



HAL
open science

Uncertainty of emission measurements for manual and automatic reference methods. Comparison between uncertainty budget approach and inter-laboratory field test approach

Jean Poulleau, Cécile Raventos, Frans Blank, Lukas Emmenegger, Richard Gould, Hakan Kassman, Emile Pilage, Serge Reynaud, Joern Rokkjaer, Michael Waeber

► To cite this version:

Jean Poulleau, Cécile Raventos, Frans Blank, Lukas Emmenegger, Richard Gould, et al.. Uncertainty of emission measurements for manual and automatic reference methods. Comparison between uncertainty budget approach and inter-laboratory field test approach. Workshop on Quality Assurance Quality Control and Accreditation, May 2003, Prague, Czech Republic. ineris-00972425

HAL Id: ineris-00972425

<https://ineris.hal.science/ineris-00972425>

Submitted on 3 Apr 2014

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

UNCERTAINTY OF EMISSION MEASUREMENTS FOR MANUAL AND AUTOMATIC REFERENCE METHODS

COMPARISON BETWEEN UNCERTAINTY BUDGET APPROACH AND INTER-LABORATORY FIELD TEST APPROACH

Jean Poulleau (INERIS, F) with the collaboration of Cécile Raventos (INERIS), Frans Blank (KEMA, NL), Lukas Emmenegger (EMPA, CH), Richard Gould (Environmental Agency, GB), Hakan Kassman (SwedPower, S), Emile Pilage (KEMA, NL), Serge Reynaud (CETIAT, F), Joern Rokkjaer (Eurofins, DK), Michael Waeber (TÜV München, D)

1. INTRODUCTION

Many European laboratories are nowadays accredited according to the new quality assurance standard ISO EN 17025 which requires that the operator identifies all components of the uncertainty of the method implemented and makes a reasonable estimation of the overall uncertainty attached to the measurement results.

This estimation has to be based on the knowledge of the performance characteristics of the method. Two techniques are proposed:

- Systematic evaluation of factors that influence the result and their associated standard uncertainty on the basis of theoretical knowledge and practical experience.
- In-field comparison between laboratories

The Guide to the expression of uncertainty in measurement and the recent ISO 14956 provide tools to estimate the uncertainty from actual or claimed values of all performance characteristics of a method and the way to calculate the overall uncertainty of the method. When the overall uncertainty has been calculated, the method must be tested under field conditions in order to verify that its performance data and calculated measurement uncertainty comply with results obtained under field conditions (ISO 14956 & 9). The ISO 5725-2 provides the guidelines and tools to plan these intra or inter-laboratory campaigns.

Today most CEN standards identify the major sources of uncertainty contributing to the measurand and often provide criteria for acceptance related to the main performance characteristics as well as to the overall uncertainty. Examples of uncertainty budget set up according to the GUM approach are provided and performance characteristics in the field of the method are also given. Finally repeatability and reproducibility data as a function of the concentration are provided.

The aim of this presentation is to give a comparison of the GUM approach which gives an overall uncertainty calculated through an uncertainty budget and the field approach which gives repeatability and reproducibility uncertainties. Two examples will be shown from the experiences within CEN TC264 WG16 by means of a manual reference method for SO₂ and an automatic reference method for NO_x.

2. UNCERTAINTY BUDGETS / FIELD VALIDATION : THE COMPARISON

2.1 UNCERTAINTY BUDGET ACCORDING TO GUM OR ISO 14956

Performance characteristics indicate the deviation from a perfect measurement and therefore contribute to the uncertainty of the measurement result. The combined impact of the performance characteristics on the measurement result is quantified by measurement uncertainty the calculation of which is based on the law on propagation of uncertainty stipulated in the GUM.

The operator has to follow several steps:

- Determine the analytical function relating the measured value to the input quantities.
- Identify all major sources of uncertainty contributing to any of the input quantities or to the measurand directly.
- Calculate or evaluate uncertainty components expressed in standard uncertainties of input and influence quantities.
- Calculate the combined standard uncertainty and the expanded uncertainty.

2.1.1 NO_x standard (automatic method)

2.1.1.1 Presentation of the standard

This draft European standard describes a reference method for sampling and determining the content of nitrogen oxides (NO_x) in ducts and stacks emitting to the atmosphere by means of a continuous analyser using the chemiluminescence principle. The specific components, the requirements for the sampling system and the chemiluminescence analyser are described.

The chemiluminescence analyser is combined with an extractive sampling system and a gas conditioning system. A representative sample of gas is taken from the stack with a sampling probe and conveyed to the analyser through the sampling line and gas conditioning system.

Five different sampling and conditioning configurations in order to avoid water condensation in the measuring system are proposed and considered as equivalent.

2.1.1.2 Establishment of the uncertainty budget

When this European standard is used as a reference method, the user must demonstrate that :

- the performance characteristics of the method given in Table 1 are lower than the associated performance criteria, and,
- the overall uncertainty calculated by combining values of selected performance characteristics by means of an uncertainty budget is less than 10% at the emission limit value, before correction on dry basis and to O₂ reference concentration (when corrections are relevant).

The values of the selected performance characteristics have to be evaluated by means of both a laboratory test and field test. Performance criteria are given in Table 1 (annex).

An uncertainty budget must be established to determine whether the analyser and its associated sampling system fulfils the requirements for a maximum allowable overall uncertainty (10% at the emission limit value). This uncertainty budget must be drawn up according to the procedures described in ISO 14956 or GUM, taking into account all the relevant characteristics included in the calculation of overall uncertainty given in Table 1.

2.1.2 SO₂ standard

2.1.2.1 Presentation

This proposed European standard describes a manual reference method. A representative sample of gas is extracted via a temperature-controlled probe. The sample is filtered and drawn through hydrogen peroxide absorber solutions for a specified time and at a controlled flow rate. The sulphur dioxide in the sampled gas is absorbed and oxidised to sulphate ion. The mass concentration of sulphate in the absorption solutions is subsequently determined using ion chromatography or by titration with a barium perchlorate solution using Thorin as an indicator.

2.1.2.2 Uncertainty budgets

The specific components and requirements for the measuring system are described. A number of performance characteristics with associated minimum performance criteria are given for the sampling system (see Table 2 in annex). The overall uncertainty of the method must meet the specifications given in this European Standard.

When this European standard is used as a reference method, the user has to demonstrate that:

- performance characteristics of the method given in Table 2 are lower than the performance criteria, and,
- the overall uncertainty calculated by combining values of selected performance characteristics by means of an uncertainty budget is less than $\pm 20\%$ at the emission limit value.

The values of the selected performance characteristics shall be evaluated:

- for the sampling step: by means of laboratory tests in order to determine uncertainty of the calibration of the equipment and by means of field tests in order to determine other parameters
- for the analytical step: by means of laboratory tests taking the standard deviation of repeatability calculated during an interlaboratory comparison. A maximum performance criteria is given in the following Table 3 (in annex).

The overall uncertainty for this method used as a reference shall be lower than $\pm 20\%$ at the emission limit value.

2.2 FIELD VALIDATION ACCORDING TO ISO 5725-2

Field validation is a valuable complement to the determination of the overall uncertainty according to the GUM approach and can validate this first approach.

Furthermore field validation must be used when some uncertainty components are difficult to evaluate or when the measurement process cannot always be modelled (sampling, losses in the line, leakage, etc.). Field validation can facilitate the studying of the influence of influent parameters.

Finally parallel measurements implemented by one or several teams can reveal the existence of systematic deviation which was not obvious when implementing the GUM approach.

ISO 5725-2 describes the method to be followed when carrying out such parallel measurements and it gives the tools to evaluate the repeatability and reproducibility of the method.

For stack measurements, the characteristics of the flue gases are not constant. Therefore the repeatability in the field is calculated from results given by parallel measurements implemented by the same team and operator.

Repeatability standard deviation s_r , internal confidence interval (CI_r) and repeatability in the field r are calculated according to ISO 5725-2, from the results of the double measurements implemented by the same laboratory.

$$CI_r = t_{0,95;n-1} \cdot s_r \qquad r = \sqrt{2} \cdot t_{0,95;n-1} \cdot s_r$$

where:

- CI_r : internal confidence interval
- s_r : repeatability standard deviation
- $t_{0,95;n-1}$: student factor for a level of confidence of 95% and a degree of freedom of n-1 (n: number of double measurements)
- r : repeatability in the field

Reproducibility standard deviation s_R , external confidence interval (CI_R) and reproducibility in the field R are calculated according to ISO 5725-2, from the results of parallel measurements performed simultaneously by several laboratories.

$$CI_R = t_{0,95;np-1} \cdot s_R \qquad R = \sqrt{2} \cdot t_{0,95;np-1} \cdot s_R$$

where:

- CI_R external confidence interval
- s_R : repeatability standard deviation
- $t_{0,95;np-1}$: student factor for a level of confidence of 95% and a degree of freedom of np-1 (n: number of measurements; p: number of laboratories)
- R : reproducibility in the field

3. COMPARISON BETWEEN GUM APPROACH AND FIELD TEST RESULTS

The overall combined uncertainty U_c obtained from the GUM approach is compared to the CI_r and CI_R obtained from six field tests performed on waste incineration installations, co-incineration installations and large combustion plants. Four different European measuring teams took part to each field test.

The comparison is made for SO_2 and NO_x measurements for Field Tests 5 and 6. Here each participating team prepared its own uncertainty budget drawn up for the specific conditions of each site and for the specific characteristics of its sampling and analytical measurement devices.

3.1 COMPARISON FOR AN AUTOMATIC METHOD (NOX)

The tests performed in 6 different stacks have led to the equations:

$$CI_r = 0,029 C + 2 \text{ mg/m}_0^3 \quad \text{and} \quad CI_R = 0,0377 C + 4,4 \text{ mg/m}_0^3$$

Tables 4 and 5 summarises the results of the uncertainty budgets of the 4 laboratories participating in field tests 5 and 6.

As seen in these tables, the overall uncertainties vary considerably.

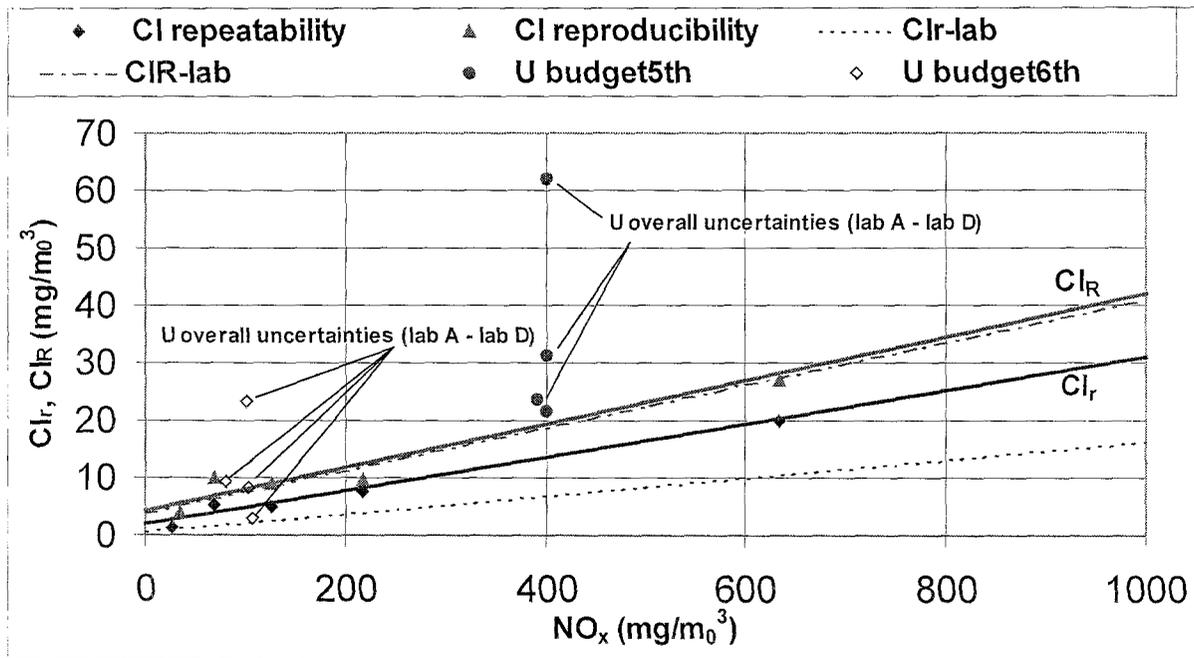


Figure 1 — Comparison for an automated method

The main reason is that the performance characteristics are not known by the laboratory implementing the uncertainty budget calculation with a sufficient accuracy at the measured concentration. Actually the performance characteristics determined by test houses are often expressed in % of the range and correspond to the maximum deviation found on all the range. Moreover, some test houses give certificates that only stipulate if the instrument fulfils the criteria or not and no actual performance characteristics are given. It seems essential to know the performance characteristics of the analyser at different levels of concentration: at the Emission Limit Value but also at lower values (the regulation will demand lower ELV in the future). In concrete terms, the determination of the performance characteristics at 20, 40, 60 and 80% of the range seems to be necessary.

If the present situation persists where the information available from the test houses is very limited, then the implementation of the uncertainty budgets can be biased and there is no more interest to do the exercise. To illustrate and quantify the importance of this problem, let us consider the example of the performance characteristics of "lack of fit".

The results of the "lack of fit" test is :

- Deviation at 20% of the range (20% of 1000ppm) : -3 ppm
- Deviation at 40% of the range (20% of 1000ppm) : 10 ppm
- Deviation at 60% of the range (20% of 1000ppm) : 15 ppm
- Deviation at 80% of the range (20% of 1000ppm) : -5 ppm

As we can notice, the maximum deviation is 15 ppm and corresponds to 1,5% of the range.

1. Some test houses may report that the instrument behaviour is satisfactory because the maximum deviation in lack of fit is lower than the criterion (2% of full range).
2. Other test houses may report that the maximum deviation is 15 ppm and corresponds to 1,5% of the range.
3. Other test houses may give the values at each different tested concentrations which is much more valuable for the labs.

Let us presume an uncertainty budget at 200 ppm. According to the available information, the contribution of the parameter "lack of fit" may strongly differ:

1. Hypothesis 1: the result is given with an uncertainty of +/- 2% of the full range (+/- 20 ppm)
2. Hypothesis 2: the result is given with an uncertainty of +/- 1,5% of the full range (+/- 15 ppm)
3. Hypothesis 3: the result is given with an uncertainty of +/- 3 ppm

The uncertainty contribution of "lack of fit" which should correspond to Hypothesis 3 is multiplied by a factor 5 in Hypothesis 2 and multiplied by a factor 7 in Hypothesis 1.

Thus the overall uncertainty U_c determined by the uncertainty budget can lead to very high values compared to the data from repeatability and reproducibility in the field tests (1 to 3 times CI_R). This phenomenon should be reduced when the budget is established at concentrations close to the full range. It seems that Lab. B for field test 5 and Lab. A for field test 6 were in configuration 1 or 2 (they have a tremendous contribution for some performance characteristics in comparison with the other laboratories).

Another factor that may create some deviation between both uncertainty approaches is the fact that the operator sometimes does not know the range of variation of influent parameters such as the ambient temperature, voltage, flow-rate, atmospheric pressure, etc. during the field experiments. These parameters are not often controlled. Therefore, the operator uses a "standard" range of variation of these parameters that is wider than the actual range encountered in the field. Thus the contribution of these parameters can be maximised by a factor of two or more.

3.2 COMPARISON FOR A MANUAL METHOD (SO₂)

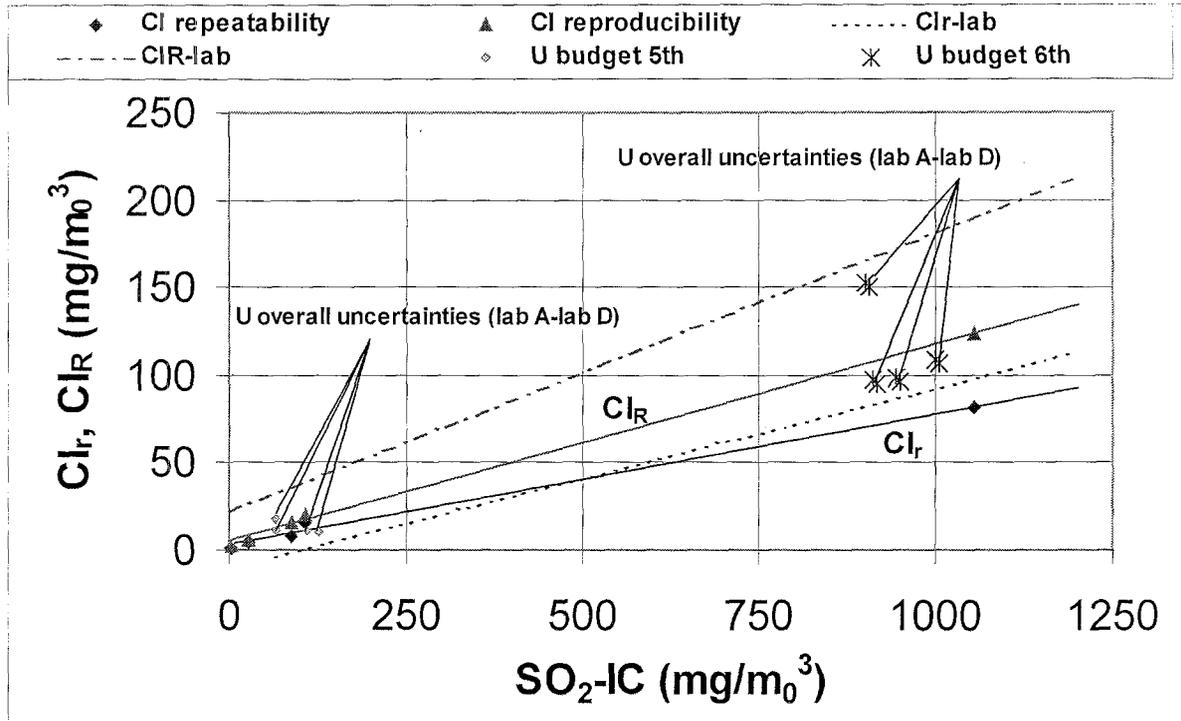


Figure 2 — Comparison for a manual method

The tests performed in 6 different stacks have led to the equations:

$$Cl_r = 0,08 C + 3 \text{ mg/m}_0^3 \quad \text{and} \quad Cl_{R-lab} = 0,113 C + 5,4 \text{ mg/m}_0^3$$

Tables 6 and 7 summarises the results of the uncertainty budgets of the 4 laboratories participating in field tests 5 and 6 for the manual method. It is observed for SO₂ manual method that, the results provided by the uncertainty budget can be very close to what is established in the field during an intercomparison. The main reason for this is that the most important component of the uncertainty budget is the uncertainty of analysis, which has already been determined by interlaboratory tests. All the other components have a rather minor effect on the overall uncertainty and are well known owing to on-going QA/QC metrological controls, regularly performed in each laboratory.

4. CONCLUSIONS

The GUM approach is very convenient to study the parameters making the major contribution to the overall uncertainty in order to focus the attention on them.

But it requires several minimum conditions to lead to realistic overall uncertainty data:

1. to be trained to handle uncertainty budgets
2. to have sufficient information on the performance characteristics of the method
3. to know which are the variation range of influent parameters in the field to make the comparison with field approach consistent

These three minimum conditions to obtain reliable results from the GUM approach are not easy to fulfil. In this presentation, it has been demonstrated that the laboratories need to have available enough information on performance characteristics at the studied concentration. It must be noted that the level of information given by test houses is often not suitable to establish an accurate uncertainty calculation for automatic methods. This problem, demonstrated by the present study, must be taken into consideration by the CEN TC264/WG22.

The overall uncertainty calculated through an uncertainty budget can, however, be close to the repeatability confidence interval obtained during field tests, when the previous conditions are met. However it is generally lower than the reproducibility confidence interval since systematic deviations due to the implementation of the method are not considered.

Our final conclusion will be to reinforce the requirement of ISO 14956: test the method under field conditions in order to verify that its performance data and measurement uncertainty calculated according to an uncertainty budget, comply with results obtained under field conditions.

5. REFERENCES

Example of an uncertainty budget for NO_x at a specific site of CENTC264 WI264043

Example of an uncertainty budget for SO₂ at a specific site of CENTC264 WI264042

6. ANNEX

Tables1 to 7

Table 1 — Relevant performance characteristics of the analyser and criteria to be evaluated

Performance characteristic	Lab. test	Field test	Performance criteria	Performance characteristic
Response time	X		≤ 200 s	
Detection limit	X		$\leq \pm 2$ % of the range	
Lack of fit	X		$\leq \pm 2$ % of the range	X
Zero drift	X		$\leq \pm 2$ % of the range/ 24 hours	X
Span drift	X		$\leq \pm 2$ % of the range/ 24 hours	X
Sensitivity to atmospheric pressure	X		≤ 3 % of the range for 2 kPa	X
Sensitivity to sample volume flow of sample pressure	X		(1)	X
Sensitivity to ambient temperature	X		≤ 3 % of the range/10 K	X
Sensitivity to electric voltage	X		≤ 2 % of the range/10V	X
Interferents (2)	X		Total $\leq \pm 4$ % of the range	X
Converter efficiency	X		≥ 95 %	X
Losses and leakage in the sampling and conditioning system		X	≤ 2 % of the measured value	X
Standard deviation of repeatability in laboratory at zero	X		≤ 1 % of the range	X (3)
Standard deviation of repeatability in laboratory at span level	X		≤ 2 % of the range	X (3)
Uncertainty of calibration gas		X	≤ 2 %	X

(1) The tested volume flow range or pressure is defined in the manufacturer's recommendations.

(2): interferents that shall be tested are at least those given in table 2

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

Table 2 — Relevant performance characteristics of the sampling procedure

Performance characteristic	Lab. Test	Field test	Performance criterion
SAMPLING			
Choice of the sampling point when the flow gas is not homogeneous		X	
Determination of the volume of the absorption solution		X	$\leq \pm 1 \%$ of the volume of solution
Volume gas meter: uncertainty of sample volume ⁽²⁾ uncertainty of temperature ⁽²⁾ uncertainty of absolute pressure ⁽²⁾	X ⁽¹⁾ X ⁽¹⁾ X ⁽¹⁾		$\leq \pm 2 \%$ of the volume of gas sampling ⁽¹⁾ $\leq \pm 2,5 \text{ K}$ ⁽¹⁾ $\leq \pm 1 \%$ of the absolute pressure ⁽¹⁾
Absorption efficiency ⁽³⁾		X	$> 95\%$
Leak in the sampling line		X	$\leq 2\%$ of the nominal flow rate
Value of the field blank		X	$\leq 10 \%$ of VLE

⁽¹⁾: Performance criteria corresponding to the uncertainty of calibration.

⁽²⁾: The uncertainty of the sampled volume is a combination of uncertainties due to: calibration, drift (random drift, drift between 2 calibrations), resolution, reading.

The uncertainty of temperature and absolute pressure at the gas volume meter is a combination of uncertainties due to: calibration, drift (random drift, drift between 2 calibrations), resolution, reading, and repeatability.

⁽³⁾: This characteristic is an assurance quality check to quantify the absorption efficiency in the first absorber; but it doesn't quantify a possible loss of absorption, and therefore it is not included in calculation of overall uncertainty

Table 3— Performance characteristics of analyse procedure

Performance characteristic	Lab. Test	Field test	Performance criterion
Standard deviation of the repeatability of the analysis of sulphate ions	X		$\leq 7 \%$ of the measured value (value of quantity of sulphate ions in the solution; in $\text{mg SO}_4^{2-}/\text{l}$)

Uncertainty components	Lab A	Lab B	Lab C	Lab D
	Variance			
Lack of fit	8.33	33.33	5.88	4.08
Zero drift	0.00	0.00	0.00	0.00
Span drift	3.00	33.33	2.08	0.04
Sensitivity to sample flow rate	5.33	3.00	0.40	0.07
Sensitivity to atmospheric pressure	0.85	0.00	0.33	0.00
Sensitivity to ambient temperature	8.33	65.33		
Sensitivity to electric voltage	1.92	8.33	2.08	0.33
Interferent NH3	0.19	0.85	0.33	0.08
Interferent CO2	0.02	0.02	0.16	0.08
Standard deviation of repeatability of measurement	9.00	25.00	4.00	0.00
calibration gas	0.93	3.64	3.42	3.26
Converter efficiency	0.58	0.73	0.58	2.58
Drift between 2 controls	0.33	0.48	0.33	0.33
Standard deviation of repeatability of converter efficiency	0.25	0.25	0.25	2.25
Studied concentration of NOx (ppm at O2ref)	194.8	194.8	194.8	189.9
Studied concentration of NOx (mg/m3 at O2ref)	400	400	400	390
Overall uncertainty: U(CNOx,mg/m3)	31.20	62.00	21.60	23.79
Overall uncertainty: U(C _{NOx,ppm}) %	7.80	15.50	5.40	6.1

Table 4 — Field Test 5: Uncertainty budgets

Uncertainty components	Lab A	Lab B	Lab C	Lab D
	Variance			
Lack of fit	5.33	0.33	0.06	0.08
Zero drift	0.00	0.00	0.00	0.00
Span drift	3.00	0.33	0.02	0.96
Sensitivity to sample flow rate	5.33	0.01	0.00	0.00
Sensitivity to atmospheric pressure	0.85	0.00	0.00	1.92
Sensitivity to ambient temperature	3.00	0.48		0.21
Sensitivity to electric voltage	1.92	0.08	0.02	0.00
Interferent NH3	0.19	0.00	0.08	0.01
Interferent CO2	0.00	0.00	0.16	0.03
Standard deviation of repeatability of measurement	4.00	0.25	0.04	0.36
calibration gas	0.06	0.15	0.00	0.00
Converter efficiency	0.58	0.73	0.58	1.21
Drift between 2 controls	0.33	0.48	0.33	0.96
Standard deviation of repeatability of converter efficiency	0.25	0.25	0.25	0.25
Studied concentration of NOx (ppm at O2ref)	48.7	39.0	51.6	50.2
Studied concentration of NOx (mg/m3 at O2ref)	100.0	80.1	106.0	103
Overall uncertainty: U(CNOx,mg/m3)	23.4	9.5	3.0	8.3
Overall uncertainty: U(C _{NOx,ppm}) %	23.40	7.60	3.20	8.6

Table 5 — Field Test 6: Uncertainty budgets

Uncertainty components	Lab A			Lab B			Lab C			
	Standard uncertainty	Relative standard uncertainty	Relative standard variance	Standard uncertainty	Relative standard uncertainty	Relative standard variance	Standard uncertainty	Relative standard uncertainty	Relative standard variance	Standard uncertainty
Volume of solution (u in ml)										
Sample solution	0.277	4.62E-03	2.13E-05	0.370	4.62E-03	2.13E-05	0.058	5.77E-04	3.33E-07	1.062
Analyse (u in mg SO ₄ ²⁻ /l solution)										
Sample solution	4.121	0.08	0.0064	5.557	0.05	2.50E-03	0.189	0.05	2.50E-03	5.700
Volume of gas sampling (u in m ³)										
Uncertainty of adjustment	0.00035			0.00060			0.00045			0.00097
Drift between 2 adjustments	0.00020			0.00035			0.00000			0.00000
Standard deviation of repeatability of measurement	1.05E-04			1.80E-04			9.00E-05			1.94E-04
Resolution	0.000			0.000			0.000			0.000
Reading	0.0006			0.0006			0.0003			0.0006
Standard deviation of mean	0.0009	0.026	6.87E-04	0.0011	0.018	3.28E-04	0.0006	0.014	1.87E-04	0.0013
Temperature at gas volume meter (u in K)										
Uncertainty of adjustment	1.00			0.25			1.50			0.75
Drift between 2 adjustments	0.000			0.000			0.000			0.000
Std deviation of repeat. of measurement	0.020			0.020			0.003			0.000
Resolution	0.2887			0.0029			0.2887			0.2887
Reading	0.000			0.000			0.289			0.289
Standard deviation of mean	1.000			0.566			0.707			0.082
Standard deviation of mean	1.444	4.98E-03	2.48E-05	0.619	2.15E-03	4.62E-06	1.708	5.73E-03	3.28E-05	0.858
Relative pressure at gas volume meter (u in Pa)										
Uncertainty of adjustment	0.75			0.75			0.50			0.75
Drift between 2 adjustments	0.000			0.000			0.577			0.289
Std deviation of repeat. of measurement	0.300			0.300			1.000			0.000
Resolution	0.144			0.144			2.887			1.443
Reading	0.000			0.000			2.887			1.443
Standard deviation of mean	7.07	u (Prel)/Pm		1.02	u (Prel)/Pm		0.00	u (Prel)/Pm		0.00
Standard deviation of mean	7.119	7.41E-05	5.50E-09	1.309	1.36E-05	1.86E-10	4.272	4.63E-04	2.14E-07	2.194
Atmospheric Pressure (u in Pa)										
Overall uncertainty of adjustment	50.0			85.0			25.0			10.0
Drift between 2 adjustments	34.6			34.6			1.7			34.6
Resolution	0.00			0.00			0.87			2.89
Reading	28.87			2.89			0.87			2.89
Standard deviation of mean	67.3	u (P _{atm})/P _m		100.00	u (P _{atm})/P _m		7.07	u (P _{atm})/P _m		14.14
Standard deviation of mean	67.3	7.01E-04	4.92E-07	135.8	1.41E-03	2.00E-06	26.1	2.82E-03	7.97E-06	38.9
Field blank (in mg/m ³ (n))	0.026			0.054			0.016			0.002
Corr fb (in mg/m ³ (n) at O ₂ ,ref)										
Studied concentration (mg/m ³ (n) at 11% O ₂)	66.0			110.0			67			125.1
Field blank (mg SO ₂ /m ³ (n) at 11% O ₂)	0.3			1.0			0.3			0
Overall uncertainty: U(C _n) %	16.9			10.7			10.5			10.5
Overall uncertainty: U(C _{n,th,corr}) %	17.4			11.6			10.9			10.5
Overall uncertainty: U(C _{n,th,corr}) mg/m ³ (n)	11.5			12.8			7.3			13.1

Table 6 — Field Test 5: Uncertainty budgets

Uncertainty components	Lab A		Lab B		Lab C		Lab D	
	Standard uncertainty	Relative standard variance						
Volume of solution (u in ml)								
Sample solution	0.277	2.13E-05	0.370	2.13E-05	0.058	3.33E-07	0.231	2.13E-05
Analyse (u in mg SO₄²⁻/l solution)								
Sample solution	56.587	0.0064	51.571	2.50E-03	2.916	2.50E-03	15.009	0.0025
Volume of gas sampling (u in m³)								
Uncertainty of adjustment	0.00035		0.00060		0.00045		0.00120	
Drift between 2 adjustments	0.00020		0.00035		0.00000		0.00069	
Standard deviation of repeatability of measurement	1.05E-04		1.80E-04		9.00E-05		3.60E-04	
Resolution	0.000		0.000		0.000		0.000	
Reading	0.0006		0.0006		0.0003		0.0006	
	0.0009	6.87E-04	0.0011	3.28E-04	0.0006	1.87E-04	0.0016	1.89E-04
Temperature at gas volume meter (u in K)								
Uncertainty of adjustment	1.00		0.25		1.50		1.50	
Drift between 2 adjustments	0.000		0.000		0.000		0.000	
Std deviation of repeat. of measurement	0.020		0.020		0.003		0.020	
Resolution	0.2887		0.0029		0.2887		0.2887	
Reading	0.000		0.000		0.289		0.000	
Standard deviation of mean	1.000		0.566		0.707		0.707	
	1.444	2.51E-05	0.619	4.62E-06	1.708	3.59E-05	1.683	3.49E-05
Relative pressure at gas volume meter (u in Pa)								
Uncertainty of adjustment	0.75		0.75		0.50		0.75	
Drift between 2 adjustments	0.000		0.000		0.577		0.577	
Std deviation of repeat. of measurement	0.300		0.300		1.000		1.000	
Resolution	0.144		0.144		2.887		2.887	
Reading	0.000		0.000		2.887		2.887	
Standard deviation of mean	7.07		1.02		0.00		0.00	
	7.119	5.50E-09	1.309	1.78E-10	4.272	1.95E-07	4.308	1.98E-07
Atmospheric Pressure (u in Pa)								
Overall uncertainty of adjustment	50.0		85.0		2.5		25.0	
Drift between 2 adjustments	34.6		34.6		1.7		1.7	
Resolution	0.00		0.00		0.87		0.87	
Reading	28.87		2.89		0.87		2.89	
Standard deviation of mean	0.00		100.00		7.07		0.00	
	67.3	4.92E-07	135.8	1.92E-06	7.8	6.48E-07	25.2	6.80E-06
Field blank (in ng/m³(n))	0.026		0.108		0.011		0.080	
Corrb (in mg/m³(n) at O₂,ref)								
Studied concentration (mg/m³(n) at 11%O₂)	900.0		1000.0		94		911	
Field blank (mg SO ₂ /m ³ (n) at 11%O ₂)	0.3		2.0		0.2		1.5	
Overall uncertainty: U(C _n) %	16.9		10.7		10.5		10.5	
Overall uncertainty: U(C _{n(meas)}) %	17.0		10.9		10.5		10.7	
Overall uncertainty: U(C _{n(air)}) mg/m ³ (n)	153.0		109.0		99.1		97.5	

Table 7 — Field Test 6: Uncertainty budgets