	21-Mar-13	12:21	12:51	2.8	4.8	3.3
17	21-Mar-13	13:21	13:51	3.3	5.1	4.0
18	21-Mar-13	14:21	14:51	3.0	4.7	3.6
19						
20						
21						
22						
23						
24						
25						
Total # of measurements				17	17	17
Minimum				2.5	1.2	3.1
Maximum				3.6	5.3	4.4
Average				3.0	3.6	3.6
Intercept (a)				**0.00**		
Slope (b)				**1.207**		
Lower limit						0.0
Upper limit						4.8

Force through zero	no	yes/no (if range >15%)		
Emission limit value	30	mg/m03		
95% CI on ELV	10	%		
Reference O2 conc.	11	vol(%)		
	ijkw	lijn	marge	
	0	0	3	
	15	17	2	
		11%		

Dust

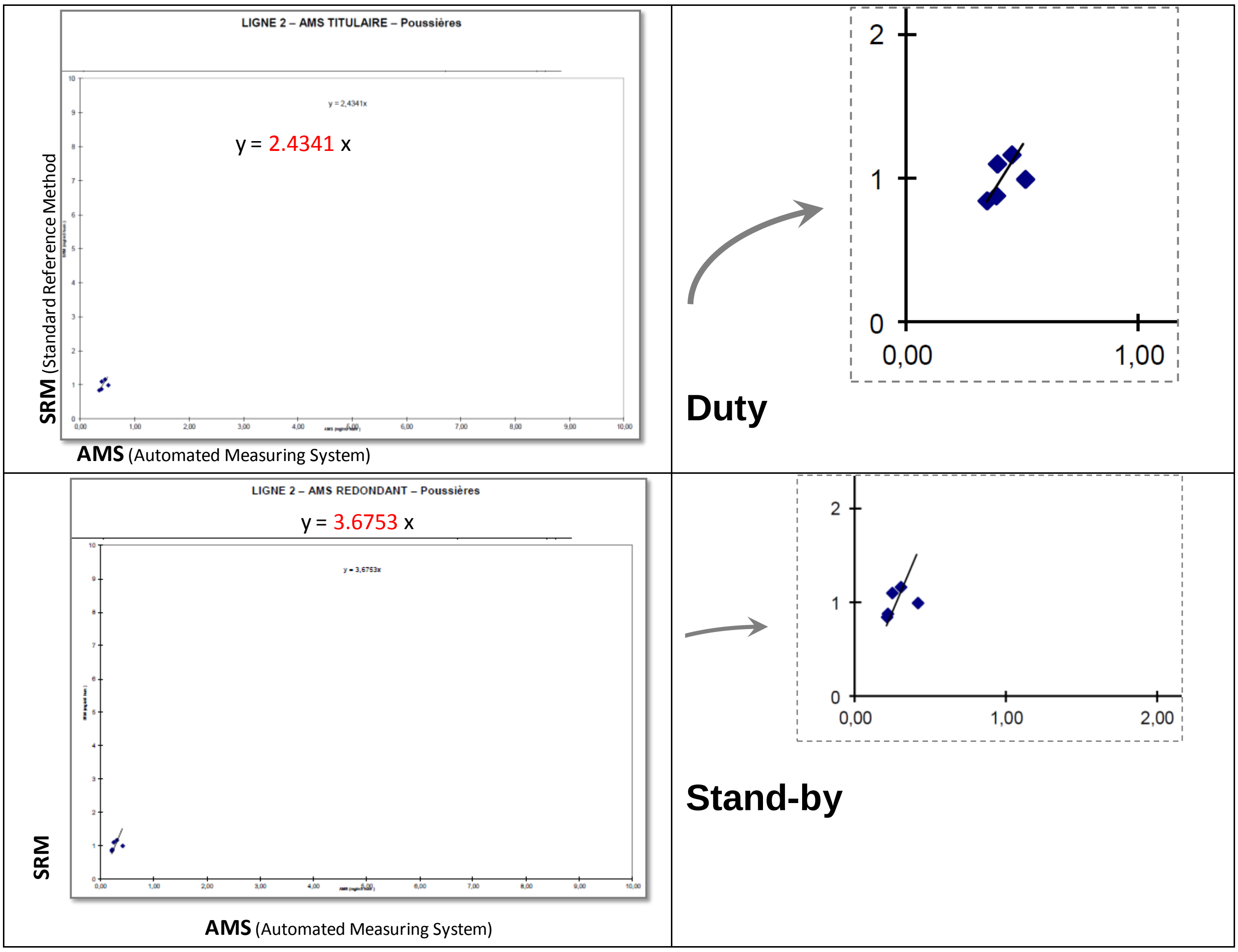
Examples 1 to 5: The narrow concentration range covered during the measurements, also is at a relatively low concentration level, leading to calibration functions whose slopes can be very different than 1, and even negative in some cases.

This can be linked to measurements close to (sometimes under) the LoQ and hence associated to high uncertainties.

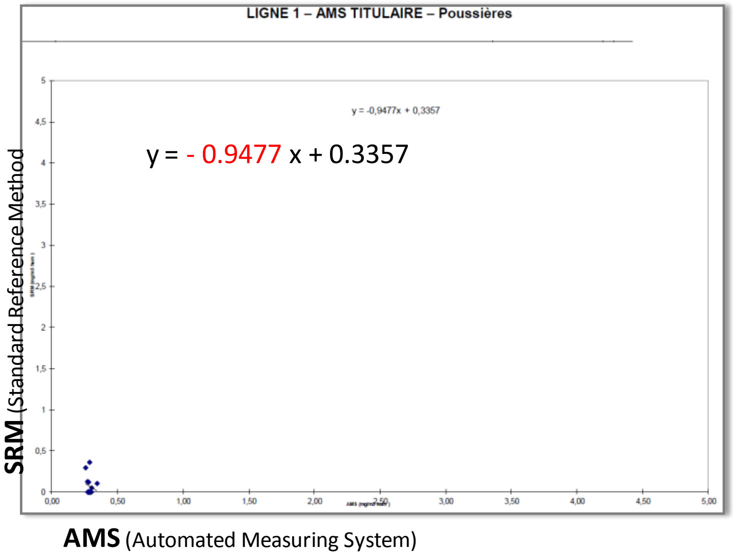
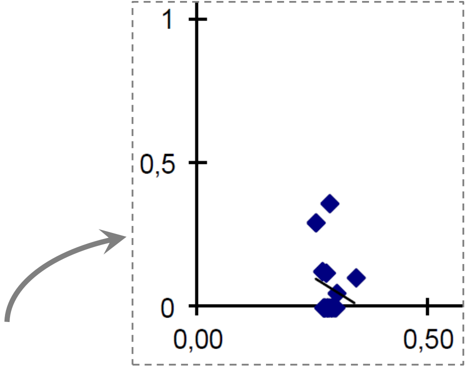
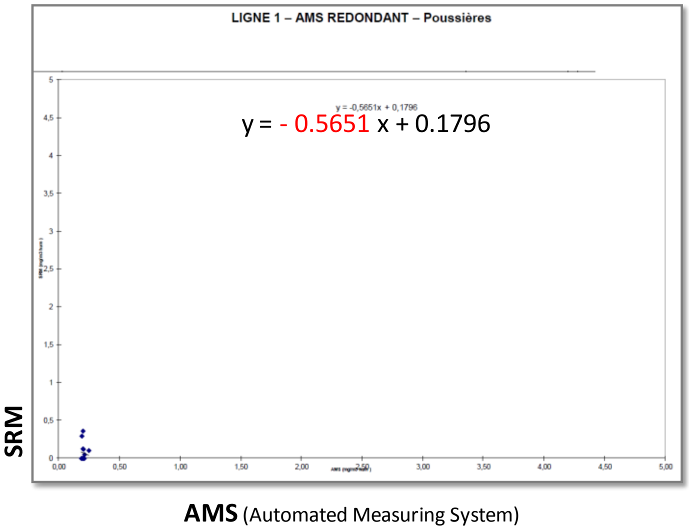
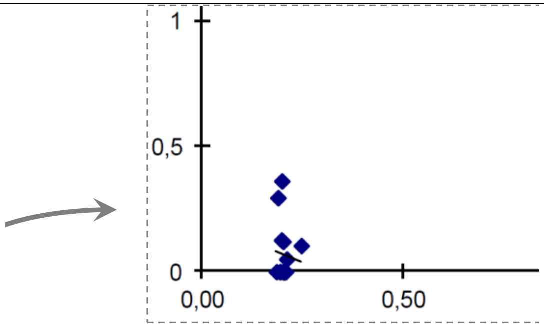
Also, the lack of reference materials prevents adding calibration points that could “increase” the calibration function.

Although the graphical representation of the SRM and AMS comparison shows results anomalies, the variability test is still fulfilled because although the concentrations are low with respect to the ELV, the differences between SRM and AMS are also small in absolute values.

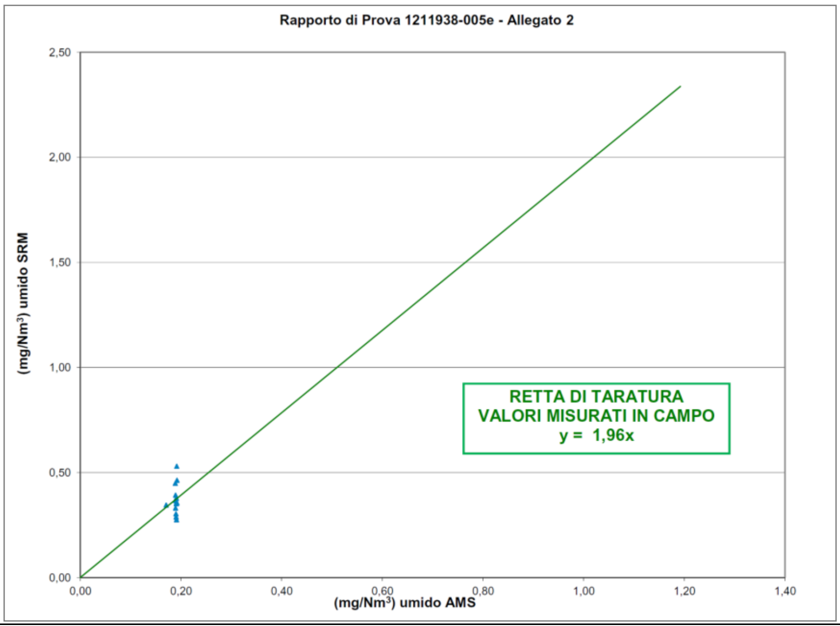
Example 1 (Plant S02 – line 2 – duty and standby)



Example 2 (Plant S01 – line 1 – duty and standby)

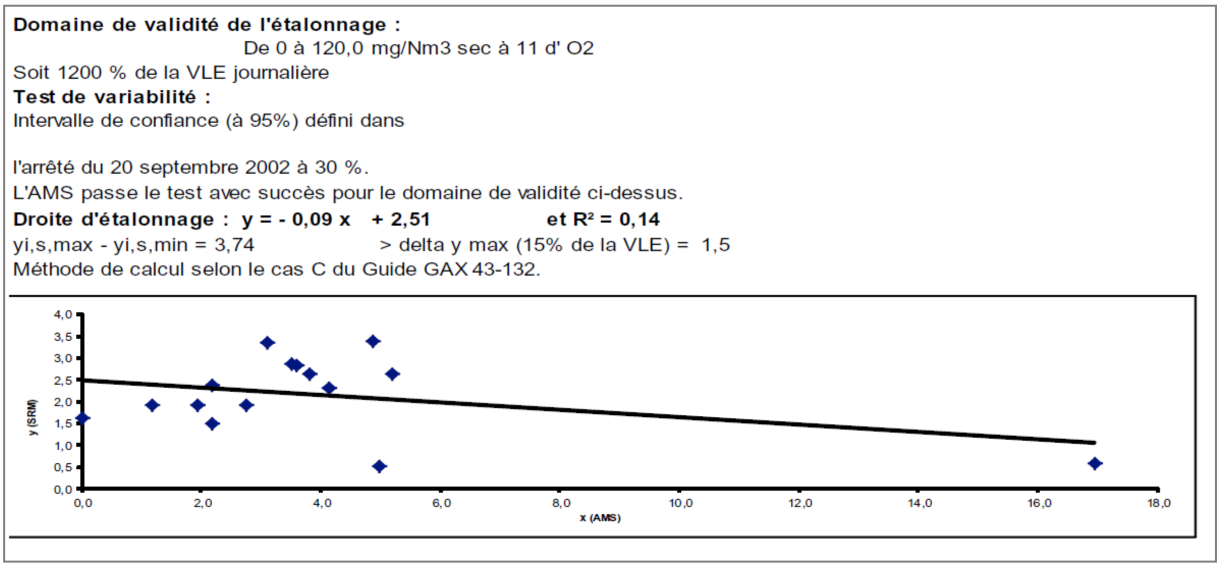
	 **Duty**
	 **Stand-by**

Example 3 (Plant I01 – line 1)

	The AMS's measurements are constant. For the AMS, as for the SRM, the concentrations likely are close to, or even below, their LoQ. It is thanks to a zero measurement that a function can be obtained.

Example 4 (Plant S04 – line 1 standby)

The AMS fulfilled the variability test but the slope is negative, which would lead, when applying the calibration function, to corrected values increasingly lower as the AMS reads a higher value, which is not consistent.



Domaine de validité de l'étalonnage :
De 0 à 120,0 mg/Nm3 sec à 11 d' O2
Soit 1200 % de la VLE journalière
Test de variabilité :
Intervalle de confiance (à 95%) défini dans

l'arrêté du 20 septembre 2002 à 30 %.
L'AMS passe le test avec succès pour le domaine de validité ci-dessus.
Droite d'étalonnage : y = - 0,09 x + 2,51 et R² = 0,14
yi,s,max - yi,s,min = 3,74 > delta y max (15% de la VLE) = 1,5
Méthode de calcul selon le cas C du Guide GAX 43-132.

Example 5 (Plant G02 – line 4 duty)

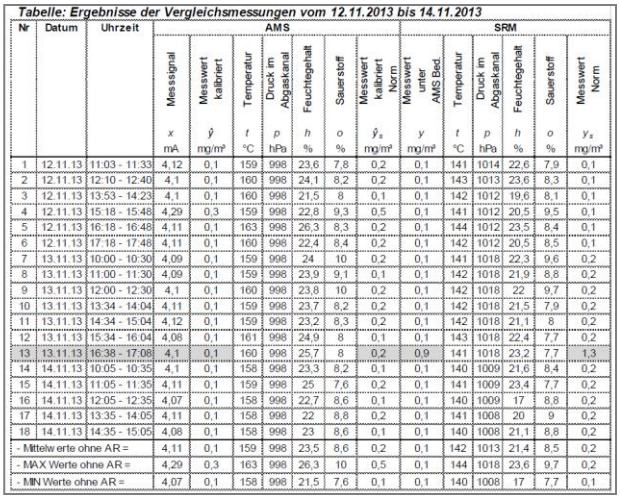
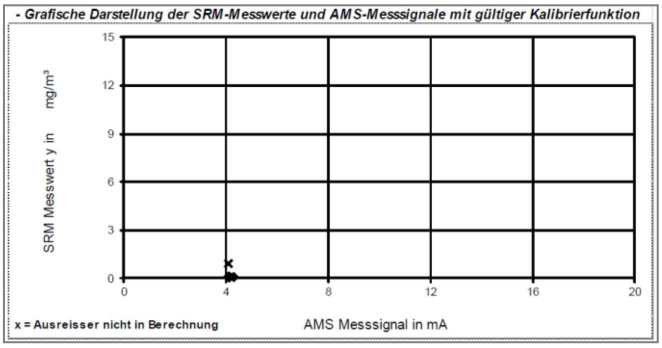


Tabelle: Ergebnisse der Vergleichsmessungen vom 12.11.2013 bis 14.11.2013

Nr	Datum	Uhrzeit	AMS							SRM					
			Messsignal x mA	Messwert kalibriert $\hat{y}$ mg/m^3	Temperatur t °C	Druck im Abgaskanal p hPa	Feuchtegehalt h %	Sauerstoff o %	Messwert kalibriert Norm $\hat{y}_s$ mg/m^3	Messwert unter AMS Bed. y mg/m^3	Temperatur t °C	Druck im Abgaskanal p hPa	Feuchtegehalt h %	Sauerstoff o %	Messwert Norm y_s mg/m^3
1	12.11.13	11:03 - 11:33	4,12	0,1	159	998	23,6	7,8	0,2	0,1	141	1014	22,6	7,9	0,1
2	12.11.13	12:10 - 12:40	4,1	0,1	160	998	24,1	8,2	0,2	0,1	143	1013	23,6	8,3	0,1
3	12.11.13	13:53 - 14:23	4,1	0,1	160	998	21,5	8	0,1	0,1	142	1012	19,6	8,1	0,1
4	12.11.13	15:18 - 15:48	4,29	0,3	159	998	22,8	9,3	0,5	0,1	141	1012	20,5	9,5	0,1
5	12.11.13	16:18 - 16:48	4,11	0,1	163	998	26,3	8,3	0,2	0,1	144	1012	23,5	8,4	0,1
6	12.11.13	17:18 - 17:48	4,11	0,1	160	998	22,4	8,4	0,2	0,1	142	1012	20,5	8,5	0,1
7	13.11.13	10:00 - 10:30	4,09	0,1	159	998	24	10	0,2	0,1	141	1018	22,3	9,6	0,2
8	13.11.13	11:00 - 11:30	4,09	0,1	159	998	23,9	9,1	0,1	0,1	142	1018	21,9	8,8	0,2
9	13.11.13	12:00 - 12:30	4,1	0,1	160	998	23,8	10	0,2	0,1	142	1018	22	9,7	0,2
10	13.11.13	13:34 - 14:04	4,11	0,1	159	998	23,7	8,2	0,2	0,1	142	1018	21,5	7,9	0,2
11	13.11.13	14:34 - 15:04	4,12	0,1	159	998	23,2	8,3	0,2	0,1	142	1018	21,1	8	0,2
12	13.11.13	15:34 - 16:04	4,08	0,1	161	998	24,9	8	0,1	0,1	143	1018	22,4	7,7	0,2
13	13.11.13	16:38 - 17:08	4,1	0,1	160	998	25,7	8	0,2	0,9	141	1018	23,2	7,7	1,3
14	14.11.13	10:05 - 10:35	4,1	0,1	158	998	23,3	8,2	0,1	0,1	140	1009	21,6	8,4	0,2
15	14.11.13	11:05 - 11:35	4,11	0,1	159	998	25	7,6	0,2	0,1	141	1009	23,4	7,7	0,2
16	14.11.13	12:05 - 12:35	4,07	0,1	158	998	22,7	8,6	0,1	0,1	140	1009	17	8,8	0,2
17	14.11.13	13:35 - 14:05	4,11	0,1	158	998	22	8,8	0,2	0,1	141	1008	20	9	0,2
18	14.11.13	14:35 - 15:05	4,08	0,1	158	998	23	8,6	0,1	0,1	140	1008	21,1	8,8	0,2
- Mittelwerte ohne AR =			4,11	0,1	159	998	23,5	8,6	0,2	0,1	142	1013	21,4	8,5	0,2
- MAX Werte ohne AR =			4,29	0,3	163	998	26,3	10	0,5	0,1	144	1018	23,6	9,7	0,2
- MIN Werte ohne AR =			4,07	0,1	158	998	21,5	7,6	0,1	0,1	140	1008	17	7,7	0,1



y = 0.91 x -3.64 (x in mA)

therefore y = 1.213 x (x in µg/Nm^3)

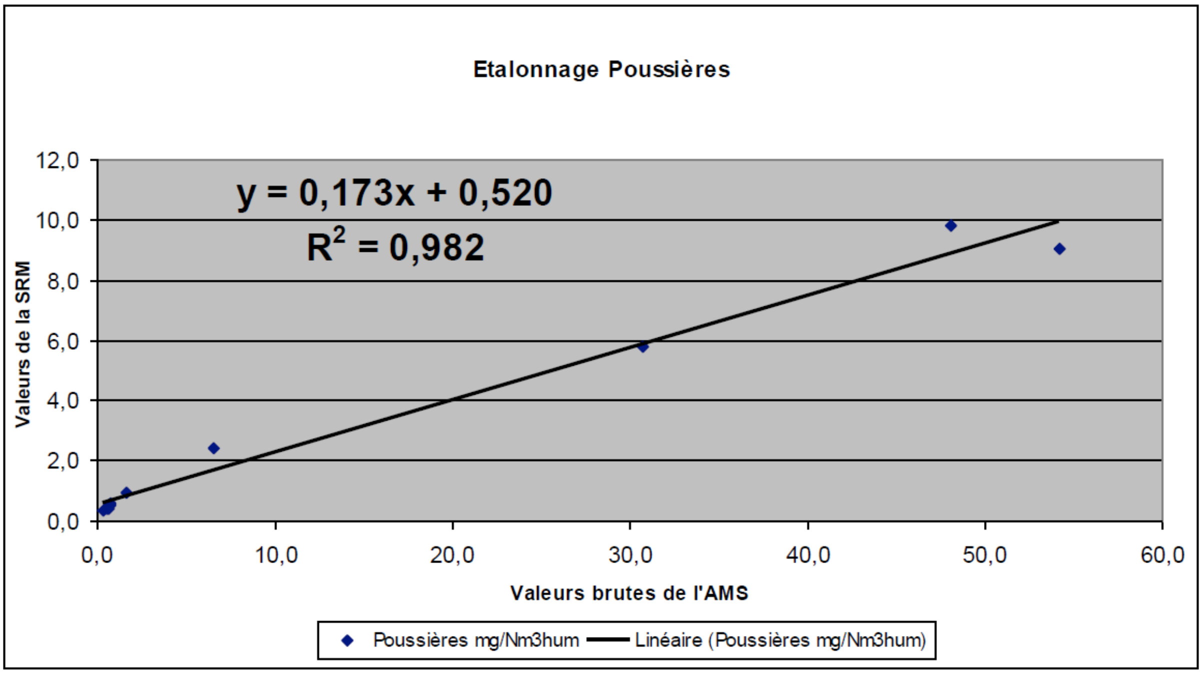
All the SRM’s values are equal to 0.1 mg/Nm³, likely because they are near, or below, the LoQ.

The function was determined by with a zero measurement.

Example 6: The concentration range covered during measurement is wider, giving a calibration function that could seem satisfactory: $R^2 = 0.9825$, but the slope is very different from 1: 0.173, and the intercept point is 0.5 mg/Nm³, which is high for levels under 2 mg/Nm³.

The 3 highest measurements likely were obtained by enriching (spiking) or by changing the installation's operating conditions. The differences between SRM and AMS can be caused by the used particulates, resulting from these changed conditions, and that would have different physical characteristics than those in the duct (the optical AMSs are very sensitive to particulates' physical characteristics), or because a lack of a reference material, the AMS could not be tuned, explaining the measurement bias.

Example 6 (Plant S03 – line 2)

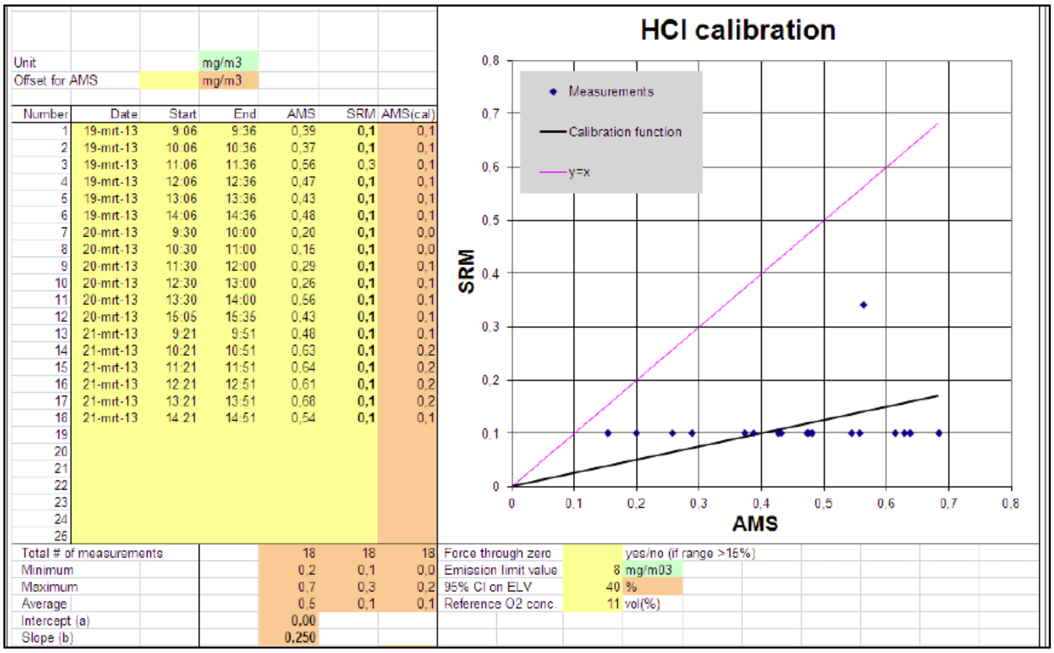


HCl

Example 1: The measured concentrations are low: < 1 mg/Nm³. The SRM's measurements are constant. Both for the AMS and the SRM, the concentrations likely are close to, or below, their LoQs.

It is thanks to a zero measurement that a non-nil slope can be obtained. This slope nevertheless is 0.25, hence very far from 1.

Example 1 (Plant N03)



Unit		mg/m3	
Offset for AMS		mg/m3	

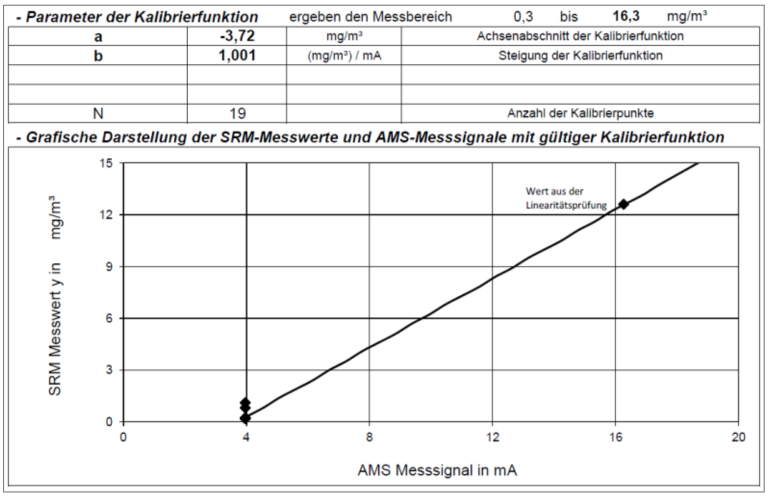
Number	Date	Start	End	AMS	SRM	AMS(cal)
1	19-mrt-13	9:06	9:36	0,39	0,1	0,1
2	19-mrt-13	10:06	10:36	0,37	0,1	0,1
3	19-mrt-13	11:06	11:36	0,56	0,3	0,1
4	19-mrt-13	12:06	12:36	0,47	0,1	0,1
5	19-mrt-13	13:06	13:36	0,43	0,1	0,1
6	19-mrt-13	14:06	14:36	0,48	0,1	0,1
7	20-mrt-13	9:30	10:00	0,20	0,1	0,0
8	20-mrt-13	10:30	11:00	0,15	0,1	0,0
9	20-mrt-13	11:30	12:00	0,29	0,1	0,1
10	20-mrt-13	12:30	13:00	0,26	0,1	0,1
11	20-mrt-13	13:30	14:00	0,56	0,1	0,1
12	20-mrt-13	15:05	15:35	0,43	0,1	0,1
13	21-mrt-13	9:21	9:51	0,48	0,1	0,1
14	21-mrt-13	10:21	10:51	0,63	0,1	0,2
15	21-mrt-13	11:21	11:51	0,64	0,1	0,2
16	21-mrt-13	12:21	12:51	0,61	0,1	0,2
17	21-mrt-13	13:21	13:51	0,68	0,1	0,2
18	21-mrt-13	14:21	14:51	0,54	0,1	0,1
19						
20						
21						
22						
23						
24						
25						
Total # of measurements				18	18	18
Minimum				0,2	0,1	0,0
Maximum				0,7	0,3	0,2
Average				0,5	0,1	0,1
Intercept (a)				0,00		
Slope (b)				0,250		

Force through zero		yes/no (if range >15%)
Emission limit value	8	mg/m03
95% CI on ELV	40	%
Reference O2 conc.	11	vol(%)

Example 2: The concentrations are low (SRM measurements from 0.2 to 1.1 mg/Nm³), the varition range is limited and the AMS gave constant measures of 3.96mA, or -0.04 mg/Nm³, which is a negative value. Adding a span gas measurement value for calibration at 13 mg/Nm³ gives a calibration function with a correct slope, but the AMS and SRM correlation is difficult to assess because the concentrations likely are close to, or below, both measurement instruments' LoQs.

Example 2 (Plant G02)

y = 1.001 x -3.72 (x in mA) - or y = 1.068 x – 0.284 (x in µg/Nm^3)



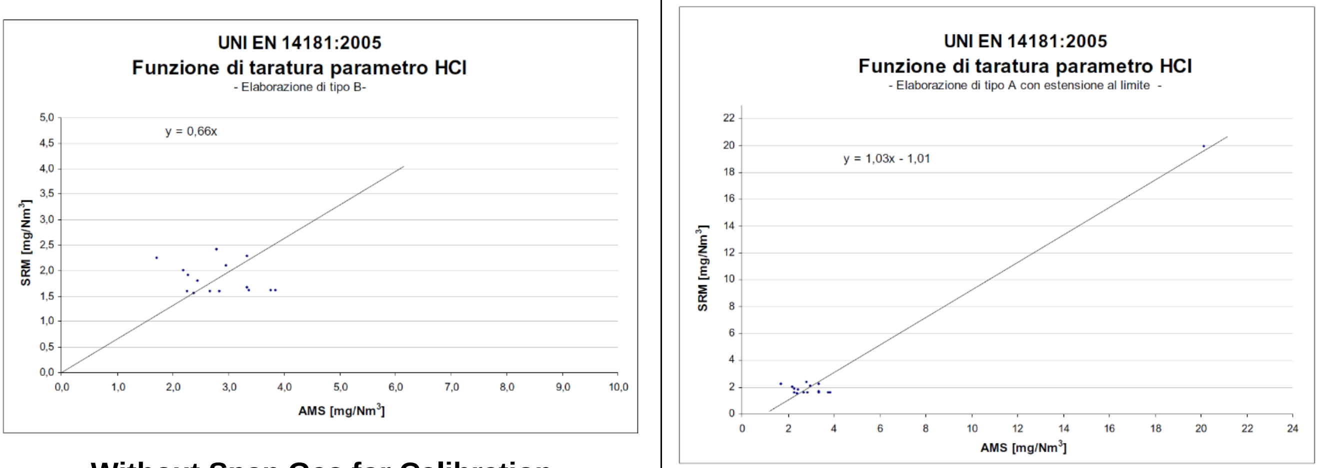
- Parameter der Kalibrierfunktion ergeben den Messbereich 0,3 bis **16,3** mg/m³

a	**-3,72**	mg/m³	Achsenabschnitt der Kalibrierfunktion
b	**1,001**	(mg/m³) / mA	Steigung der Kalibrierfunktion
N	19		Anzahl der Kalibrierpunkte

- Grafische Darstellung der SRM-Messwerte und AMS-Messsignale mit gültiger Kalibrierfunktion

Example 3: As for example 2, adding measurements from span gaz values for calibration leads to a function with a slope near 1 (instead of 0.66), but with an intercept of -1, or relatively high given the concentration level.

Example 3 (Plant I03 – line 4)

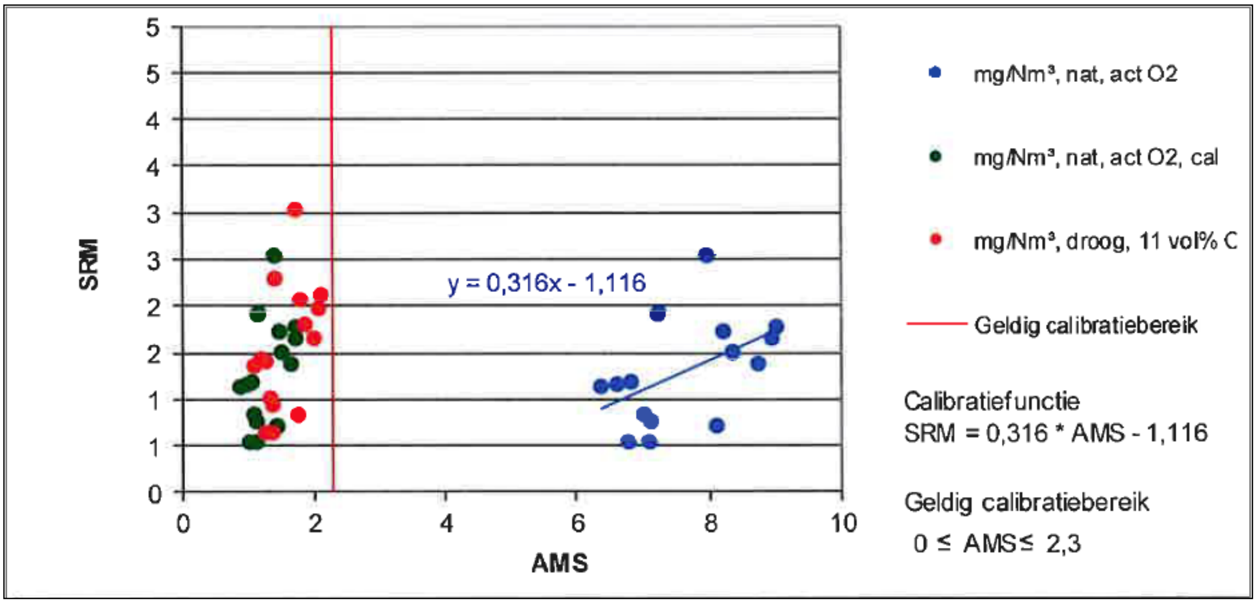


Without Span Gas for Calibration

With Span Gas for Calibration

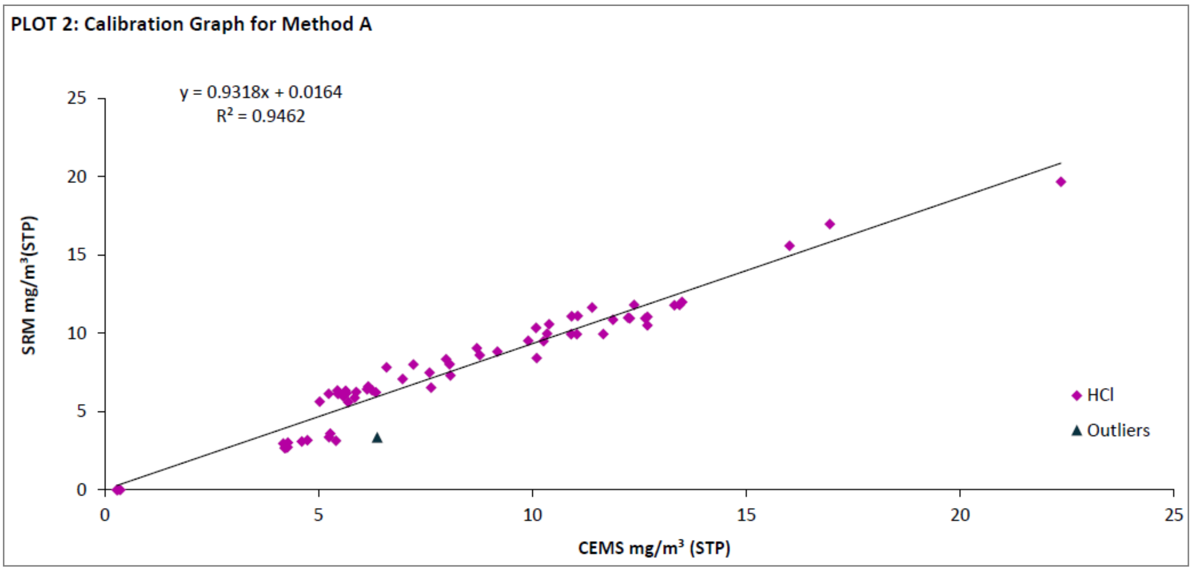
Example 4: The concentration range covered during the test is limited: the SRM measurements are between 0.5 and 2.5 mg/Nm³. The AMS measures the highest values, from 6 to 9 mg/Nm³. This yields a calibration function whose slope is very different from 1: 0.316, and whose intercept is high given the concentration. Also, the points' dispersion shows a weak correlation between SRM and AMS.

Example 4 (Plant B01)



Example 5: The concentration range covered during the test is larget and at a higher concentration level: 5 to 22 mg/Nm³, giving a satisfactory calibration function.

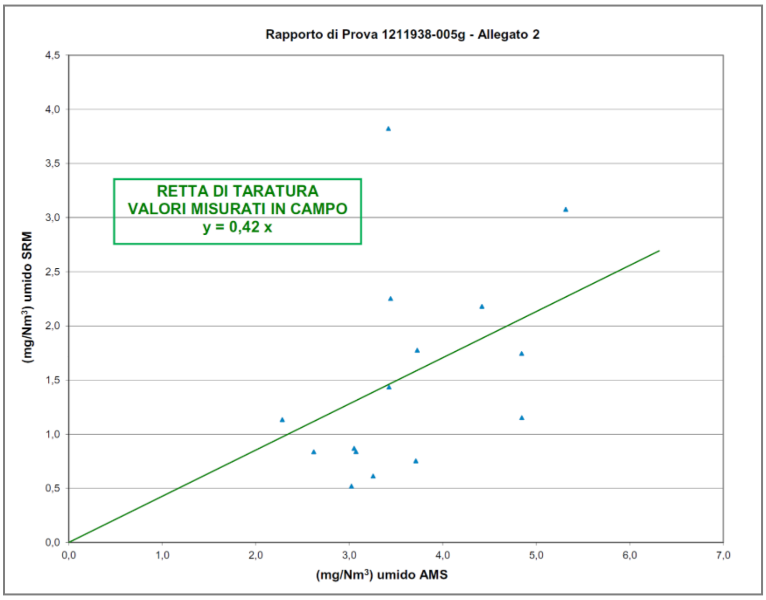
Example 5 (Plant U01 – line 1)



SO_2

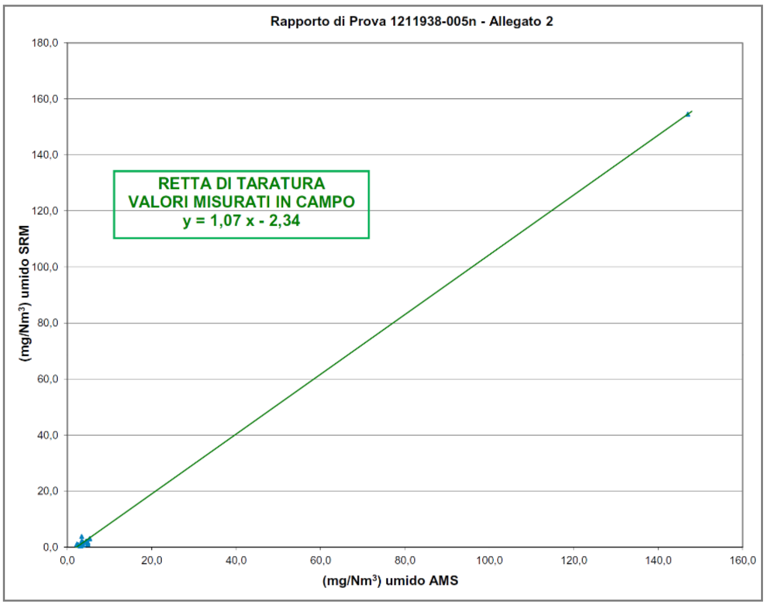
Example 1: The measured concentrations are low: < 4 mg/Nm³, and the covered concentration range is limited. The resulting function has a slope very different from 1, although the zero measurement likely "improves" the function.

Example 1 (Plant I01 – line 1 - duty)



Example 2: The obtained slope of 1 is linked to the inclusion of span gas injection measurements for calibration at 150 mg/Nm³ (a very high concentration level compared to the Daily ELV which is 40 mg/Nm³). It could appear satisfactory but the intercept of -2.3 shows that for the site's concentration level, the SRM and AMS measurements are offset.

Example 2 (Plant I01 – line 1 – standby)

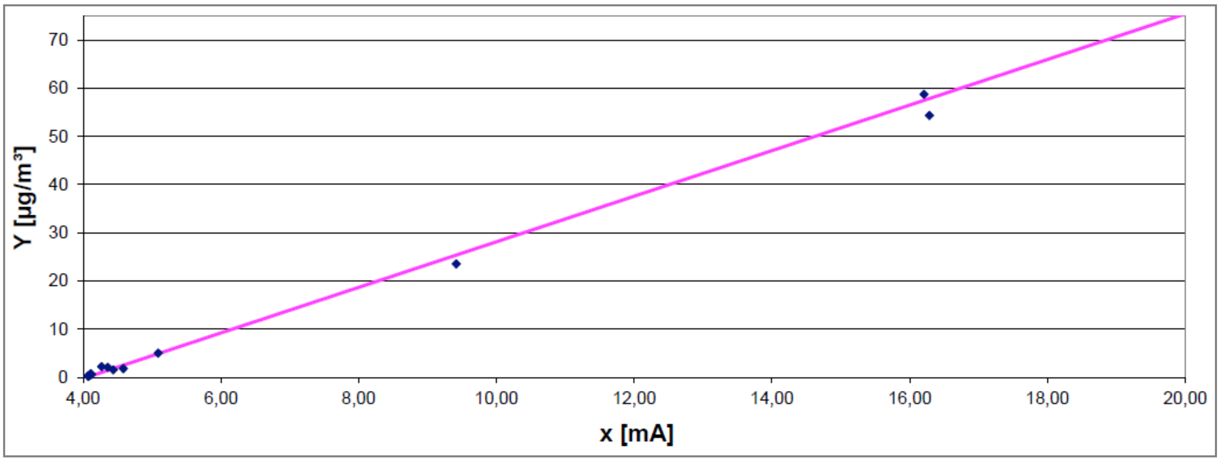


Hg

Example 1: The concentration range covered is relatively wide: 0-40 µg/Nm³, giving a satisfactory function with a slope very near 1. For low concentration levels, < 0.5 µg/Nm³, the SRM and AMS measurements show a difference.

Example 1 (Plant G01 – line 2 - duty)

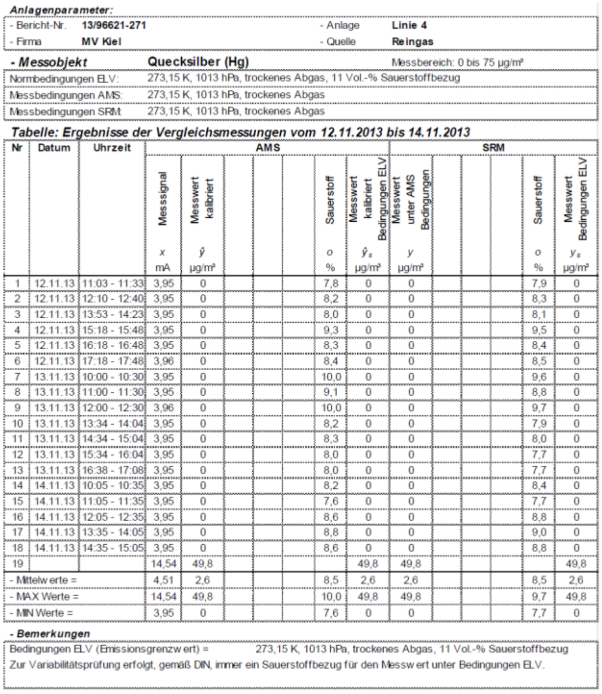
y = 4.73 x -19.15 (x in mA) or y = 1.009 x – 0.240 (x in µg/Nm^3)



Example 2: All the AMS and SRM measurements are zero, likely because they are under their respective LoQs.

It is through span gas injection that the calibration function is calculated. However, this raises the question on what calibrated values will be given for concentrations above the AMS's LoQ.

Example 2 (Plant G02 – line 4 - duty)



Anlagenparameter:

- Bericht-Nr.	**13/96621-271**	- Anlage	**Linie 4**
- Firma	**MV Kiel**	- Quelle	**Reingas**

- Messobjekt **Quecksilber (Hg)** Messbereich: 0 bis 75 µg/m³

Normbedingungen ELV:	273,15 K, 1013 hPa, trockenes Abgas, 11 Vol.-% Sauerstoffbezug
Messbedingungen AMS:	273,15 K, 1013 hPa, trockenes Abgas
Messbedingungen SRM:	273,15 K, 1013 hPa, trockenes Abgas

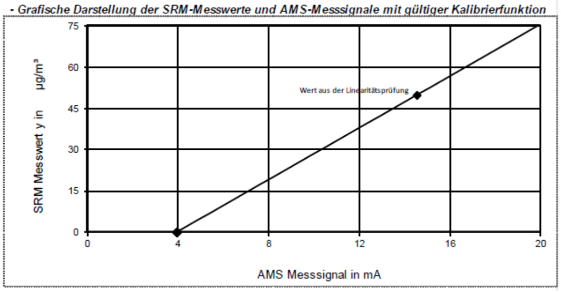
Tabelle: Ergebnisse der Vergleichsmessungen vom 12.11.2013 bis 14.11.2013

Nr	Datum	Uhrzeit	AMS							SRM					
			Messsignal x mA	Messwert kalibriert $\hat{y}$ µg/m³				Sauerstoff o %	Messwert kalibriert Bedingungen ELV $\hat{y}_s$ µg/m³	Messwert unter AMS Bedingungen y µg/m³				Sauerstoff o %	Messwert Bedingungen ELV y_s µg/m³
1	12.11.13	11:03 - 11:33	3,95	0				7,8	0	0				7,9	0
2	12.11.13	12:10 - 12:40	3,95	0				8,2	0	0				8,3	0
3	12.11.13	13:53 - 14:23	3,95	0				8,0	0	0				8,1	0
4	12.11.13	15:18 - 15:48	3,95	0				9,3	0	0				9,5	0
5	12.11.13	16:18 - 16:48	3,95	0				8,3	0	0				8,4	0
6	12.11.13	17:18 - 17:48	3,96	0				8,4	0	0				8,5	0
7	13.11.13	10:00 - 10:30	3,95	0				10,0	0	0				9,6	0
8	13.11.13	11:00 - 11:30	3,95	0				9,1	0	0				8,8	0
9	13.11.13	12:00 - 12:30	3,96	0				10,0	0	0				9,7	0
10	13.11.13	13:34 - 14:04	3,95	0				8,2	0	0				7,9	0
11	13.11.13	14:34 - 15:04	3,95	0				8,3	0	0				8,0	0
12	13.11.13	15:34 - 16:04	3,95	0				8,0	0	0				7,7	0
13	13.11.13	16:38 - 17:08	3,95	0				8,0	0	0				7,7	0
14	14.11.13	10:05 - 10:35	3,95	0				8,2	0	0				8,4	0
15	14.11.13	11:05 - 11:35	3,95	0				7,6	0	0				7,7	0
16	14.11.13	12:05 - 12:35	3,95	0				8,6	0	0				8,8	0
17	14.11.13	13:35 - 14:05	3,95	0				8,8	0	0				9,0	0
18	14.11.13	14:35 - 15:05	3,95	0				8,6	0	0				8,8	0
19			14,54	49,8					49,8	49,8					49,8
- Mittelwerte =			4,51	2,6				8,5	2,6	2,6				8,5	2,6
- MAX Werte =			14,54	49,8				10,0	49,8	49,8				9,7	49,8
- MIN Werte =			3,95	0				7,6	0	0				7,7	0

- Bemerkungen

Bedingungen ELV (Emissionsgrenzwert) = 273,15 K, 1013 hPa, trockenes Abgas, 11 Vol.-% Sauerstoffbezug

Zur Variabilitätsprüfung erfolgt, gemäß DIN, immer ein Sauerstoffbezug für den Messwert unter Bedingungen ELV.



y = 4.703 x -18.61 (x in mA)

or y = 1.003 x – 0.202 (x in µg/Nm^3)

ANNEX D

Calculation of the uncertainty associated with a concentration expressed on dry gas and at an oxygen reference concentration

Calculation of the uncertainty associated with a concentration expressed on dry gas and at an oxygen reference concentration

Uncertainty associated with a concentration expressed on dry gas

The concentration of a measured component expressed for dry gas is calculated according to Formula (D.1):

$$C_{\mathrm{dry}} = C_{\mathrm{wet}} \frac{100\%}{100\% - h_{\mathrm{m}}} \qquad \text{(D.1)}$$

where

C_{dry} is the concentration expressed on dry basis;

C_{wet} is the concentration expressed on wet basis;

h_{m} is the volume fraction of water vapour.

The uncertainty associated with a concentration expressed on dry gas is calculated according to Formula (D.2):

$$u^2(C_{\mathrm{dry}}) = \left(C_{\mathrm{dry}}\right)^2 \times \left(\frac{u^2(C_{\mathrm{wet}})}{\left(C_{\mathrm{wet}}\right)^2} + \frac{u^2(h_{\mathrm{m}})}{(100\% - h_{\mathrm{m}})^2} \right) \qquad \text{(D.2)}$$

where :

$u(C_{\mathrm{dry}})$ is the uncertainty associated with a concentration expressed on dry gas;

$u(C_{\mathrm{wet}})$ is the uncertainty associated with a concentration expressed on wet gas;

$u(h_{\mathrm{m}})$ is the uncertainty associated with the water vapour volume fraction.

Table D.1 — Calculation of the uncertainty on dry gas

Concentration C_{wet} of the measured component:	100 mg/Nm^3 on wet basis
Standard uncertainty of the concentration $u(C_{\mathrm{wet}})$:	6% of measured value
Standard uncertainty of the water vapour content $u(h_{\mathrm{m}})$:	10% of measured value

Water vapour content h_{m} %	**Concentration on dry basis** C_{dry} mg/Nm^3	**Standard uncertainty** $u(C_{\mathrm{dry}})$ mg/Nm^3	**Relative standard uncertainty** $u_{\mathrm{rel}}(C_{\mathrm{dry}})$ %
1	101.01	6.06	**6.00**
2	102.04	6.13	**6.00**
3	103.09	6.19	**6.01**
4	104.17	6.27	**6.01**
5	105.26	6.34	**6.02**
6	106.38	6.42	**6.03**
7	107.53	6.50	**6.05**
8	108.70	6.59	**6.06**
9	109.89	6.68	**6.08**
10	111.11	6.78	**6.10**
11	112.36	6.88	**6.13**
12	113.64	6.99	**6.15**
13	114.94	7.11	**6.18**
14	116.28	7.23	**6.22**
15	117.65	7.36	**6.25**
16	119.05	7.49	**6.30**
17	120.48	7.64	**6.34**
18	121.95	7.79	**6.39**
19	123.46	7.95	**6.44**
20	125.00	8.13	**6.50**
21	126.58	8.31	**6.56**
22	128.21	8.50	**6.63**
23	129.87	8.70	**6.70**
24	131.58	8.92	**6.78**
25	133.33	9.15	**6.86**
26	135.14	9.40	**6.95**
27	136.99	9.66	**7.05**
28	138.89	9.93	**7.15**
29	140.85	10.22	**7.26**
30	142.86	10.53	**7.37**
31	144.93	10.86	**7.50**
32	147.06	11.21	**7.63**
33	149.25	11.59	**7.76**
34	151.52	11.98	**7.91**
35	153.85	12.40	**8.06**

Uncertainty associated with a concentration expressed at an oxygen reference concentration

The concentration of a measured component for oxygen reference conditions is calculated according to Formula (D.3):

$$C_{\mathrm{corr}} = C_{\mathrm{m}} \times \frac{21\% - (o_{\mathrm{ref}})_{\mathrm{dry}}}{21\% - (o_{\mathrm{m}})_{\mathrm{dry}}} \tag{D.3}$$

where

C_{corr}	is the concentration expressed at oxygen reference conditions;
$(o_{\mathrm{ref}})_{\mathrm{dry}}$	is the oxygen reference concentration expressed as a volume fraction on dry basis;
C_{m}	is the measured concentration at the actual volume fraction of oxygen;
$(o_{\mathrm{m}})_{\mathrm{dry}}$	is the actual volume fraction of oxygen in the dry flue gas.

The uncertainty associated with a concentration expressed on dry gas is calculated according to Formula (D.4):

$$u^2(C_{\mathrm{corr}}) = (C_{\mathrm{corr}})^2 \times \left(\frac{u^2(C_{\mathrm{m}})}{(C_{\mathrm{m}})^2} + \frac{u^2((o_{\mathrm{m}})_{\mathrm{dry}})}{(21\% - (o_{\mathrm{m}})_{\mathrm{dry}})^2} \right) \tag{D.4}$$

where

$u(C_{\mathrm{corr}})$	is the uncertainty associated with a concentration expressed at a oxygen reference concentration;
$u(C_{\mathrm{m}})$	is the uncertainty associated with a concentration at the actual volume fraction of oxygen;
$u((o_{\mathrm{m}})_{\mathrm{dry}})$	is the uncertainty associated with the actual volume fraction of oxygen in the flue gas on dry basis.

The uncertainty associated to the concentration expressed at a reference oxygen volume fraction depends on the uncertainty of the measurement carried out at the actual oxygen volume fraction, and on the uncertainty of measurement of oxygen. It increases with the oxygen volume fraction in the sample gas as shown in Table D.2.

Table D.2 — Calculation of the uncertainty of a concentration expressed at an oxygen reference concentration

Concentration C_m of the measured component:	100	mg/Nm^3 at actual oxygen content
Standard uncertainty of the concentration $u(C_\mathrm{m})$:	4.7	% of the measured value
Relative standard uncertainty of the oxygen content $u_\mathrm{rel}(o_\mathrm{m})$:	2.5	%
Oxygen reference volume concentration o_ref:	11	%

Oxygen volume content o_m %	**Concentration at o_ref = 11%** (calculated with o_m) C_corr mg/Nm^3	**Standard uncertainty** $u(C_\mathrm{corr})$ mg/Nm^3	**Relative standard uncertainty** $u_\mathrm{rel}(C_\mathrm{corr})$ %
5	**62.50**	2.98	**4.76**
6	**66.67**	3.20	**4.81**
7	**71.43**	3.47	**4.86**
8	**76.92**	3.80	**4.95**
9	**83.33**	4.22	**5.06**
10	**90.91**	4.75	**5.22**
11	**100.00**	5.45	**5.45**
12	**111.11**	6.40	**5.76**
13	**125.00**	7.77	**6.21**
14	**142.86**	9.80	**6.86**
15	**166.67**	13.03	**7.82**
16	**200.00**	18.56	**9.28**
17	**250.00**	29.05	**11.62**
18	**333.33**	52.40	**15.72**
19	**500.00**	121.05	**24.21**
20	**1000.00**	502.20	**50.22**

ANNEX E

Summary sheets showing SRMs’ and AMSs’ performances

E1: Summary Sheet O_2

Oxygen O_2

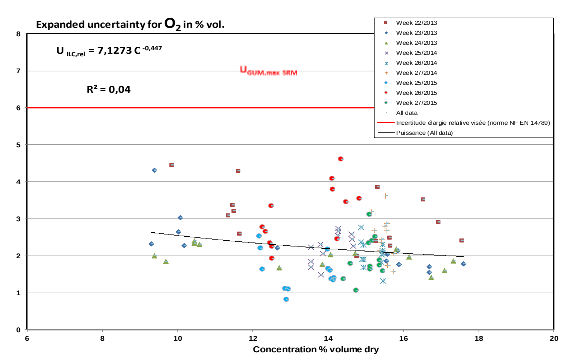
SRM

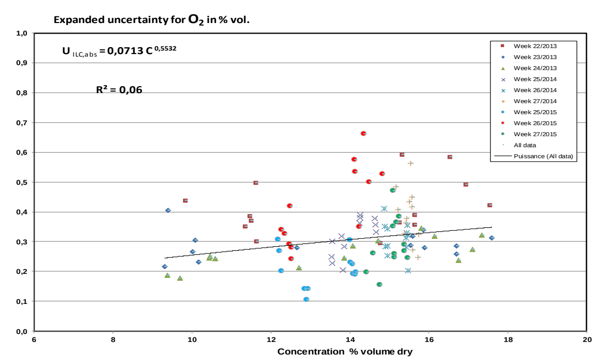
NF EN 14789 - Paramagnetic Method

[1] Average value of Paramagnetic AMSs

[2] EN 14789 Standard's Requirement

SRM implementation characteristics	
(1)LoQ in % volume	(2) U_{max} (GUM) in relative %
0,020	6





AMS

[4] GA X 43-132 recommendations (no IED requirements)

[5] when the concentration at which the uncertainty calculation was performed is not mentioned in the certificate, it is assumed that it was equal to the mentioned concentration (grey cells)

Mandated confidence interval by the IED	none
Uncertainty recommended by GA X 43-132 at the level of the measured concentrations	15% [4]

		Values obtained during certification			
	Paramagnetic	Full scale (% volume)	LoQ (% volume)	U (GUM) (relative %)	[5] C_U (% volume)
Para-1	Servomex Group Ltd: mini MP 5200	25	0,06	2,1	25
Para-2	Servomex Group Ltd: Servomex 4900 Multi gas analyser	25	<0.1	2,3	25
Para-3	SICK MAIHAK GmbH: MAC GMS 800 Multi-Component Analyser	25	<0.1	2,36	25
Para-4	ABB Ltd: Endura AZ20/AZ30	25	<0.04	2,6	25
Para-5	ABB: AO2000 Magnos 206	10	0	4,2	10
Para-6	HORIBA: ENDA-5000	25	0,01	2,2	25
Para-7	HORIBA: PG 250	25	NC	2,3	25
Para-8	HORIBA: PG 350 E	25	0,02	2	25
Para-9	Siemens Production: Oxymat 6	5 and 25	0,01	0,32	25
Para-10	Emerson Process Management Manufacturing GmbH & Co. OHG: NGA 2000 MLT3/4	5 and 25	0,01	2,8	25
Para-11	Environnement SA: MIR9000 Multi-gas Analyser Type 2 SEC Probe & MIR9000 CLD optionType 2	10 and 25	0,02	2,7	25
Para-12	Environnement SA: MIR-IS Multi-gas Analyser Type 2 SEC	10 and 25	0,02	0,28	25
	Zirconia probe				
ZIRC-1	Dr Födisch MCA 04	25	0,06	2,3	25
ZIRC-2	Dr Födisch MCA 10	25	<0.5	1,7	25
ZIRC-3	FUJI ZFK8 + ZKM	25	NC	2,7	25
ZIRC-4	FUJI ZRE et ZRE/ZFK7+ ZKM	25	0,02	2,9	25
ZIRC-5	ABB Ltd: ENDURA AZ20	25	0,04	2,6	25
ZIRC-6	Environnement SA: MIR9000 H	25	NC	1,8	25
ZIRC-7	SICK MAIHAK GmbH: MCS 100E PD	21	0,03	3	10
ZIRC-8	SICK MAIHAK GmbH: MCS 100E FT	21	0,008	2,8	21
ZIRC-9	ABB : Advance CEMAS FTIR – NT (ACF-NT) (CEM 1230KL)	25	0,04	2,4	25
ZIRC-10	Gasmet Technologies Oy: DX 4000, CX 4000 OXITEC 500E SME 5	25	0,04	2,4	25
ZIRC-11	Pillard: Oxatex 3107 C67	21	NC	2,9	21
ZIRC-12	Emerson Process Management Rosemount analytical, Inc.: Model 6888A with zirconia probe	25	NC	2,4	25
ZIRC-13	Emerson Process Management Rosemount analytical, Inc.: Oxymitter 4000 With operator Interface LOI	25	<0.5	3,2	25
ZIRC-14	Opsis AB: 02000 Oxygen analyser	25	0,04	4,8	25
ZIRC-15	Protea LTD: ProtIR 204M Mobile FTIR	25	0,02	NC	-
ZIRC-16	SICK MAIHAK GmbH: MCS 100E HW	21	0,07	0,53	10
ZIRC-17	SICK MAIHAK GmbH: SIDOR Multi Gas Analyser with OXOR-P modules	25	0,06	1,1	10
ZIRC-18	Environnement SA: MIR-FT Multi-gas Analyser	25	0,2	0,7	25
	Electrochemical cell				
C.elec-1	ABB: AO2000 El sensor	10	0,004	4,2	10
C.elec-2	Land Instruments International Ltd: FGAII Flue Gas Analyser & ChillerProbe	25	0,03	3,11	25
C.elec-3	SICK MAIHAK GmbH: SIDOR Multi Gas Analyser with OXOR-E module	25	0,12	1,4	10
C.elec-4	Siemens Production Automatisation S.A.S.: ULTRAMAT 23 Multi-component gas analyser with acetic acid cell for O_2	25	0,01	0,6	25

E2: Summary Sheet CO

Carbon Monoxide CO

SRM

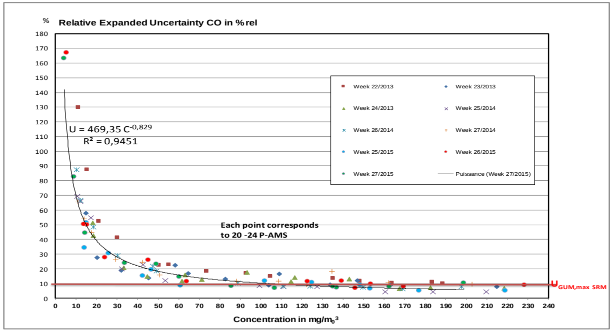
NF EN 15058

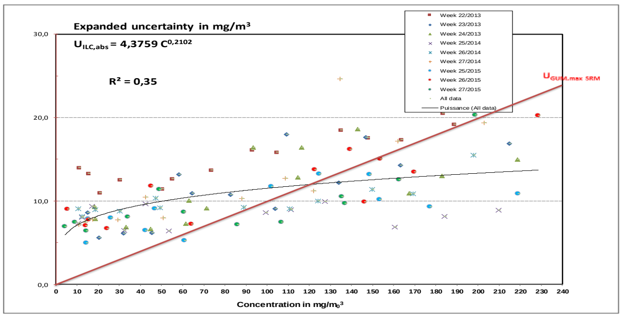
[1] Minimum ELV based on the median of AMSs measuring according to the SRM and assuming that Min. ELV = 10 LoQ
[2] Estimated expanded uncertainty based on the method's reproducibility

SRM implementation characteristics	
[1] Min ELV based on AMSs' LoQs in mg/Nm^3	U_{max} (GUM) in %
8,0	6

Values obtained through ILCs organised at INERIS			
C_{SRM} in mg/Nm^3	10	20	50
[2] U in %	70	39	18

C_{SRM}: Concentration level





AMS

[3] Assuming that the Minimum ELV = 5 LoQ
[4] when the concentration at which the uncertainty calculation was performed is not mentioned in the certificate, it is assumed that it was equal to 50 mg/Nm³ (grey cells)

75 % of the P relative uncertainty mandated by the IED at the Daily ELV:	7,5%

		Values obtained during certification				
	Non-Dispersive InfraRed (NDIR)	Full scale (mg/Nm^3)	LoQ (mg/Nm^3)	[3] Min ELV (mg/Nm^3)	U(GUM) %	[4] C_U (mg/Nm^3)
NDIR-1	ABB Automation Products GmbH: Advance Optima AO2000	75	0,03	0,15	8,5	50
NDIR-2	ABB Automation Products GmbH: EL3000	75	0,3	1,5	8,5	50
NDIR-3	HORIBA: ENDA-5000	50	1,2	6	5,6	50
NDIR-4	Siemens Production Automatisation S.A.S.: ULTRAMAT 23	50	2,4	12	7,9	80
NDIR-5	SICK MAIHAK GmbH: MAC GMS 800 (UNOR)	75	0,9	4,5	7,4	50
NDIR-6	SICK MAIHAK GmbH: MAC GMS 800 (MULTOR)	200	0,8	4	7,5	50
NDIR-7	Siemens Production Automatisation S.A.S.: ULTRAMAT 6 Multi-component gas analyser	50	0,8	4	7,3	50
NDIR-8	Emerson Process Management Manufacturing GmbH & Co. OHG: NGA 2000 MLT3/4	75	1,8	9	7,8	50
	Gas Filter Correlation InfraRed (GFCIR)					
GFCIR-1	SICK MAIHAK GmbH: MCS 100E HW Multi-Component Analyser	75	0,5	2,5	5,8	50
GFCIR-2	SICK MAIHAK GmbH: MCS 100E PD Multi-Component Analyser	50	0,6	3	6	50
GFCIR-3	Environnement SA: MIR-IS Multi-gas Analyser Type 2 SEC	75	0,1	0,5	5,3	50
GFCIR-4	Environnement SA: MIR9000 Multi-gas Analyser Type 2 SEC Probe & MIR9000 CLD optionType 2	75	0,1	0,5	7,9	50
GFCIR-5	Environnement SA: MIR9000 H	75	NC	-	8	50
GFCIR-6	Servomex Group Ltd: Servomex 4900 Multigas Analyser	75	2,8	14	5,5	50
GFCIR-7	HORIBA: PG 250	75	0,27	1,35	3.5 or 9.3	50
GFCIR-8	HORIBA: PG 350E	75	0,3	1,5	6,7	50
GFCIR-9	Dr Födisch MCA 04 Dualwavelength method and Gas filter correlation	75	<1.5	<7.5	7,5	50
GFCIR-10	Dr Födisch MCA 10 Dualwavelength method and Gas filter correlation	75	0,09	0,45	7,5	50
GFCIR-11	Siemens Production Automatisation S.A.S.: ULTRAMAT / OXYMAT 6 Multi-component analyser	50	0,8	4	7,3	50
GFCIR-12	FUJI Electric Co Ltd: ZRE et ZRE/ZFK7	125	0,15	0,75	12,5	50
GFCIR-13	SICK MAIHAK GmbH: SIDOR Multi Gas Analyser with OXOR-E & OXOR-P modules	75	1,3	6,5	5,2	50
GFCIR-14	SICK MAIHAK GmbH: GM35 In-situ Gas Analyser Model Cross-Duct & Model Measuring Probe GMP	75	1,3	6,5	6,9	50
GFCIR-15	Unit	187	0,8	4	7,5	50
	Fourrier Transform InfraRed (FTIR)					
FTIR-1	Gasmet Technologies OY: GASMET Multi gas analyser CX 4000, DX4000 or CEM II	75	0,3	1,5	6	50
FTIR-2	ABB Automation GmbH: Advance CEMAS FTIR – NT (ACF-NT) Multigas Continous Emission Monitor	75	0,5	2,5	9,8	50
FTIR-3	SICK MAIHAK GmbH: MCS 100 FT	75	0,6	3	8,7	50
FTIR-4	MKS Intruments Inc,: MGS 300	75	0,6	3	6,2	50
FTIR-5	General Impianti GL: GIGAS 10M	75	NC	-	9	50
FTIR-6	Environnement SA: MIR-FT Multi-gas Analyser	75	0,2	1	2,8	50
FTIR-7	Protea LTD: ProtIR 204M Mobile FTIR multigas analyser	75	0,09	0,45	NC	NC
	Differential Optical Absorption Spectroscopy (DOAS)					
DOAS	OPSIS: AR 650	75	2,4	12	6,9	50
	Electrochemical cell					
ElecC	Land Instruments International Ltd: FGAII Flue Gas Analyser & ChillerProbe	150	3,6	18	20,6	50

Different values on the TÜV and MCERTS certificates

Data from QAL2 control reports

Cavg, ELV, S_D: expressed in mg/Nm^3 on dry gas at 11% O_2
Min ELV calculated = S_D x 1.96 x 100 / P - Min ELV calculated with SD,min= SD,min x 1.96 x 100 / P

Cavg measured by SRM (mg/Nm^3)	Number of measurements [AMS/SRM]	Site's ELV (mg/Nm^3)	Min ELV by data reprocessing (mg/Nm^3)	Min ELV calculated by S_D (mg/Nm^3)	Min ELV calculated by $S_{D,min}$ (mg/Nm^3)	Minimum expanded uncertainty to fulfil the variability test (%)
24,7	17	50	23,6	14,4	7,7	2,9
24,7	18	50	23,5	13,5	12,6	2,8

Min ELV >> than calculated based on the certificate, but cannot be tested lower by data reprocessing because only 3 data pairs are left for the test (lowest concentrations measured around 20 mg/Nm³)

Cavg measured by SRM (mg/Nm^3)	Number of measurements [AMS/SRM]	Site's ELV (mg/Nm^3)	Min ELV by data reprocessing (mg/Nm^3)	Min ELV calculated by S_D (mg/Nm^3)	Min ELV calculated by $S_{D,min}$ (mg/Nm^3)	Minimum expanded uncertainty to fulfil the variability test (%)
21,7	15	50	18,6	25,2	22,5	5,2
25,6	16	50	17,7	22,5	11,8	4,6
51,6	18	50	Not fulfilled variability test			
48,2	17	50	16,0	17,1	8,0	3,5

Min ELV >> than calculated based on the certificate, but cannot be tested lower by data reprocessing because only 3 data pairs are left for the test (lowest concentrations measured around 15 mg/Nm³)

Cavg measured by SRM (mg/Nm^3)	Number of measurements [AMS/SRM]	Site's ELV (mg/Nm^3)	Min ELV by data reprocessing (mg/Nm^3)	Min ELV calculated by S_D (mg/Nm^3)	Min ELV calculated by $S_{D,min}$ (mg/Nm^3)	Minimum expanded uncertainty to fulfil the variability test (%)
8,8	18	50	29,2	28,4	-	5,8
8,8	15	50	20,1	21,5	19,5	4,4

Cavg measured by SRM (mg/Nm^3)	Number of measurements [AMS/SRM]	Site's ELV (mg/Nm^3)	Min ELV by data reprocessing (mg/Nm^3)	Min ELV calculated by S_D (mg/Nm^3)	Min ELV calculated by $S_{D,min}$ (mg/Nm^3)	Minimum expanded uncertainty to fulfil the variability test (%)
5,9	6	30	6,8	6,1	-	2,2
5,9	6	30	6,0	3,5	4,7	1,2

E3: Summary Sheet NO_x

Nitrogen Oxide NO_x

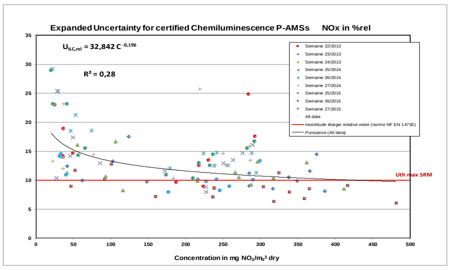
SRM

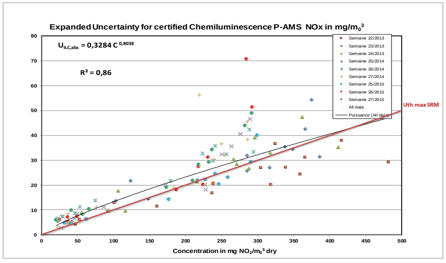
NF EN 14792: Chemiluminescence

[1] Minimum ELV based on the median of AMSs measuring according to the SRM and assuming that Min. ELV = 10 LoQ

[2] Estimated expanded uncertainty based on the method's reproducibility

SRM implementation characteristics	
[1] Min ELV based on AMSs' LoQs in mg/Nm^3	U_{max} (GUM) in %
17	10





AMS

[3] Assuming that the Minimum ELV = 5 LoQ

[4] when the concentration at which the uncertainty calculation was performed is not mentioned in the certificate, it is assumed that it was equal to 200 mg/Nm³ (grey cells)

75 % of the P relative uncertainty mandated by the IED at the Daily ELV:	15%

		Values obtained during certification				
		Full scale (mg/Nm^3)	LoQ (mg/Nm^3)	[3] Min ELV (mg/Nm^3)	U(GUM) %	[4] C_U (mg/Nm^3)
	Chemiluminescence Reference Method NF EN 14792					
Chemilu-1	Eco Physics AG: Eco Physics CLD 82Mh & 822Mh chemiluminescence NO/NO$_x$ analyser	90	0,7	3,5	19	33
Chemilu-2	Environnement SA: MIR9000 Multi-gas Analyser Type 2	100	0,08	0,4	7,2	20
Chemilu-3	Environnement SA: MIR9000 CLD optionType 2, range 9000 CD	20	NC	-	6,1	20
Chemilu-4	Emerson Process Management Manufacturing GmbH & Co. OHG: NGA 2000 MLT3/4	200	7,2	36	9,2	131
Chemilu-5	Emerson Process Management Manufacturing GmbH & Co. OHG: NGA 2000 CLD	134	<2.7	<13.5	12,5	100
Chemilu-6	HORIBA: PG 350E	134	<2.7	<13.5	6,6	131
Chemilu-7	HORIBA: PG 250	134	0,2	1	8,5	131
	Non-Dispersive InfraRed (NDIR)					
NDIR-1	ABB Automation Products GmbH: AO2000 Series Multigas Analysers with SCC-K NO/NO$_2$ converter	100	0,28	1,4	7,9	200
NDIR-2	ABB Automation Products GmbH: EL3000 Series Multigas Analysers with SCC-K NO/NO$_2$ converter	150	0,12	0,6	7,9	200
NDIR-3	Siemens Production Automatisation S.A.S.: ULTRAMAT 23 Multi-component gas analyser	250	8	40	10,4	32,6
NDIR-4	Siemens Production Automatisation S.A.S.: ULTRAMAT / OXYMAT 6 Multi-component analyser	100	1,6	8	10,6	32,6
NDIR-5	HORIBA: ENDA-5000	100	0,4	2	5,1	131
NDIR-6	SICK MAIHAK GmbH: MAC GMS 800 UNOR	100	1,6	8	11,7	50
NDIR-7	SICK MAIHAK GmbH: MAC GMS 800 MULTOR	250	8	40	11,9	200
NDIR-8	SICK MAIHAK GmbH: MAC GMS 800 DEFOR	50	0,2	1	11,1	30
NDIR-9	FUJI Electric Co Ltd: ZRE et ZRE/ZFK7	268	0,6	3	14,7	200
NDIR-10	Siemens Production Automatisation S.A.S.: ULTRAMAT 6 Multi-component gas analyser	100	1,6	8	10,6	32,6
	Gas Filter Correlation InfraRed (GFCIR)					
GFCIR-1	SICK MAIHAK GmbH: MCS 100E HW Multi-Component Analyser	15	0,6	3	7,0	130
GFCIR-2	SICK MAIHAK GmbH: MCS 100E PD Multi-Component Analyser	50	0,4	2	6	130
GFCIR-3	Servomex Group Ltd: Servomex 4900 Multigas Analyser	268	0,8	4	7,3	
GFCIR-4	Dr Födisch MCA 04 Dualwavelength method and Gas filter correlation	200	0,8	4	11,4	98
GFCIR-5	Dr Födisch MCA 10 Dualwavelength method and Gas filter correlation	200	<4	<20	5,9	130
GFCIR-6	Siemens AG.: Set CEM CERT 7MB 1957 with SIPROCESS UV600_7MB2621 module	50	NC	-	8,5	100
GFCIR-7	Environnement SA: MIR9000 Multi-gas Analyser Type 2 SEC Probe & MIR9000 CLD optionType 2	20	0,02	0,1	7,2	20
GFCIR-8	Environnement SA: MIR9000 H	200	NC	-	12,6	100
GFCIR-9	Environnement SA: MIR-IS Multi-gas Analyser Type 2 SEC	100	0,08	0,4	4,8	
GFCIR-10	Kittiwake Procal Ltd: Procal 2000 Series Continuous Emission Monitor with ACU MK3 Control Unit or with Procal 1000 Control Unit	320	2	10	11,6	
GFCIR-11	SICK MAIHAK GmbH: SIDOR Multi Gas Analyser with OXOR-E or OXOR-P modules	75	3,9	19,5	6,1	130
	Fourrier Transform InfraRed (FTIR)					
FTIR-1	MKS Intruments Inc,: MGS 300	200	0,8	4	6,8	131
FTIR-2	General Impianti GL: GIGAS 10M	200	NC	-	9,1	131
FTIR-3	ABB Automation GmbH: Advance CEMAS FTIR – NT (ACF-NT)	200	4,5	22,5	8,2	131
FTIR-4	Gasmet Technologies OY: GASMET Multi gas analyser CX 4000 , DX4000 & EN4000 Multi-gas analyser	200	2,4	12	6,5	131
FTIR-5	SICK MAIHAK GmbH: MCS 100 FT	200	1,5	7,5	9,5	131
FTIR-6	Protea LTD: ProtIR 204M Mobile FTIR multigas analyser	200	2,2	11	NC	NC
FTIR-7	Environnement SA: MIR-FT Multi-gas Analyser	200	1,8	9	9,8	
	UV Absorption					
UV-1	AMETEK Process Instruments: Model 910 Hot/Wet Multi-Gas Mass Flow CEM / Model 920 Hot/Wet Multi-Gas CEM / Model 919 Hot/Wet Single-Gas CEM Model 919 Hot/Wet Single-Gas CEM / Model 909 Hot/Wet Single-Gas Mass Flow CEM	670	2	10	12,1	268
UV-2	ABB Automation: AO2000- Limas11 UV canal NO and NO$_2$	33,5	0,54	2,7	4,65	
UV-3	Siemens Sensors & Communications: SIPROCESS UV600	50	0,2	1	11,1	
	Differential Optical Absorption Spectroscopy (DOAS)					
DOAS-1	OPSIS AB: AR 602 Z/N GM32 In-situ Multi-Component Analyser (Cross Duct version)	150	0,6	3	4,5	100
DOAS-2	SICK Maihak GmbH: GM32 In-situ Multi-Component Analyser (Cross Duct version)	70	0,3	1,5	11,6	40
DOAS-3	SICK Maihak GmbH: GM32 In-situ Multi-Component Analyser (GMP measuring probe version)	70	0,4	2	11,8	40
	Electrochemical cell					
ElecC	Land Instruments International Ltd: FGAII Flue Gas Analyser & ChillerProbe	200	2,1	10,5	12,7	130

Data from QAL2 control reports

Cavg, ELV, S_D: expressed in mg/Nm^3 on dry gas at 11% O_2

Min ELV calculated = S_D x 1.96 x 100 / P - Min ELV calculated with SD,min= SD,min x 1.96 x 100 / P

➡ GFCIR-1

Cavg measured by SRM (mg/Nm^3)	Number of measurements [AMS/SRM]	Site's ELV (mg/Nm^3)	Min ELV by data reprocessing (mg/Nm^3)	Min ELV calculated by S_D (mg/Nm^3)	Min ELV calculated by S_D,min (mg/Nm^3)	Minimum expanded uncertainty to fulfil the variability test (%)
74,1	18	80	43.0 *	26,3	29,9	6,9
74,1	18	80	44.3 *	13,5	17,7	3,5

***: Min ELV >> than calculated based on the certificate, but cannot be tested lower by data reprocessing because only 3 data pairs are left for the test (lowest concentrations measured around 40 mg/Nm³)**

➡ GFCIR-7

Cavg measured by SRM (mg/Nm^3)	Number of measurements [AMS/SRM]	Site's ELV (mg/Nm^3)	Min ELV by data reprocessing (mg/Nm^3)	Min ELV calculated by S_D (mg/Nm^3)	Min ELV calculated by S_D,min (mg/Nm^3)	Minimum expanded uncertainty to fulfil the variability test (%)
166,9	18	200	141.9 *	64,4	93,6	6,6
168,4	17	200	144.0 *	77,8	101,0	7,9
187,1	18	200	184,8	138,7	163,8	14,4
187,1	18	200	152.1 *	46,6	2,8	4,8

***: Min ELV >> than calculated based on the certificate, but, except for the 3rd case, the ELV cannot be tested lower by data reprocessing because only 3 data pairs are left for the text (lowest concentrations measured around 60 mg/Nm³ for the first 2 and 40 mg/Nm³ for the last)**

➡ FTIR-3

Cavg measured by SRM (mg/Nm^3)	Number of measurements [AMS/SRM]	Site's ELV (mg/Nm^3)	Min ELV by data reprocessing (mg/Nm^3)	Min ELV calculated by S_D (mg/Nm^3)	Min ELV calculated by S_D,min (mg/Nm^3)	Minimum expanded uncertainty to fulfil the variability test (%)
67,8	17	80	67.9 *	30,7	13,5	8,0
67,8	15	80	69,0	76,1	64,3	19,6

***: Min ELV >> than calculated based on the certificate, but cannot be tested lower by data reprocessing because only 3 data pairs are left for the test (lowest concentrations measured around 60 mg/Nm³)**

➘ FTIR-7

Cavg measured by SRM (mg/Nm^3)	Number of measurements [AMS/SRM]	Site's ELV (mg/Nm^3)	Min ELV by data reprocessing (mg/Nm^3)	Min ELV calculated by S_D (mg/Nm^3)	Min ELV calculated by S_D,min (mg/Nm^3)	Minimum expanded uncertainty to fulfil the variability test (%)
78,2	17	70	*	12,6		
78,2	18	70	*	5,3		

***: impossible to test lower ELVs because at 69 mg/Nm^3, only 2 data pairs are left**

E4: Summary Sheet TOC

Total Organic Compounds TOC

SRM

EN 12619

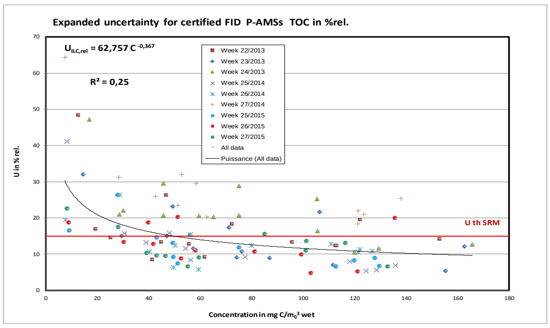
[1] Minimum ELV based on the median of AMSs measuring according to the SRM and assuming that Min. ELV = 10 LoQ

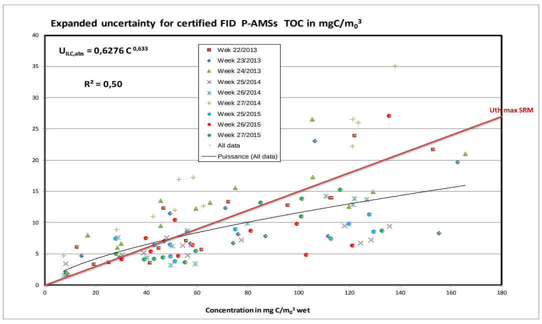
[2] Estimated expanded uncertainty based on the method's reproducibility

SRM implementation characteristics	
[1] Min ELV based on AMSs' LoQs in mg/Nm^3	U_{max} (GUM) in %
0,40	15

Values obtained through ILCs organised at the INERIS or when validating the EN 12619 Standard						
C_{SRM} in mg/Nm^3	1.0 - 5.0	5.0 - 10.0	10.0 - 20.0	20 - 120	120 - 170	
[2] U TOC in %	50	30	20			EN 12619
[2] U TOC in %			23	13	10	INERIS ILC

C_{SRM}: Concentration level





AMS

75 % of the P relative uncertainty mandated by the IED at the Daily ELV:	23%

[4] Assuming that Min ELV = 5 LQ

		Values obtained during certification				
	FID	Full scale (mg/Nm^3)	LoQ (mg/Nm^3)	[3] Min ELV (mg/Nm^3)	U(GUM) %	[4] C_U (mg/Nm^3)
FID-1	SK Elektronik GmbH: Thermo FID	15	0,06	0,3	11,8	10
FID-2	ABB Automation GmbH: AO2000 MultiFID 14	10	0,036	**0,18**	**18,2**	10
FID-3	SICK AG: GMS810-FIDOR TOC analyser	15	0,06	0,3	8,6	10
FID-4	SICK AG: MCS 100 FT FID	15	<0.03	<0.15	21	10
FID-5	Dr Födisch MCA 04	15	0,012	0,06	12,8	10
FID-6	Dr Födisch MCA 10	15	0,012	0,06	8,7	10
FID-7	Environnement SA: Graphite 52 M	15	0,06	**0,3**	**8,7**	10

FTIR

FTIR-1	ABB Automation GmbH: Advance CEMAS FTIR – NT (ACF-NT)	15	0,042	0,21	18,2	10

Data from QAL2 control reports

Cavg, ELV, S_D: expressed in mg/Nm^3 on dry gas at 11% O_2

Min ELV calculated = S_D x 1.96 x 100 / P - Min ELV calculated with SD,min= SD,min x 1.96 x 100 / P

➡

Cavg measured by SRM (mg/Nm^3)	Number of measurements [AMS/SRM]	Site's ELV (mg/Nm^3)	**Min ELV by data reprocessing (mg/Nm^3)**	**Min ELV calculated by S_D (mg/Nm^3)**	**Min ELV calculated by S_D,min (mg/Nm^3)**	**Minimum expanded uncertainty to fulfil the variability test (%)**
1,2	13	10	**4,6**	**4,4**	**-**	
1,2	17	10	Does not fulfil the variability test			

➡

Cavg measured by SRM (mg/Nm^3)	Number of measurements [AMS/SRM]	Site's ELV (mg/Nm^3)	**Min ELV by data reprocessing (mg/Nm^3)**	**Min ELV calculated by S_D (mg/Nm^3)**	**Min ELV calculated by S_D,min (mg/Nm^3)**	**Minimum expanded uncertainty to fulfil the variability test (%)**
0,94	18	10	**1,7**	**1,6**	**-**	**4,9**
0,91	18	10	**4,2**	**4,0**	**-**	**12,3**
0,91	18	10	**1,3**	**2,5**	**1,4**	**7,6**
0,91	18	10	**1,7**	**3,6**	**1,6**	**11,1**

Non-certified FID Analyser

SICK MAIHAK - EUROFID 3000

Cavg measured by SRM (mg/Nm^3)	Number of measurements [AMS/SRM]	Site's ELV (mg/Nm^3)	**Min ELV by data reprocessing (mg/Nm^3)**	**Min ELV calculated by S_D (mg/Nm^3)**	**Min ELV calculated by S_D,min (mg/Nm^3)**	**Minimum expanded uncertainty to fulfil the variability test (%)**
1,6	15	10	**3,5**	**3,4**	**-**	**10,4**
1,6	15	10	**3,2**	**3,3**	**3,1**	**10,2**

Non-certified FTIR Analyser

Environnement SA Analyser - MIR FT (certified for other parameters)

Cavg measured by SRM (mg/Nm^3)	Number of measurements [AMS/SRM]	Site's ELV (mg/Nm^3)	**Min ELV by data reprocessing (mg/Nm^3)**	**Min ELV calculated by S_D (mg/Nm^3)**	**Min ELV calculated by S_D,min (mg/Nm^3)**	**Minimum expanded uncertainty to fulfil the variability test (%)**
0,8	6	10	**0,8**	**0,6**	**0,3**	**1,9**
0,8	6	10	**0,8**	**0,8**	**0,0**	**2,5**

Min ELV >> than calculated based on the certificate, but cannot be tested lower by data reprocessing because only 3 data pairs are left for the test (lowest concentrations measured around 20 mg/Nm³)

E5: Summary sheet Dust

Dust

SRM

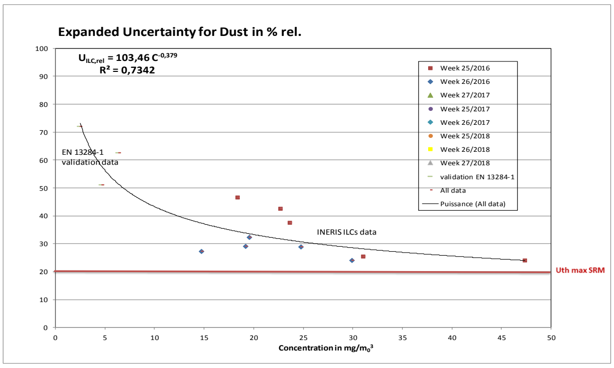
NF EN 13284-1 Manual method: filter sampling and gravimetric determination

(1) Assuming a Min ELV = 10 LoQ

(2) Based on 1 hour of sampling and of 1 m³ sampled

(3) Requirement mandated by the Standard being revised

	SRM implementation characteristics			
	Analytical LoQ in mg	(1) LoQ in mg/Nm^3	(2) Min ELV in mg/Nm^3	(3) U_{max} (GUM) in %
filter	1,0	1,0	34,0	20%
rinsing	2,0	2,0		


Expanded Uncertainty for Dust in % rel.

AMS

(5) Assuming that the Minimum ELV = 5 LoQ

(6) when the concentration at which the uncertainty calculation was performed is not mentioned in the certificate, it is assumed that it was equal to 10 mg/Nm³ (grey cells)

75 % of the P relative uncertainty mandated by the IED at the Daily ELV:	23%

		Values obtained during certification				
	Opacity measurement / transmission	Full scale (mg/Nm^3)	LoQ (mg/Nm^3)	(3) Min ELV (mg/Nm^3)	U(GUM) %	(4) C_U (mg/Nm^3)
TRANS-1	PCME Ltd Stack 710	15	NC	-	6,8	10
TRANS-2	Pillard: OPASTOP EM--D 5100	20	NC	-	13,4	10
TRANS-3	HORIBA EM-D 5100	15	NC	-	5,2	10
TRANS-4	CODEL D-CEM2100 model	15	0,00018	0,0009	6	10
TRANS-5	Land Instruments 4500 MKIII	15	0,06	0,3	6,8	10
TRANS-6	SICK AG: FWE 200	15	0,06	0,3	6,2	10
TRANS-7	SICK AG: DUSTHUNTER T200	15	0,06	0,3	8,4	10
TRANS-8	SICK AG: DUSTHUNTER T100	15	0,06	0,3	6	10
TRANS-9	SICK AG: DUSTHUNTER C 200	15	0,06	0,3	8,4	10
TRANS-10	SICK AG: DUSTHUNTER SF100	15	0,078	0,39	7	10
TRANS-11	DURAG GmbH: D-R 290	15	0,06	0,3	5,2	10
	Diffusion optics					
DIFF-1	SICK AG: DUSTHUNTER SP100	18	0,022	0,11	3,9	10
DIFF-2	DURAG GmbH: D-R 300	3	<0.006	<0.03	0,9	3
DIFF-3	DURAG GmbH: D-R 320	7,5	NC	-	7	5
DIFF-4	SICK AG: DUSTHUNTER C 200	15	0,06	0,3	7	10
DIFF-5	DURAG GmbH: D-R 800	15	<0.03	<0.15	5,3	15
DIFF-6	DURAG GmbH: D-R 820	15	0,9	4,5	12,3	10
DIFF-7	PCME Limited: PCME QAL 181	15	0,078	0,39	6,4	10
DIFF-8	Dr Födisch PFM 06ED	15	NC	-	12,3	10
DIFF-9	SICK AG: DUSTHUNTER SB100	15	0,23	1,15	5,3	10
	Triboelectric probe					
TRIBO-1	DURAG D-RX 250	15	<0.03	<0.15	8,2	10
TRIBO-2	PCME Limited QAL 991	7,5	0,012	0,06	9,5	5
TRIBO-3	PCME 980	15	<0.03	<0.15	NC	-

Data from QAL2 control reports

Cavg, ELV, S_D: expressed in mg/Nm^3 on dry gas at 11% O_2
Min ELV calculated = S_D x 1.96 x 100 / P - Min ELV calculated with SD,min= SD,min x 1.96 x 100 / P

Cavg measured by SRM (mg/Nm^3)	Number of measurements [AMS/SRM]	Site's ELV (mg/Nm^3)	Min ELV by data reprocessing (mg/Nm^3)	Min ELV calculated by S_D (mg/Nm^3)	Min ELV calculated by S_D,min (mg/Nm^3)	Minimum expanded uncertainty to fulfil the variability test (%)
3,6	17	10	3,1 *	3,7	1,1	11,2
3,6	17	10	3,1 *	3,7	1,1	11,4
3,6	17	10	3,1 *	3,6	1,9	11,0
3,6	17	10	3,1 *	3,6	1,9	11,0

***: Min ELV >> than calculated based on the certificate, but cannot be tested lower by data reprocessing because only 3 data pairs are left for the test (lowest concentrations measured around 40 mg/Nm³)**

Cavg measured by SRM (mg/Nm^3)	Number of measurements [AMS/SRM]	Site's ELV (mg/Nm^3)	Min ELV by data reprocessing (mg/Nm^3)	Min ELV calculated by S_D (mg/Nm^3)	Min ELV calculated by S_D,min (mg/Nm^3)	Minimum expanded uncertainty to fulfil the variability test (%)
0,12	16	5	1,5	1,4	-	8,4
0,12	16	5	1,5	1,4	-	8,4

Cavg measured by SRM (mg/Nm^3)	Number of measurements [AMS/SRM]	Site's ELV (mg/Nm^3)	Min ELV by data reprocessing (mg/Nm^3)	Min ELV calculated by S_D (mg/Nm^3)	Min ELV calculated by S_D,min (mg/Nm^3)	Minimum expanded uncertainty to fulfil the variability test (%)
4,3	16	10	2,7	4,4	2,3	13,7
4,3	16	10	3,4	4,0	3,2	12,4
6.6 *	7	10	4,0	4,8	-	15,9
6.6 *	7	10	5,1	6,1	-	20,0

***: average concentration increased by results made by doping the effluent for 2 trials**

OLDHAM Analyser - EP 1000 Model (no certification data available)

Cavg measured by SRM (mg/Nm^3)	Number of measurements [AMS/SRM]	Site's ELV (mg/Nm^3)	Min ELV by data reprocessing (mg/Nm^3)	Min ELV calculated by S_D (mg/Nm^3)	Min ELV calculated by S_D,min (mg/Nm^3)	Minimum expanded uncertainty to fulfil the variability test (%)
0,12	16	5	1,5	1,4	-	8,4
0,12	16	5	1,5	1,4	-	8,4

E6: Summary Sheet SOx

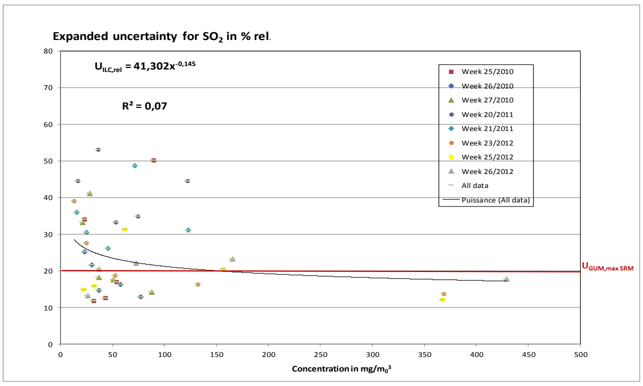
Sulphur Dioxide SO_2

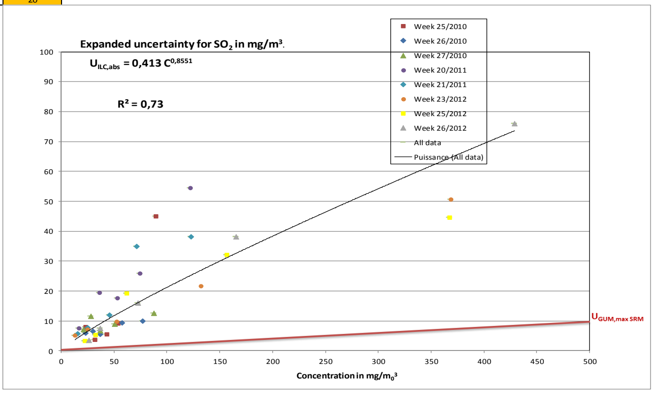
SRM

NF EN 14791 Manual method: bubbling and ionic chromatography

(1) Assuming the Min ELV = 10 LQ
(2) Based on 1 hour sampling
(3) Estimated expanded uncertainty based on the method's reproducibility

SRM implementation characteristics			
Analytical LoQ in mg	(1) LoQ in mg/Nm³	(2) Min ELV in mg/Nm³	(3) U_{max} (GUM) in %
0,1	0,167	1,667	20





AMS

75 % of the P relative uncertainty mandated by the IED at the Daily ELV:	15%

(4) Assuming that the Minimum ELV = 5 LoQ

		Values obtained during certification				
		Full scale (mg/Nm³)	LoQ (mg/Nm³)	(3) Min ELV (mg/Nm³)	U(GUM) %	(4) C_U (mg/Nm³)
	Non-Dispersive InfraRed (NDIR)					
NDIR-1	ABB Automation Products GmbH: URAS 26 (AO2000-EL3000)	75	0,39	1,95	10,2	50
NDIR-2	Siemens Production Automatisation S.A.S.: ULTRAMAT 6 Multi-component gas analyser	75	0,9	4,5	7,6	50
NDIR-3	HORIBA: ENDA-5000	75	0,3	1,5	8,8	50
NDIR-4	SICK MAIHAK GmbH: MAC GMS 800 UNOR	75	0,6	3	11,5	50
NDIR-5	SICK MAIHAK GmbH: MAC GMS 800 DEFOR	75	0,6	3	10,9	50
NDIR-6	SICK MAIHAK GmbH: MAC GMS 800 MULTOR	250	7	35	10,7	150
NDIR-7	Siemens Production Automatisation S.A.S.: ULTRAMAT 23 Multi-component gas analyser	400	8	40	7,9	200
NDIR-8	Emerson Process Management Manufacturing GmbH & Co. OHG: NGA 2000 MLT3/4	120	2,7	13,5	15,3	50
	Gas Filter Correlation InfraRed (GFCIR)					
GFCIR-1	SICK MAIHAK GmbH: MCS 100E HW Multi-Component Analyser	75	0,8	4	7,8	50
GFCIR-2	SICK MAIHAK GmbH: MCS 100E PD Multi-Component Analyser	10	0,2	1	9	50
GFCIR-3	Siemens Production Automatisation S.A.S.: ULTRAMAT / OXYMAT 6 Multi-component analyser	75	0,9	4,5	7,6	50
GFCIR-4	Dr Födisch MCA 04 Dualwavelength method and Gas filter correlation	75	<1.5	<7.5	11,4	50
GFCIR-5	Dr Födisch MCA 10 Dualwavelength method and Gas filter correlation	75	<1.5	<7.5	7,7	50
GFCIR-1	Environnement SA: MIR9000 Multi-gas Analyser Type 2 SEC Probe & MIR9000 CLD optionType 2	75	0,3	1,5	8,3	50
GFCIR-2	Servomex Group Ltd: Servomex 4900 Multigas Analyser	572	3	15	13,7	200
GFCIR-3	HORIBA: PG 350E	143	<2.9	<14.5	13,8	60
GFCIR-4	Siemens AG.: Set CEM CERT 7MB 1957 with SIPROCESS UV600_7MB2621 module	400	NC	-	13,3	200
GFCIR-5	Environnement SA: MIR9000 H	500	NC	-	13,2	200
GFCIR-6	Environnement SA: MIR-IS Multi-gas Analyser Type 2 SEC	75	0,3	1,5	4,1	50
GFCIR-7	FUJI Electric Co Ltd: ZRE and ZRE/ZFK7	571	0,5	2,5	6,9	200
GFCIR-8	HORIBA: PG 250	460	22,9	114,5	16,7	33,3
GFCIR-9	Kittiwake Procal Ltd : Procal 2000 Series Continuous Emission Monitor with ACU MK3 Control Unit or with Procal 1000 Control Unit	429	2,3	11,5	11,7	200
GFCIR-10	SICK MAIHAK GmbH: SIDOR Multi Gas Analyser with OXOR-E ou OXOR-P modules	150	2,2	11	7,4	50
	Fourrier Transform InfraRed (FTIR)					
FTIR-1	Gasmet Technologies OY : GASMET Multi gas analyser CX 4000 , DX4000 & EN4000 Multi-gas analyser	75	0,9	4,5	9,4	50
FTIR-2	ABB Automation GmbH: Advance CEMAS FTIR – NT (ACF-NT)	75	1,35	6,75	10	50
FTIR-3	MKS Intruments Inc,: MGS 300	75	0,9	4,5	7	50
FTIR-4	Protea LTD: ProtIR 204M Mobile FTIR multigas analyser	75	0,06	0,3	NC	NC
FTIR-5	Genral Impianti GL: GIGAS 10M	75	NC	-	11,5	50
FTIR-6	SICK MAIHAK GmbH: MCS 100 FT	75	0,5	2,5	10,5	50
FTIR-7	Environnement SA: MIR-FT Multi-gas Analyser	75	0,4	2	4,4	50
	Non-Dispersive UltraViolet (NDUV)					
NDUV-1	AMETEK Process Instruments: Model 910 Hot/Wet Multi-Gas Mass Flow CEM / Model 920 Hot/Wet Multi-Gas CEM / Model 919 Hot/Wet Single-Gas CEM	571	<5.7	<29	14	200
	Gas Filter Correlation UltraViolet (GFCUV)					
GFCUV-1	ABB Automation Products GmbH: LIMAS 11 UV	75	3,7	18,5	11,4	50
GFCUV-2	Siemens Sensors & Communications: SIPROCESS UV600	75	0,6	3	11	50
	Differential Optical Absorption Spectroscopy (DOAS)					
DOAS-1	OPSIS AB: AR 602 Z/N GM32 In-situ Multi-Component Analyser (Cross Duct version)	75	0,3	1,5	5,2	50
DOAS-2	SICK Maihak GmbH: GM32 In-situ Multi-Component Analyser (Cross Duct version)	75	0,8	4	13,3	30
DOAS-3	SICK Maihak GmbH: GM32 In-situ Multi-Component Analyser (GMP measuring prob version)	75	1,14	5,7	13,6	35

Data from QAL2 control reports

Cavg, ELV, S_D: expressed in mg/Nm³ on dry gas at 11% O_2
Min ELV calculated = S_D x 1.96 x 100 / P - Min ELV calculated with SD,min= SD,min x 1.96 x 100 / P

Cavg measured by SRM (mg/Nm³)	Number of measurements [AMS/SRM]	Site's ELV (mg/Nm³)	Min ELV by data reprocessing (mg/Nm³)	Min ELV calculated by S_D (mg/Nm³)	Min ELV calculated by S_D,min (mg/Nm³)	Minimum expanded uncertainty to fulfil the variability test (%)
20,2	18	50	15.2 *	12,7	4,0	5,2
20,2	17	50	14.0 *	10,8	9,3	4,4

***: Min ELV >> than calculated based on the certificate, but cannot be tested lower by data reprocessing because only 3 data pairs are left for the test (lowest concentrations measured around 14 mg/Nm³)**

Cavg measured by SRM (mg/Nm³)	Number of measurements [AMS/SRM]	Site's ELV (mg/Nm³)	Min ELV by data reprocessing (mg/Nm³)	Min ELV calculated by S_D (mg/Nm³)	Min ELV calculated by S_D,min (mg/Nm³)	Minimum expanded uncertainty to fulfil the variability test (%)
9,99	16	50	25,1	25,0	24,3	10,2
10,9	18	50	7,1	12,5	6,9	5,1
10,9	18	50	Does not fulfil the variability test			
10,9	18	50	18,0	16,5	17,5	6,7

Cavg measured by SRM (mg/Nm³)	Number of measurements [AMS/SRM]	Site's ELV (mg/Nm³)	Min ELV by data reprocessing (mg/Nm³)	Min ELV calculated by S_D (mg/Nm³)	Min ELV calculated by S_D,min (mg/Nm³)	Minimum expanded uncertainty to fulfil the variability test (%)
7,2	19	50	20,6	22,5	20,4	9,2
7,2	19	50	27,6	26,2	27,0	10,7

Cavg measured by SRM (mg/Nm³)	Number of measurements [AMS/SRM]	Site's ELV (mg/Nm³)	Min ELV by data reprocessing (mg/Nm³)	Min ELV calculated by S_D (mg/Nm³)	Min ELV calculated by S_D,min (mg/Nm³)	Minimum expanded uncertainty to fulfil the variability test (%)
7,7	6	35	10,2	10,2	9,3	6,2
7,7	6	35	10,7	9,2	9,7	5,6

E7: Summary Sheet HCl

Hydrogen Chloride HCl

SRM

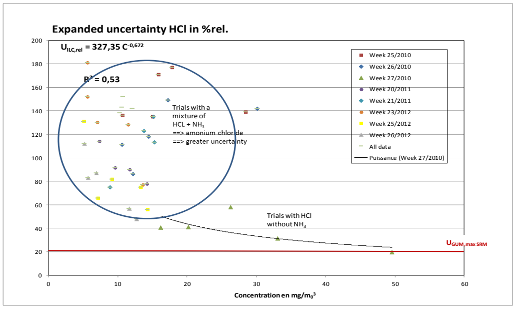
NF EN 1911 Manual method: bubbling sampling and ionic chromatography analysis

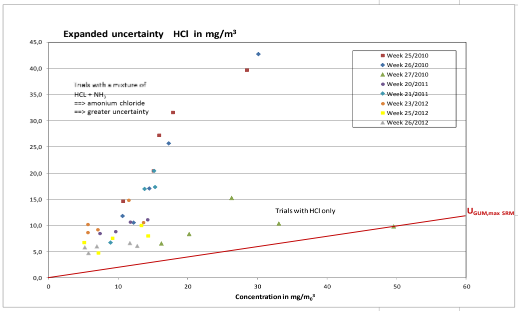
(1) Assuming the Min ELV = 10 LoQ

(2) Based on 1 hour sampling

(3) Estimated expanded uncertainty based on the method's reproducibility

SRM implementation characteristics de la SRM			
Analytical LoQ in mg	(1) LoQ in mg/Nm^3	(2) Min ELV in mg/Nm^3	(3)U_{max} (GUM) in %
0.05-0.2	0.083-0.33	0.83-3.3	20





AMS

(4) Assuming that the Minimum ELV = 5 LoQ

(5) when the concentration at which the uncertainty calculation was performed is not mentioned in the certificate, it is assumed that it was equal to 10 mg/Nm³ (grey cells)

75 % of the P relative uncertainty mandated by the IED at the Daily ELV:	30%

		Values obtained during certification				
		Full scale (mg/Nm^3)	LoQ (mg/Nm^3)	(3) Min ELV (mg/Nm^3)	U(GUM) %	(4) C_U (mg/Nm^3)
	Gas Filter Correlation InfraRed (GFCIR)					
GFCIR-1	SICK AG: MCS 100E PD	10	0,3	1,5	10	10
GFCIR-2	SICK AG: MCS 100E HW	15	0,23	1,15	8,6	10
GFCIR-3	Dr Födisch MCA 04	15	0,42	2,1	12,5	10
GFCIR-4	Dr Födisch MCA 10	15	0,042	0,21	12,8	10
GFCIR-5	Environnement SA: MIR-IS	15	0,0078	0,039	7,9	10
GFCIR-6	Environnement SA: MIR9000	15	0,0078	0,039	11,9	10
	Fourrier Transform InfraRed (FTIR)					
FTIR-1	Gasmet Technologies OY: CX 4000, DX4000 & EN4000	15	0,18	0,9	12	10
FTIR-2	ABB Automation GmbH: Advance CEMAS FTIR – NT (ACF-NT)	15	0,32	1,6	11,8	10
FTIR-3	MKS Instruments Inc: MGS300	15	0,24	1,2	8,1	10
FTIR-4	Protea Ltd: MGS300 ProtIR-204M	15	0,51	2,55		
FTIR-5	SICK AG: MCS 100 FT	15	0,16	0,8	12,2	10
FTIR-6	Environnement SA: MIR-FT	15	0,06	0,3	8,8	10
	Tunable Diode Laser Absorption Spectroscopy (TDLAS)					
TDLAS -1	Neo monitors AS: LaserGas II monitor	15	0,06	0,3	7,7	10
TDLAS -2	Siemens: LDS 6	15	0,06	0,3	13,4	10
	Differential Optical Absorption Spectroscopy (DOAS)					
DOAS-1	OPSIS: AR 650	15	1,08	5,4	12,5	10

Data from QAL2 control reports

Cavg, ELV, S_D: expressed in mg/Nm^3 on dry gas at 11% O_2

Min ELV calculated = S_D x 1.96 x 100 / P - Min ELV calculated with SD,min= SD,min x 1.96 x 100 / P

Cavg measured by SRM (mg/Nm^3)	Number of measurements [AMS/SRM]	Site's ELV (mg/Nm^3)	Min ELV by data reprocessing (mg/Nm^3)	Min ELV calculated by S_D (mg/Nm^3)	Min ELV calculated by S_D,min (mg/Nm^3)	Minimum expanded uncertainty to fulfil the variability test (%)
2,3	16	10	2,4	1,7	2,2	7,0
2,3	17	10	2,2	1,3	1,9	5,5

Cavg measured by SRM (mg/Nm^3)	Number of measurements [AMS/SRM]	Site's ELV (mg/Nm^3)	Min ELV by data reprocessing (mg/Nm^3)	Min ELV calculated by S_D (mg/Nm^3)	Min ELV calculated by S_D,min (mg/Nm^3)	Minimum expanded uncertainty to fulfil the variability test (%)
9.0 *	17	10	5,2	4,4	4,8	18,2
20.4 *	17	10	5,2	5,1	4,8	20,9
12.1 *	18	10	6,8	6,6	6,4	27,7
11.2 *	17	10	9,6	9,2	-	38,1

***: average concentration increased by trials made by doping the effluent**

Cavg measured by SRM (mg/Nm^3)	Number of measurements [AMS/SRM]	Site's ELV (mg/Nm^3)	Min ELV by data reprocessing (mg/Nm^3)	Min ELV calculated by S_D (mg/Nm^3)	Min ELV calculated by S_D,min (mg/Nm^3)	Minimum expanded uncertainty to fulfil the variability test (%)
1,3	19	10	3,8	5,0	3,7	20,2
1,3	19	10	3,7	4,3	3,6	17,4

Cavg measured by SRM (mg/Nm^3)	Number of measurements [AMS/SRM]	Site's ELV (mg/Nm^3)	Min ELV by data reprocessing (mg/Nm^3)	Min ELV calculated by S_D (mg/Nm^3)	Min ELV calculated by S_D,min (mg/Nm^3)	Minimum expanded uncertainty to fulfil the variability test (%)
1,3	16	8	4,9	4,8	-	24,3
1,3	16	8	4,9	4,7	-	24,1

E8: Summary Sheet HF

Hydrofluoric Acid HF

SRM

NF X 43-304 Manual method

(1) Assuming Min ELV = 10 LoQ
(2) Based on 1 hour sampling
(3) Estimated expanded uncertainty based on the method's reproducibility

	SRM implementation characteristics			
	Analytical LoQ in mg	(1) LoQ in mg/Nm^3	(2) Min ELV in mg/Nm^3	(3) U_{max} (GUM) in %
filter	0.05-0.1	0.083-0.17	0.83-1.7	-
bubblers	0.025-0.05	0.041-0.08	0.83-1.7	-

AMS

75 % of the P relative uncertainty mandated by the IED at the Daily ELV:	30%

(4) Assuming Min ELV = 5 LoQ

		Values obtained during certification				
		Full scale (mg/Nm^3)	LoQ (mg/Nm^3)	(3) Min ELV (mg/Nm^3)	U(GUM) %	(4) C_U (mg/Nm^3)
	Gas Filter Correlation InfraRed (GFCIR)					
GFCIR-1	Dr Födisch MCA 10	20	0,096	0,48	10,6	10
	Fourrier Transform InfraRed (FTIR)					
FTIR-1	ABB Automation GmbH: Advance CEMAS FTIR – NT (ACF-NT)	5	0,2	1	31,5	2
FTIR-2	General Impianti GL GIGAS 10M	5	NC	-	19,9	2
FTIR-3	Gasmet Technologies OY: CX 4000, DX4000 & EN4000	3	<0.006	<0.03	18,4	1
FTIR-4	MKS Instruments Inc: MGS300	3	0,06	0,3	19,3	1
FTIR-5	SICK AG: MCS 100 FT	3	0,16	0,8	30,3	1
	Tunable Diode Laser Absorption Spectroscopy (TDLAS)					
TDLAS-1	SICK AG: GM700-2	5	NC	-	37,9	1
TDLAS-2	Unisearch associates LasIR	5	NC	-	16,4	1
TDLAS-3	Neo monitors AS: LaserGas II monitor	2	0,008	0,04	10,8	1
	Differential Optical Absorption Spectroscopy (DOAS)					
DOAS-1	OPSIS: AR 650	3	0,16	0,8	18,4	1

Data from QAL2 control reports

Cavg, ELV, S_D: expressed in mg/Nm^3 on dry gas at 11% O_2
Min ELV calculated = S_D x 1.96 x 100 / P - Min ELV calculated with SD,min= SD,min x 1.96 x 100 / P

Non-certified FTIR Analyser

Environnement SA Analyser - MIR FT (certified for other parameters)

Cavg measured by SRM (mg/Nm^3)	Number of measurements [AMS/SRM]	Site's ELV (mg/Nm^3)	Min ELV by data reprocessing (mg/Nm^3)	Min ELV calculated by S_D (mg/Nm^3)	Min ELV calculated by S_D,min (mg/Nm^3)	Minimum expanded uncertainty to fulfil the variability test (%)
0,1	6	1	0,2	0,020	-	0,8
0,1	6	1	0,1	0,005	-	0,2

E9: Summary Sheet NH_3

Ammonia NH_3

SRM

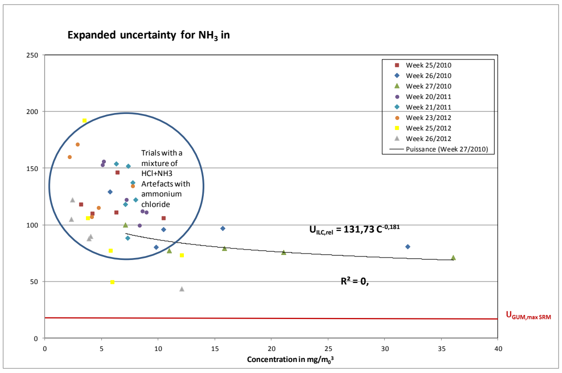
NF X 43-303 Manual method

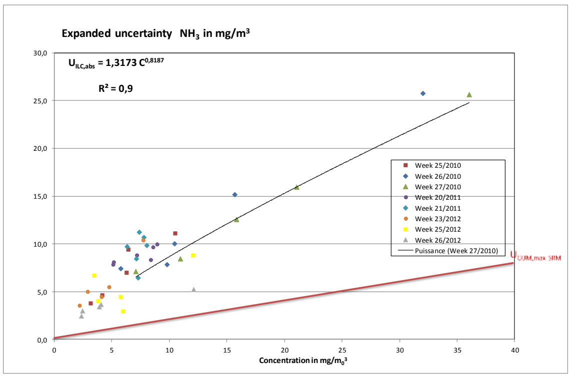
[1] Assuming Min ELV = 10 LoQ

[2] Based on 1 hour sampling

[3] Estimated expanded uncertainty based on the method's reproducibility

SRM implementation characteristics			
Analytical LoQ in mg/l	[1] LoQ in mg/Nm^3	[2] Min ELV in mg/Nm^3	[3]U_{max} (GUM) in %
0,05	0,083	0,833	-





AMS

75 % of the P relative uncertainty mandated by the IED at the Daily ELV:	30%

[4] Assuming Min ELV = 5 LoQ

		Values obtained during certification				
		Full scale (mg/Nm^3)	LoQ (mg/Nm^3)	[3] Min ELV (mg/Nm^3)	U(GUM) %	[4] C_U (mg/Nm^3)
	Non-Dispersive InfraRed (NDIR)					
NDIR-1	SICK AG: MCS 100E HW Multi-Component Analyser	20	0,22	1,1	12,4	10
	Gas Filter Correlation InfraRed (GFCIR)					
GFCIR-1	Environnement SA: MIR-9000 H	15	NC	-	6,9	10
GFCIR-2	Dr Födisch MCA 04	30	<0.06	<0.3	22,4	10
GFCIR-3	Dr Födisch MCA 10	10	0,012	0,06	14,2	5
	Fourrier Transform InfraRed (FTIR)					
FTIR-1	ABB Automation GmbH: Advance CEMAS FTIR – NT (ACF-NT)	15	0,68	3,4	12,5	10
FTIR-2	Environnement SA: MIR-FT	15	0,24	<1.2	6,6	10
FTIR-3	Protea Ltd: ProtIR 204 M	15	0,84	4,2	NC	NC
FTIR-4	Genral Impianti Ltd: GIGAS 10M	15	NC	-	10,6	10
FTIR-5	SICK AG: MCS 100 FT	10	0,092	0,46	6,4	10
FTIR-6	MKS Instruments Inc: MGS300	10	0,2	1	6,2	10
FTIR-7	Gasmet Technologies OY: CX 4000, DX4000 & EN4000	15	0,12	0,6	9,6	10
	Tunable Diode Laser Absorption Spectroscopy (TDLAS)					
TDLAS-1	Siemens SAS: LDS 6 Ammonia	20	0,88	4,4	19,7	10
TDLAS-2	Neo monitors AS: LaserGas II monitor	10	NC	-	5,4	10
TDLAS-3	Servomex Group Ltd: Servo tough Laser SP Model 2930	10	0,04	0,2	5,4	10
	Differential Optical Absorption Spectroscopy (DOAS)					
DOAS-1	OPSIS: AR 650	20	0,64	3,2	24,5	10
DOAS-2	OPSIS AB: AR 602Z	10	NC	-	5,5	10

Data from QAL2 control reports

Cavg, ELV, S_D: expressed in mg/Nm^3 on dry gas at 11% O_2

Min ELV calculated = S_D x 1.96 x 100 / P - Min ELV calculated with SD,min= SD,min x 1.96 x 100 / P

Cavg measured by SRM (mg/Nm^3)	Number of measurements [AMS/SRM]	Site's ELV (mg/Nm^3)	Min ELV by data reprocessing (mg/Nm^3)	Min ELV calculated by S_D (mg/Nm^3)	Min ELV calculated by S_D,min (mg/Nm^3)	Minimum expanded uncertainty to fulfil the variability test (%)
0,7	18	30	0,8	2,0	0,7	2,7
0,7	18	30	1,0	1,7	0,9	2,2

Cavg measured by SRM (mg/Nm^3)	Number of measurements [AMS/SRM]	Site's ELV (mg/Nm^3)	Min ELV by data reprocessing (mg/Nm^3)	Min ELV calculated by S_D (mg/Nm^3)	Min ELV calculated by S_D,min (mg/Nm^3)	Minimum expanded uncertainty to fulfil the variability test (%)
9,9	18	10	8,2	7,5	7,0	31,5
9,9	18	10	8,2	7,5	7,2	31,5

E10: Summary Sheet mercury

Mercury Hg

SRM

NF EN 13211 Manual method
(1) Assuming Min ELV = 10 LoQ
(2) Based on 1 hour sampling
(3) Estimated expanded uncertainty based on the method's reproducibility

	SRM implementation characteristics			
	Analytical LoQ in µg/l or µg	(1) LoQ in µg/Nm^3	(2) Min ELV in en µg/Nm^3	U_{max} (GUM) in %
filter	0.05-0.1	0.024-0.048	0.24-0.48	-
bubblers	0.5-1.0			

Values obtained through validation of EN 13211		
C_{SRM} en µg/m$_0^3$	04 - 10	40 - 100
(3) U en %	42	26

C_{SRM}: Concentration level

AMS

(4) Assuming Min ELV = 5 LoQ

Mandatory IED uncertainty at the Daily ELV (75% U_{max})	-

	Values obtained during certification				
Zeeman Effect Atomic Absorption	Full scale	LoQ	(4) Min ELV	U (GUM)	(5) C_U
SICK Maihak: MERCEM 300Z	10	0,08	0,4	2,3	30
UV CVAAS Cold Vapour Atomic Absorption Catalytic Reduction					
Mercury Instruments GmbH: SM-4	30	0,024	0,12	12,7	20
Verewa GmbH: HM 1400 TRX Mercury Analyser	45	0,2	1	8,4	30
UV DOAS Catalytic Reduction					
OPSIS AB: AR 602Z	45	0,72	3,6	10,7	30
	median	**0,14**	**0,7**	**9,55**	