



Uncertainty budget and interlaboratory field tests in SO₂ and NO_x emission measurements

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 budget and interlaboratory field tests in SO₂ and NO_x emission measurements. 6. International Conference on emission monitoring, Jun 2004, Milan, Italy. pp.NC. ineris-00972457

HAL Id: ineris-00972457

<https://ineris.hal.science/ineris-00972457>

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 budget and interlaboratory field tests in SO₂ and NO_x emission measurements

Authors

Jean Poulleau, INERIS, BP 2, 60550 Verneuil en Halatte, France – jean.poulleau@ineris.fr

Cécile Raventos, INERIS, BP 2, 60550 Verneuil en Halatte, France

Frans Blank, KEMA NV, PO Box 9035, 6800 Arnhem, Netherlands

Lukas Emmenegger, EMPA, Ueberlandstrasse 129, CH-8600 Dübendorf, Switzerland

Richard Gould, Environment Agency, Cameron House, White Cross, Lancaster LA1 4XQ, United Kingdom

Hakan Kassman, SwedPower, PO Box 1046, 611 29, Nyköping, Sweden

Emile Pilage, KEMA NV, PO Box 9035, 6800 Arnhem, Netherlands

Serge Reynaud, 25 av. des Arts, 69603 Villeurbanne, France

Joern Rokkjaer, AEA Technology, Abingdon Oxfords Ox14 3DE, United Kingdom

Michael Waeber, TUV Süddeutschland, Westendstr. 199, 80686 München, Germany

Abstract

This paper compares two techniques to assess uncertainty on emission measurements. The first one, described in ISO 14956, gives an appropriate procedure to establish uncertainty budgets from systematic assessment of factors influencing the result. The second approach consists in the quantification of the fidelity of the method during inter and intra-laboratory field experiments set out according to ISO 5725-2.

The comparison has been carried out for two reference methods described in the drafts prepared by CEN/TC264/WG16.

For the SO₂ manual reference method

Uncertainty budgets lead to very realistic overall uncertainty comparable to the repeatability and reproducibility confidence intervals determined in field tests. This agreement is reached thanks to the fact that the major contribution to the uncertainty calculation is the analysis reproducibility, determined during an inter-laboratory exercise.

For the NO_x automatic method, the comparison shows rather big discrepancies between both approaches and enlightens the conclusion that a rather good reliability can be reached using the uncertainty budget approach only if the following conditions are met:

- trained personnel to correctly establish and interpret uncertainty budgets,
- sufficient information on the performance characteristics of the method at the studied concentration,

knowledge of the variation range of influent parameters in the field, such as temperature, humidity, voltage, etc.

1. Introduction

Many European laboratories are nowadays accredited to the quality assurance standard for the competence of testing and calibration laboratories, ISO/IEC EN 17025 [15]. Among other things, this Standard requires the laboratory to identify all uncertainty components of the implemented method and gives a reasonable estimation of the overall uncertainty attached to the measurement results. For the validation of methods, mainly main techniques are proposed:

- A systematic assessment of factors influencing the result and their associated standard uncertainty on the basis of theoretical principles and practical experience.
- Interlaboratory (in-field) comparisons.

Furthermore, a thorough validation of the method will include field tests to verify that its performance data and calculated measurement uncertainty comply with results obtained under field conditions. Appropriate procedures for air quality measurements - whose output is a defined time average - are described in EN ISO 14956. These methods are well suited for the evaluation of emission measurement techniques. Finally, the ISO 5725-2 provides guidelines and tools to plan such intra or inter-laboratory campaigns [14].

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. Recent standards for ambient air measurements and their concepts with respect to uncertainty have been discussed by E. Sneek [11]. A review of the recommendations given in EN 13005, the ISO Guide to the Uncertainty of Measurement (GUM)(reference?), with special focus on ambient air and stack emission monitoring has been published by R. Beier and R. Kordecki [1]. This paper will focus on emission measurements and give examples of uncertainty budgets determined according to the GUM. The results will then be compared to performance characteristics obtained in inter and intra-laboratory field experiments.

The examples are taken from the work carried out by CEN/TC264/WG16 which is mandated to develop five standards for the measurement of O₂, CO, NO_x, H₂O and SO₂, as well as a technical report describing how to evaluate equivalent methods [6, 7, 8, 9, 10]. This paper discusses the manual reference method for SO₂ and the automatic reference method for NO_x. The extensive international laboratory and field testing provide an excellent opportunity to compare the overall uncertainty calculated through an uncertainty budget (GUM) with the field approach yielding uncertainties for (intra-laboratory) repeatability and (inter-laboratory) reproducibility.

2. Uncertainty budget

Performance characteristics indicate the deviation from a perfect measurement and therefore describe the contribution of a single element to the total uncertainty of the measurement result. The combined impact of the performance characteristics on the measurement result is quantified by the overall measurement uncertainty, the calculation of which is based on the law on propagation of uncertainty as stipulated in the GUM. Calculating the expanded uncertainty then provides a confidence interval within which the accepted reference value is expected to lie, typically with a 95% level of confidence.

To associate the expanded uncertainty with an analytical result, the laboratory has to perform the following 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 as standard uncertainties of input and influence quantities.

- Calculate the combined standard uncertainty and the expanded uncertainty.

The following paragraphs briefly describe the SO₂ and NO_x reference methods, each followed by an overview of the specific requirements that are given in the standards and the relevant EU directives with respect to measurement uncertainty.

SO₂ standard (manual method)

The draft European standard prEN 14791 describes a manual reference method. A representative sample of gas is extracted via a temperature controlled probe. It is then 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. The standard describes the specific components and requirements for sampling and analysis. For the sampling system, a number of performance characteristics with associated minimum performance criteria are given as shown in Table 1.

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

- the performance characteristics of the method are lower than the performance criteria given in Table 1, 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 and field tests in order to determine uncertainty of the calibration and other parameters, and,
- for the analytical step: by means of laboratory tests taking the standard deviation of repeatability calculated during an inter-laboratory comparison. A performance better than 7 % of the measured value is required by the standard.

NO_x standard (automatic method)

The draft European standard prEN 14792 describes a reference method by means of a continuous analyser using the chemiluminescence principle for sampling and determining the content of nitrogen oxides (NO_x) in ducts and stacks emitting to the atmosphere. 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 equivalent sampling and conditioning configurations that avoid water condensation in the measuring system are described. The standard provides minimal requirements for both, the sampling system and the chemiluminescence analyser.

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

- the performance characteristics of the method given in Table 2 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.

This means, that the values of the required performance characteristics, determined by adequate laboratory and field tests, have to be compared to the criteria given in Table 2. The uncertainty budget must be drawn up according to the procedures described in ISO 14956 or GUM.

3. Field Validation

Field validation is a valuable complementary technique to determine the overall uncertainty based on an uncertainty budget according to the GUM approach. It must be used when some uncertainty components are difficult to evaluate or when the measurement process cannot be modelled (sampling, losses in the line, leakage, etc.). Field validation can facilitate the assessment of influence parameters. Parallel (field) measurements by one or several teams often reveal the existence of systematic deviations which might not otherwise be revealed by the uncertainty budget approach.

ISO 5725-2 [14] describes the method to be followed when carrying out such parallel measurements, and it gives the statistical tools to evaluate the repeatability and reproducibility of the method. Repeatability corresponds to an intra-laboratory validation; however, this particular evaluation does not determine if there is a bias in the result since only one laboratory is involved in the test. Inter-laboratory validation provides information about the reproducibility of a given method. Since the results are provided by several laboratories, the bias between single laboratories is evaluated. For stack measurements, the characteristics of the flue gases are not constant. It is, therefore, not possible to determine repeatability from subsequent measurements of the same sample. To overcome this limitation, the internal (repeatability) confidence interval (CI_r) in the field is calculated from results obtained by parallel measurements implemented by the same team and equipment:

$$CI_r = t_{0,95;n-1} \cdot s_r \quad [1]$$

$$r = \sqrt{2} \cdot t_{0,95;n-1} \cdot s_r \quad [2]$$

where s_r is the repeatability standard deviation, $t_{0,95}$ is the Student factor at a 95% confidence level and a degree of freedom of $n-1$, with n being the number of double measurements, r is the repeatability in the field.

The external (reproducibility) confidence interval (CI_R) in the field is determined in a very similar way:

$$CI_R = t_{0,95;np-1} \cdot s_R \quad [3]$$

$$R = \sqrt{2} \cdot t_{0,95;np-1} \cdot s_R \quad [4]$$

where s_r is the reproducibility standard deviation, $t_{0,95}$ is the Student factor at a 95% confidence level and a degree of freedom of $n-1$, with n being the number of double measurements. R is the reproducibility in the field.

4. Comparison between the uncertainty budget and field test

Repeatability, i.e. the internal confidence interval (CI_r) and reproducibility given by the external confidence interval (CI_R) were determined in six field tests, performed on waste incineration installations, co-incineration installations and large combustion plants. During each field test, four different European teams performed two parallel measurements on twelve 30 min samples. CI_r and CI_R were calculated from all results after elimination of eventual outliers. CI_r and CI_R for SO_2 and NO_x were then plotted for all field tests as a function of mean stack concentration.

In the following paragraphs, a comparison is made of the expanded uncertainty for SO_2 and NO_x for analysers used during tests 5 and 6, with CI_r and CI_R from all field tests. The final two field tests were chosen because each participating team prepared its own uncertainty budget, based on a standardised protocol, which included the specific site conditions and the individual characteristics of sampling and analytical measurement devices.

SO₂ (manual method)

Tables 3 and 4 provide a summary of the relative standard uncertainty for each of the influence parameters on the overall uncertainty. As can be seen, the global quality criteria of overall uncertainty is fulfilled even though lab A (5th field test), and labs A and B (6th field test) assume an uncertainty for analysis greater than the 7% required by the standard. For all laboratories, the major contribution to the uncertainty budget comes from the analysis of sulphate, and the second most important factor is the volume of sampled gas.

The tests performed in 6 different stacks lead to the equations:

$$Cl_r = 0,08 c + 3 \text{ mg/m}_0^3 \quad [5]$$

$$Cl_R = 0,113 c + 5,4 \text{ mg/m}_0^3 \quad [6]$$

where c is the measured SO₂ concentration, given in mg/m₀³.

Figure 1 shows that for the SO₂ manual method the results provided by the uncertainty budget are very close to what has been determined 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 had been determined previously by inter-laboratory tests. All other components have a rather minor contribution to the overall uncertainty and are well known owing to on-going metrology controls, regularly performed in each laboratory.

NO_x (automated method)

The field tests performed on 6 different stacks have led to the following equations for repeatability and reproducibility:

$$Cl_r = 0.029 c + 2.0 \text{ mg/ m}_0^3 \quad [7]$$

$$Cl_R = 0.038 c + 4.4 \text{ mg/ m}_0^3 \quad [8]$$

where c is the NO_x concentration in mg/m₀³.

Additionally, all teams involved in field tests 5-6 had developed uncertainty budgets following an exhaustive list of criteria and applying the same calculation routines. The detailed results are given in Tables 6 and 7, and a graphical representation of Cl_r , Cl_R , and the overall uncertainty from the uncertainty budgets is shown in Figure 2. There are some clear discrepancies between the field results and the uncertainty budgets, the latter ones yielding distinctly higher values for most participating teams. These findings will be discussed in the following paragraphs.

The resulting relative overall uncertainty broadly varies in the range of 5.4 % to 15.5 % for field test 5. The dominating parameters are: lack of fit, sensitivity to temperature, repeatability of measurement and calibration gas. The relatively high value of Lab B is due to both technical problems of the gas analysers, and to the fact that the performance characteristics of its instrument were known and expressed as a fixed value determined at the full range (1000 ppm). All other laboratories estimated similar overall uncertainties between 5.4 % and 7.8 % of the studied concentration.

For field test 6, the resulting relative overall uncertainty broadly varies in the range of 3.2 % to 23.4 %. The overall uncertainty determined by Lab A is quite high, Lab C estimated relative low, and Lab B and D calculated 7,6 resp. 8,6 %. Here too, the laboratory did not know the relevant performance characteristics at the actual measurement range and, therefore applied fixed values determined at full range. Again, this leads to a clear overestimation considering the field results (Figure 2) and the values obtained by the other laboratories.

As shown above, the limited information on performance characteristics available from manufacturers and test houses might lead to uncertainty budgets that might be biased and, therefore, irrelevant. To illustrate and quantify the importance of this problem, the example of the performance characteristic *lack of fit* is considered. Typically, a test house or manufacturer will determine *lack of fit*, i.e. the deviation of from the true value of linearity, by calibrating the instrument with a reference gas at full range, followed by measurements of the

diluted reference gas at 20 %, 40 %, 60 %, and 80 % of the range. For a range of 1000 ppm, a hypothetical set of results is given in Table 5.

As observed in Table 5, the maximum deviation is 15 ppm and corresponds to 1,5 % of the range. However, the performance characteristics might be described as follows: (i) *lack of fit* < 2 %, because this is the performance criterion in the standard, and a typical value that many manufacturers can guarantee, (ii) *lack of fit* < 15 ppm, or (iii) *lack of fit* = 0.3 % (200 ppm), 1 % (400 ppm), 1.5 % (600 ppm), 0.5 % (800 ppm), i.e. the full information contained in Table 5.

Considering a hypothetical uncertainty budget at 200 ppm, according to the available information, the contribution of the parameter *lack of fit* in the calculation of the overall uncertainty may strongly differ according to the different ways of expressing or determining performance characteristics. It would amount to (i) ± 20 ppm, (ii) ± 15 ppm, or (iii) ± 3 ppm. This corresponds to an uncertainty contribution between 1.5 % and 10 % of 200 ppm. In other words, the way of describing the performance characteristic for lack of fit will yield a difference of a factor 7 in its contribution to overall uncertainty. It seems that the very large values of Lab. B (field test 5) and Lab. A (field test 6) of some parameters were mainly due to such unclear documentation of performance characteristics. This phenomenon is of lesser importance when the budget is established at concentrations near to the full range.

Another element that often limits the correct establishment of an uncertainty budget is the fact that the laboratory might not know the exact range of variation of influent parameters such as the ambient temperature, voltage, flow-rate or atmospheric pressure encountered during the field experiment. Since these parameters are often not measured, the laboratory might use a standardised range that is wider than the actual field values. Thus, there is a general tendency to overestimate a number of uncertainty contributions.

5. Conclusions

The establishment of an uncertainty budget is very useful to identify and study the major contribution to the overall uncertainty. As has been shown by the work performed on SO₂ analysis, uncertainty budgets that are based on sound scientific knowledge of the main contributions will give results that are consistent with repeatability and reproducibility confidence intervals determined in field tests. However several conditions must be met to obtain realistic data from uncertainty budgets:

- trained personnel to correctly establish and interpret uncertainty budgets,
- sufficient information on the performance characteristics of the method at the studied concentration,
- knowledge of the variation range of influent parameters in the field, such as temperature, humidity, voltage, etc.

Currently, the performance characteristics determined by test houses are often expressed in % of the range and correspond to the maximum deviation. Therefore, laboratories often miss the relevant figures of performance characteristics at a particular concentration. Because uncertainty budgets must frequently be established at the Emission Limit Value (ELV), it seems essential to provide at least the performance characteristics of an analyser at ELV. In view of future (lower) ELVs and applications over the whole range of an analyser, performance characteristics should be determined and given at least at 20, 40, 60 and 80% of the range. This will yield more trustworthy uncertainty budgets and better consistency with field inter- and intra laboratory tests. The necessity to obtain sufficiently detailed performance data from manufacturers should be considered in future standardisation work, such as the one currently carried out by CEN/TC264/WG22 on a certification scheme for automated measuring systems.

Finally, EN ISO 14956, states that the user of this standard must *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*. The results of CEN/TC264/WG16 show that this recommendation is critical for valid uncertainty determinations.

Acknowledgement

The authors wish to thank the members of working group 16 and its secretariat provided by the French standardization body AFNOR, the secretariat of CEN TC 264 and the CEN Management Centre. The field tests were made possible by financial support of the European.

6. References

- [1] Beier R, Korderecki R. : Uncertainty analysis in the field of ambient air and stack emission monitoring, *Gefahrstoffe-Reinhaltung der Luft*, 60 (3), 2000
- [2] ENV 13005 (1999), *Guide to the expression of uncertainty in measurement*.
- [3] Example of an uncertainty budget for NO_x at a specific site of CENTC264 WI264043
- [4] Example of an uncertainty budget for SO₂ at a specific site of CENTC264 WI264042
- [5] ISO 14956 (2002), *Air Quality – Determination of performance requirements of a measurement method derived from a stated measurement uncertainty*
- [6] prEN 14792 (2003), Stationary source emissions - Determination of mass concentration of nitrogen oxides (NO_x) - Reference method - chemiluminescence
- [7] prEN 14791 (2003), Stationary source emissions - Determination of mass concentration of sulphur dioxide - Reference method
- [8] prEN 14789 (2003), Stationary source emissions - Determination of mass concentration of oxygen (O₂) - Reference method
- [9] prEN 14790 (2003), Stationary source emissions - Determination of mass concentration of the water vapour (H₂O) - Reference method
- [10] prEN xxx, Stationary source emissions - Determination of mass concentration of carbon monoxide (CO) - Reference method, in preparation
- [12] Sneek, E. J. : Type approval of instruments and uncertainty calculations in the new EN-standards for the measurement of SO₂, NO₂, CO and O₃ in ambient air, *Gefahrstoffe-Reinhaltung der Luft*, 63 (4), 2003
- [12] Council Directive 2001/80/EC on the limitation of emissions of certain pollutants into the air from large combustion plants and Council Directive 2000/76/EC on waste incineration plants.
- [13] prEN TS14193 (2004) Stationary source emission _ Intralaboratory validation procedure for an alternative method compared to a reference method
- [14] ISO 5725-2 (1994), Application of statistics - Accuracy (trueness and precision) of measurement methods and results - Part 2 : basic method for the determination of repeatability and reproducibility of a standard measurement method.
- [15] ISO/IEC 17025 (1999), General requirements for the competence of testing and calibration laboratories.

Table 1 Relevant characteristics and minimal performance criteria for the determination of sulphur dioxide [7].

Performance characteristic	Performance criterion
Volume of the absorption solution	$\leq \pm 1 \%$ of the volume of solution
Volume gas meter: uncertainty of sample volume ⁽²⁾ uncertainty of temperature ⁽²⁾ uncertainty of absolute pressure ⁽²⁾	$\leq \pm 2 \%$ of the volume of gas sampling ⁽¹⁾ $\leq \pm 2,5 \text{ K}$ ⁽¹⁾
Absorption efficiency ⁽³⁾	$> 95\%$
Leak in the sampling line	$\leq 2\%$ of the nominal flow rate
Value of the field blank	$\leq 10 \%$ of VLE
Standard deviation of repeatability of analysis	$\leq 7 \%$
Overall uncertainty at the limit value	$\leq 20 \%$

⁽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 2 Relevant characteristics and minimal performance criteria for the determination of sulphur dioxide [6].

Performance characteristic	Performance criteria
Response time	$\leq 200 \text{ s}$
Detection limit	$\leq \pm 2 \%$ of the range
Lack of fit	$\leq \pm 2 \%$ of the range
Zero drift	$\leq \pm 2 \%$ of the range/ 24 hours
Span drift	$\leq \pm 2 \%$ of the range/ 24 hours
Sensitivity to atmospheric pressure	$\leq 3\%$ of the range for 2 kPa
Sensitivity to ambient temperature	$\leq 3\%$ of the range/10 K
Sensitivity to electric voltage	$\leq 2 \%$ of the range/10V
Interferents	Total $\leq \pm 4\%$ of the range
Converter efficiency	$\geq 95\%$
Losses and leakage in the sampling and conditioning system	$\leq 2\%$ of the measured value
Standard deviation of repeatability in laboratory at zero	$\leq 1 \%$ of the range
Standard deviation of repeatability in laboratory at span level	$\leq 2 \%$ of the range
Uncertainty of calibration gas	$\leq 2 \%$
Overall uncertainty at the ELV	$\leq 10 \%$

Table 3 Contribution of different parameters to the uncertainty budgets for SO₂ as estimated by the laboratories taking part in field test 5.

Uncertainty components	Lab A	Lab B	Lab C	Lab D
	Relative standard uncertainties in %			
Volume of solution (u in ml)	0.46	0.46	0.06	0.46
Analyse	8.00	8.00	5.00	5.00
Volume of gas sampling	2.62	1.81	1.37	1.33
Temperature at gas volume meter	0.50	0.22	0.57	0.29
Relative pressure at gas volume meter	0.01	0.00	0.05	0.00
Atmospheric Pressure	0.07	0.14	0.28	0.04
Studied concentration (mg/m ₀ ³ at 11% O ₂)	66.0	110.0	67	125.1
Field blank (mg SO ₂ /m ₀ ³ at 11% O ₂)	0.3	1.0	0.3	0
Overall uncertainty: U(C _m) %	16.9	10.7	10.5	10.5
Overall uncertainty: U(C _{m,fb,corr}) %	17.4	11.6	10.9	10.5
Overall uncertainty: U(C _{m,fb,corr}) mg/m ₀ ³	11.5	12.8	7.3	13.1

Table 4 Contribution of different parameters to the uncertainty budgets for SO₂ as estimated by the laboratories taking part in field test 6.

Uncertainty components	Lab A	Lab B	Lab C	Lab D
	Relative standard uncertainties			
Volume of solution	0.46%	0.46%	0.06%	0.46%
Analyse	8.00%	5.00%	5.00%	5.00%
Volume of gas sampling	2.62%	1.81%	1.37%	1.37%
Temperature at gas volume meter	0.50%	0.21%	0.60%	0.59%
Relative pressure at gas volume meter	0.01%	0.00%	0.04%	0.04%
Atmospheric Pressure	0.07%	0.14%	0.08%	0.26%
Studied concentration (mg/m ₀ ³ at 11% O ₂)	900	1000	944	911
Field blank (mg SO ₂ /m ₀ ³ at 11% O ₂)	0.3	2.0	0.2	1.5
Overall uncertainty: U(C _m) %	16.9	10.7	10.5	10.5
Overall uncertainty: U(C _{m,fb,corr}) %	17.0	10.9	10.5	10.7
Overall uncertainty: U(C _{m,fb,corr}) mg/m ₀ ³	153.0	109.0	99.1	97.5

Table 5 Hypothetical example of measurements to determine "lack of fit".

C _{ref} [ppm]]	C _{meas} [ppm]	C _{ref} - C _{meas} [ppm]	C _{ref} - C _{meas} / C _{ref} * 100 [%]	C _{ref} - C _{meas} / 1000 * 100 [%]
200	197	3	1.5	0.3
400	410	-10	-2.5	-1.0
600	615	-15	-2.5	-1.5
800	795	5	0.6	0.5
1000	1000	0	0.0	0.0

C_{ref} : concentration of reference gas supplied to the instrument

C_{meas}: concentration determined by the instrument that had been previously been calibrated with a 1000 ppm standard

Table 6 Uncertainty budgets for NO_x set up by the laboratories taking part in field test 5

	Lab A	Lab B	Lab C	Lab D
Uncertainty components	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 NH ₃	0.19	0.85	0.33	0.08
Interferent CO ₂	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 NO _x (ppm at O ₂ ref)	194.8	194.8	194.8	189.9
Studied concentration of NO _x (mg/m ³ at O ₂ ref)	400	400	400	390
Overall uncertainty: U(CNO _x ,mg/m ³)	31.20	62.00	21.60	23.79
Overall uncertainty: U(CNO _x ,ppm) %	7.80	15.50	5.40	6.1

Table 7 Uncertainty budgets for NO_x set up by the laboratories taking part in field test 6

	Lab A	Lab B	Lab C	Lab D
Uncertainty components	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 NH ₃	0.19	0.00	0.08	0.01
Interferent CO ₂	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 NO _x (ppm at O ₂ ref)	48.7	39.0	51.6	50.2
Studied concentration of NO _x (mg/m ³ at O ₂ ref)	100.0	80.1	106.0	103
Overall uncertainty: U(CNO _x ,mg/m ³)	23.4	9.5	3.0	8.3
Overall uncertainty: U(CNO _x ,ppm) %	23.40	7.60	3.20	8.6

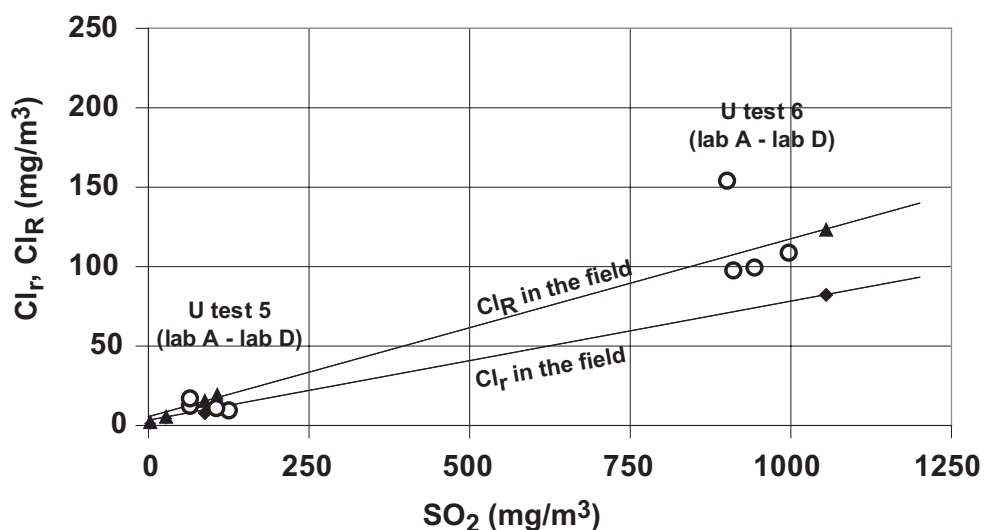


Figure 1

Repeatability (Cl_r), reproducibility (Cl_R) and overall uncertainty (U) for SO_2 measurements done in field test 5 and field test 6. The lines are linear regressions of the data obtained through field tests 2-6. The open circles are the calculated overall uncertainties of field test 5 and 6.

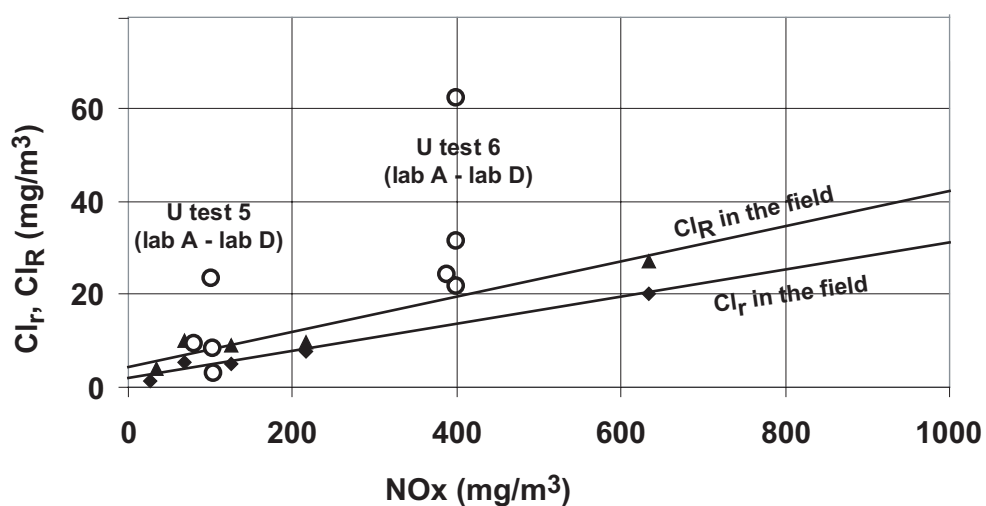


Figure 2

Repeatability (Cl_r), reproducibility (Cl_R) and overall uncertainty (U) for NO_x measurements done in field test 5 and field test 6. The lines are linear regressions of the data obtained through field tests 2-6. The open circles are the calculated overall uncertainties of field test 5 and 6.