



Key comparison for measurement of stack gas

CCQM-K71
Final report

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Summary

Industrial stack gas emission measurements are important for process control, control of air pollution, and for implementing legislation regarding the carbon dioxide emission rights. Measurements are typically performed using a range of process analysers for carbon monoxide (CO), carbon dioxide (CO₂), nitrogen oxides (NO_x), sulphur dioxide (SO₂) and miscellaneous hydrocarbons. The calibration of these analysers is often performed using a series of binary mixtures of each component in nitrogen. For reasons of efficiency as well as a better match with true stack gas, the use of multi component mixtures for this purpose would be preferred.

The data from gravimetric preparation have been used as the basis for establishing the key comparison reference value.

Most of the participating NMIs mastered the challenges set in this key comparison well. IPQ reported results for CO, CO₂ and SO₂ only. INMETRO took part in this comparison as a pilot study.

The results for carbon monoxide showed serious deviations for INMETRO (-26.5% relative), VNIIM (+12.7% relative), and IPQ (-3.9% relative), with none of the cases demonstrating equivalence with the KCRV. Two other results inconsistent with the KCRV were reported by NMISA and KRISS.

For carbon dioxide, all laboratories except IPQ reported results consistent with the KCRV.

For propane, INMETRO reported a seriously deviating result (-6.0% relative). NMISA and VNIIM also reported deviating results (in absolute sense more than 1% relative). None of these three results were consistent with the KCRV.

Three results for nitrogen monoxide were not consistent with the KCRV: KRISS, VNIIM and NMISA. With the exception of CENAM, none of the results differed more than 1% relative from the KCRV.

For sulphur dioxide, two results were not consistent with the KCRV: NIM and VNIIM. Only one result deviated by more than 1% relative from the reference value (NIM).

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1 Introduction

Industrial stack gas emission measurements are important for process control, control of air pollution, and for implementing legislation regarding the carbon dioxide emission rights. Measurements are typically performed using a range of process analysers for carbon monoxide (CO), carbon dioxide (CO₂), nitrogen oxides (NO_x), sulphur dioxide (SO₂) and miscellaneous hydrocarbons. The calibration of these analysers is often performed using a series of binary mixtures of each component in nitrogen. For reasons of efficiency as well as a better match with true stack gas, the use of multicomponent mixtures for this purpose would be preferred.

The measurement of stack gas is a challenging task, as the various components may interfere in the measurement of other components. The challenge for the participating national metrology institutes is to control these interferences during the measurement (characterisation) of the mixtures in this international key comparison. Binary mixtures have been part of previous key comparisons, such as CCQM-K1 [1] (carbon monoxide, carbon dioxide, nitrogen monoxide, and sulphur dioxide) and CCQM-K52 (carbon dioxide) [2]. Carbon monoxide, carbon dioxide and propane have also been the subject of a key comparison in the form of a multicomponent mixture: CCQM-K3 [3] (automotive mixtures).

Just as in other key comparisons in gas analysis, the values as obtained from gravimetric preparation in accordance with ISO 6142 [4] are taken as the reference values.

2 Design of the key comparison

2.1 Field of measurement

Amount-of-substance

2.2 Subject

Key comparison in the field of industrial emission measurements (stack gas)

2.3 Participants

Table 1 lists the participants in this key comparison.

Table 1: List of participants

Acronym	Country	Institute
INMETRO ¹	BR	Instituto Nacional de Metrologia, Normalização e Qualidade Industrial, Xerém RJ, Brasil
NIM	CN	National Institute of Metrology, Beijing, PR China
KRISS	KR	Korea Research Institute of Standards and Science, Daejeon, South-Korea
CENAM	MX	Centro Nacional de Metrologia, Queretaro, Mexico
VSL	NL	Van Swinden Laboratorium B.V., Delft, the Netherlands
IPQ	PT	Instituto Português da Qualidade, Monte de Caparica, Portugal
VNIIM	RU	D.I. Mendeleev Institute for Metrology, St. Petersburg, Russia
NMISA	SA	National Metrology Institute of South Africa, Pretoria, South Africa
SMU	SK	Slovak Institute of Metrology, Bratislava, Slovak Republic
NPL	UK	National Physical Laboratory, Teddington, Middlesex, United Kingdom
NIST	US	National Institute of Standards and Technology, Gaithersburg, United States

2.4 Measurement standards

A suite of mixtures has been gravimetrically prepared for this comparison. Table 2 lists the nominal composition of the mixture used (expressed as amount of substance fractions).

Table 2: Nominal composition of the mixtures

Component	x
Nitrogen monoxide	10-100 $\mu\text{mol/mol}$
Carbon dioxide	100-160 mmol/mol
Carbon monoxide	10-100 $\mu\text{mol/mol}$
Propane	1-10 $\mu\text{mol/mol}$
Sulphur dioxide	20-200 $\mu\text{mol/mol}$

The mixtures were prepared gravimetrically and subsequently verified. The preparation of the mixtures was carried out using the normal procedure for the preparation of gas mixtures [5]. After preparation, the mixtures were verified by comparing the key comparison mixtures with PSMs from the standards maintenance programme. The mixtures were verified against binary and multicomponent mixtures.

2.5 Measurement protocol

The laboratories were requested to use their normal procedure for the measurement of the gas mixture composition. For participation in this key comparison, it had been requested that participants determine all components in the mixture, and not just a subset. The participants were asked to perform at least three measurements, on different days with independent calibrations. Laboratories were allowed to use the same set of measurement standards for these calibrations.

The participants were also requested to describe their methods of measurement, and the models used for evaluating the measurement uncertainty. A typical numerical example of the evaluation of measurement uncertainty had to be included for each component. It was not required to reproduce all numerical data underlying

¹ Participated in this international comparison as a pilot study

the results reported and the uncertainties thereof, but the report of the evaluation of measurement uncertainty should at least allow addressing which components had been included in the evaluation, and reviewing their impact on the uncertainty of the results reported.

2.6 Schedule

The schedule for this key comparison reads as follows

31 December 2007	Final Registration of participants
Jan-June 2008	Preparation of gravimetric mixtures + verification measurements
July 2008	Shipment of cylinders to participating laboratories
1 December 2008	Reports due to pilot laboratory
1 December 2008	Cylinders due to pilot laboratory
January 2008	Verification measurements at pilot laboratory
December 2008	Draft A report
July 2009	Draft B report

2.7 Measurement equation

The reference values used in this key comparison are based on gravimetry, and the purity verification of the parent gases/liquids. All mixtures underwent verification prior to shipping them to the participants. After return of the cylinders, they were verified once more to reconfirm the stability of the mixtures.

In the preparation, the following four groups of uncertainty components were considered:

1. gravimetric preparation (weighing process) ($x_{i,grav}$)
2. purity of the parent gases ($\Delta x_{i,purity}$)
3. stability of the gas mixture ($\Delta x_{i,stab}$)
4. correction due to partial recovery of a component ($\Delta x_{i,nr}$)

The amount of substance fraction $x_{i,prep}$ of a particular component in mixture i , as it appears during use of the cylinder, can now be expressed as

$$x_{i,prep} = x_{i,grav} + \Delta x_{i,purity} + \Delta x_{i,stab} + \Delta x_{i,nr} \quad (1)$$

The value obtained from equation (1) is sometimes referred to as "gravimetric value". Assuming independence of the terms in equation (1), the expression for the combined standard uncertainty becomes

$$u_{i,prep}^2 = u_{i,grav}^2 + u_{i,purity}^2 + u_{i,stab}^2 + u_{i,nr}^2 \quad (2)$$

For the mixtures used in this key comparison, the following statements hold for all components involved. First of all, the preparation method was designed in such a way that

$$\Delta x_{i,nr} = 0, \quad (3)$$

and its standard uncertainty as well. Furthermore, long-term stability study data has shown that

$$\Delta x_{i,stab} = 0, \quad (4)$$

and its standard uncertainty as well. In practice, this means that the scattering of the results over time in the long-term stability study can be explained solely from the analytical uncertainty (e.g. calibration, repeatability of measurement). On this basis, using the theory of analysis of variance [7,8] the conclusion can be drawn that the uncertainty due to long-term stability can be set to zero.

Summarising, the model reduces to

$$x_{i,prep} = x_{i,grav} + \Delta x_{i,purity} \quad (5)$$

and for the associated standard uncertainty, the following expression is obtained

$$u_{i,prep}^2 = u_{i,grav}^2 + u_{i,purity}^2 \quad (6)$$

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The validity of the mixtures was demonstrated by verifying the composition as calculated from the preparation data with that obtained from (analytical chemical) measurement. In order to have a positive demonstration of the preparation data including uncertainty, the following condition should be met [4]

$$|x_{i,prep} - x_{i,ver}| \leq 2\sqrt{u_{i,prep}^2 + u_{i,ver}^2} \quad (7)$$

The factor 2 is a coverage factor (normal distribution, 95% level of confidence). The assumption must be made that both preparation and verification are unbiased. Such bias has never been observed. The uncertainty associated with the verification highly depends on the experimental design followed. In this particular key comparison, an approach has been chosen which is consistent with CCQM-K3 [3] and takes advantage of the work done in the gravimetry study CCQM-P23 [6]. All mixtures prepared in this key comparison satisfy for all components the condition given in equation (7).

The reference value of mixture i in a key comparison² can be defined as

$$x_{i,KCRV} = \langle x_{i,KCRV} \rangle + \delta x_{i,KCRV} \quad (8)$$

where

$$x_{i,KCRV} = x_{i,prep} + \Delta x_{i,ver} \quad (9)$$

Since the amount of substance fraction from preparation is used as the basis, the expectation of the correction $\langle \Delta x_{i,ver} \rangle$ due to verification can be taken as zero, which is consistent with the assumption made earlier that both preparation and verification are unbiased. Thus, (9) can be expressed as

$$x_{i,KCRV} = \langle x_{i,prep} \rangle + \delta x_{i,prep} + \delta \Delta x_{i,ver} \quad (10)$$

This expression forms the basis for the evaluation of degrees of equivalence in this key comparison. For all mixtures, it has been required that

$$\Delta x_{i,ver} = 0, \quad (11)$$

that is, there is no correction from the verification. The verification experiments have demonstrated that within the uncertainty of these measurements, the gravimetric values of the key comparison mixtures agreed with older measurement standards.

The expression for the standard uncertainty of a reference value becomes thus

$$u_{i,KCRV}^2 = u_{i,prep}^2 + u_{i,ver}^2 \quad (12)$$

The values for $u_{i,ver}$ are given in the tables containing the results of this key comparison.

2.8 Supported CMC claims

At the November 2009 meeting in Rio de Janeiro, the HFTLS statement was modified to include concentration ranges for the components in the standards.

HFTLS: "This key comparison can be used to support CMC³ claims for stack gas type multi component mixtures." The following ranges in a nitrogen matrix were suggested:

NO 10-1000 $\mu\text{mol/mol}$

CO 10-1000 $\mu\text{mol/mol}$

CO₂ 50-200 mmol/mol

C₃H₈ 1-100 $\mu\text{mol/mol}$

SO₂ 10-1000 $\mu\text{mol/mol}$.

² This definition of a reference value is consistent with the definition of a key comparison reference value, as stated in the mutual recognition arrangement (MRA) [9].

³ CMC = calibration and measurement capability

2.9 Degrees-of-equivalence

A unilateral degree of equivalence in key comparisons is defined as [9]

$$D_i = D_i = x_i - x_{\text{KCRV}}, \quad (13)$$

and the uncertainty of the difference D_i at 95% level of confidence. Here x_{KCRV} denotes the key comparison reference value, and x_i the result of laboratory i .⁴ Appreciating the special conditions in gas analysis, it can be expressed as

$$D_i = x_i - x_{i,\text{KCRV}} \quad (14)$$

The standard uncertainty of D_i can be expressed as

$$u^2(D_i) = +u_{i,\text{lab}}^2 + u_{i,\text{prep}}^2 + u_{i,\text{ver}}^2 \quad (15)$$

assuming that the aggregated error terms are uncorrelated. As discussed, the combined standard uncertainty of the reference value comprises that from preparation and that from verification for the mixture involved. A bilateral degree of equivalence is defined as [9]

$$D_{ij} = D_i - D_j \quad (16)$$

and the uncertainty of this difference at 95% level of confidence. Under the assumption of independence of D_i and D_j , the standard uncertainty of D_{ij} can be expressed as

$$u^2(D_{ij}) = +u_{i,\text{lab}}^2 + u_{i,\text{prep}}^2 + u_{i,\text{ver}}^2 + u_{j,\text{lab}}^2 + u_{j,\text{prep}}^2 + u_{j,\text{ver}}^2 \quad (17)$$

The assumption of independence is not satisfied by the preparation and verification procedures. It is well known that the use of pre-mixtures leads to correlations in the final mixtures. The standard uncertainty from verification is based on the residuals of a straight line through the data points (response versus composition), and these residuals are correlated too. However, the uncertainty of a degree of equivalence is still dominated by the uncertainty of the laboratory, so that these correlations, which certainly influence D_{ij} and its uncertainty, will have little practical impact.

⁴ Each laboratory receives one cylinder, so that the same index can be used for both a laboratory and a cylinder.

3 Results

3.1 Measurement methods

The measurement methods used by the participants are described in annex A of this report. A summary of the calibration methods, dates of measurement and reporting, and the way in which metrological traceability is established are given in tables 3–7.

Table 3: Summary of calibration methods and metrological traceability (carbon monoxide)

Laboratory	Measurements	Calibration	Traceability	Matrix standards	Measurement technique
INMETRO	07-11-2008	ISO 6143	VSL	Nitrogen	GC-NiCAT-FID
NIM	12 and 13-12-2008	Single point	Own standard	Nitrogen including 120 mmol/mol CO ₂	ND-IR
KRISS	23, 27 and 29-09-2008	Single point	Own standard	Stack gas	GC-TCD
CENAM	7, 9, 10 and 14-10-2008	ISO 6143	Own standards	Stack gas	GC-NiCAT-FID
VSL	29-01-2009 and 4 and 20-02-2009	ISO 6143	Own standards	Nitrogen	GC-NiCAT-FID
IPQ	5, 6 and 14-11-2008	ISO 6143	Own standards	Nitrogen	ND-IR
VNIIM	11, 24 and 26-12-2008	Bracketing	Own standards	Stack gas without CO ₂	GC-ECD
NMISA	18-09-2008 and 9 and 11-12-2008	ISO 6143	Own standards	Stack gas	ND-IR
SMU	11, 12 and 16-09-2008	ISO 6143	Own standards	Stack gas and binary mixtures	GC-NiCAT-FID
NPL	January 2009	Bracketing	Own standards	Stack gas	ND-IR
NIST	24 and 29-09-2008 and 2-10-2008	ISO 6143	Own standards	Nitrogen	GC-NiCAT-FID

Table 4: Summary of calibration methods and metrological traceability (carbon dioxide)

Laboratory	Measurements	Calibration	Traceability	Matrix standards	Measurement technique
INMETRO	26, 29 and 30-10-2008	ISO 6143	VSL	Nitrogen	GC-TCD
NIM	22, 23 and 24-12-2008 and 06-01-2009	Single point	Own standard	Nitrogen	ND-IR
KRISS	22, 24 and 26-09-2008	Single point	Own standard	Stack gas	GC-TCD
CENAM	2, 3 and 6-10-2008	ISO 6143	Own standards	Stack gas	GC-TCD
VSL	3-10-2008 and 31-12-2008 and 4 and 20-02-2009	ISO 6143	Own standards	Nitrogen	GC-TCD
IPQ	21-10-2008 and 18 and 19-11-2008	ISO 6143	Own standards	Nitrogen	ND-IR
VNIIM	8 and 22-12-2008	Bracketing	Own standards	Nitrogen	FT-IR
NMISA	16-09-2008 and 10 and 12-12-2008	ISO 6143	Own standards	Stack gas	ND-IR
SMU	9 and 10-09-2008 and 14-10-2008	ISO 6143	Own standards	Stack gas and binary mixtures	GC-TCD
NPL	January 2009	Bracketing	Own standards	Stack gas	GC-TCD
NIST	6, 7 and 8-10-2008	ISO 6143	Own standards	Nitrogen	GC-TCD

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Table 5: Summary of calibration methods and metrological traceability (propane)

Laboratory	Measurements	Calibration	Traceability	Matrix standards	Measurement technique
INMETRO	17, 23 and 28-10-2008	ISO 6143	Own standards	Nitrogen	GC-FID
NIM	14 and 15-01-2009	Single point	Own standard	Nitrogen including 120 mmol/mol CO ₂	GC-FID
KRISS	22, 26, 29 and 30-09-2008	Single point	Own standard	Stack gas	GC-FID
CENAM	15, 16 and 20-10-2008	ISO 6143	Own standards	Stack gas	GC-FID
VSL	3-10-2008 and 31-12-2008 and 4 and 20-02-2009	ISO 6143	Own standards	Nitrogen	GC-FID
IPQ	-	-	-	-	-
VNIIM	3 and 15-12-2008	Bracketing	Own standards	Stack gas without CO ₂	GC-FID
NMISA	26 and 27-11-2008 and 01-12-2008	ISO 6143	Own standards	Stack gas and binary mixtures	GC-FID
SMU	9 and 10-09-2008 and 14-10-2008	ISO 6143	Own standards	Stack gas and binary mixtures	GC-FID
NPL	January 2009	Bracketing	Own standards	Stack gas	GC-FID
NIST	15 and 16-10-2008	ISO 6143	Own standards	Nitrogen	GC-FID

Table 6: Summary of calibration methods and metrological traceability (nitrogen monoxide)

Laboratory	Measurements	Calibration	Traceability	Matrix standards	Measurement technique
INMETRO	28, 29 and 30-10-2008	ISO 6143	VSL	Nitrogen	ND-IR
NIM	10 and 11-12-2008	Single point	Own standards	Nitrogen	CLD
KRISS	19, 21, 27 and 30-09-2008	Single point	Own standard	Stack gas	CLD
CENAM	30 and 31-10-2008 and 3-11-2008	ISO 6143	Own standards	Stack gas	FT-IR
VSL	14, 27 and 29-10-2008 and 15-12-2008	ISO 6143	Own standards	Nitrogen	ND-UV
IPQ	-	-	-	-	-
VNIIM	5 and 18-12-2008	Bracketing	Own standards	Stack gas without CO ₂	FT-IR
NMISA	22 and 23-12-2008 and 6-01-2009	ISO 6143	Own standards	Stack gas	CLD
SMU	1 and 10-10-2008 and 6-11-2008	ISO 6143	Own standards	Stack gas and binary mixtures	CLD and FT-IR
NPL	January 2009	Bracketing	Own standards	Stack gas	CLD
NIST	21, 22 and 23-10-2008	ISO 6143	Own standards	Nitrogen	CLD

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Table 7: Summary of calibration methods and metrological traceability (sulphur dioxide)

Laboratory	Measurements	Calibration	Traceability	Matrix standards	Measurement technique
INMETRO	28, 29 and 30-10-2008	ISO 6143	VSL	Nitrogen	ND-IR
NIM	12 and 17-12-2008	Single point	Own standard	Nitrogen, some including 120 mmol/mol CO ₂	UV-fluorescence
KRISS	19, 21, 27 and 30-09-2008	Single point	Own standard	Stack gas	ND-IR
CENAM	30 and 31-10-2008 and 3-11-2008	ISO 6143	Own standards	Stack gas	FT-IR
VSL	30-09-2008 and 21-10-2008 and 6-11-2008	ISO 6143	Own standards	Nitrogen	ND-IR
IPQ	20-10-2008 and 19 and 20-11-2008	ISO 6143	Own standards and VSL	Nitrogen	ND-IR
VNIIM	5 and 18-12-2008	Bracketing	Own standards	Stack gas without CO ₂	FT-IR
NMISA	14 and 28-10-2008 and 17-12-2008	ISO 6143	Own standards	Stack gas	UV-fluorescence
SMU	30-09-2008 and 9-10-2008 and 4-11-2008	ISO 6143	Own standards	Stack gas and binary mixtures	UV-fluorescence and FT-IR
NPL	January 2009	Bracketing	Own standards	Stack gas	GC-SCD
NIST	28, 29 and 30-10-2008	ISO 6143	Own standards	Nitrogen	ND-UV

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3.2 Results

In this section, the results of the key comparison are summarised. In the tables, the following data is presented

x_{prep}	amount of substance fraction, from preparation
u_{prep}	standard uncertainty associated with x_{prep}
u_{ver}	standard uncertainty from verification
u_{KCRV}	combined standard uncertainty of reference value
x_{lab}	result of laboratory
U_{lab}	stated expanded uncertainty of laboratory, at 95% level of confidence
k_{lab}	stated coverage factor
D	difference between laboratory result and reference value
k	assigned coverage factor for degree of equivalence
$U(D)$	Expanded uncertainty associated with difference D , at 95% level of confidence ⁵

Table 8: Results and degrees-of-equivalence for carbon monoxide

Lab	Cylinder	x_{prep} μmol/mol	u_{prep} μmol/mol	u_{ver} μmol/mol	u_{KCRV} μmol/mol	x_{lab} μmol/mol	U_{lab} μmol/mol	k_{lab}	D μmol/mol	D/x	k	$U(D)$ μmol/mol	$U(D)/x$
NIST	M937423	40.083	0.034	0.06012	0.06907	40.112	0.063	2	0.03	0.07%	2	0.1518	0.38%
NIM	M937410	40.092	0.034	0.06014	0.06908	40.050	0.240	2	-0.04	-0.10%	2	0.2769	0.69%
NPL	M937411	40.047	0.034	0.06007	0.06903	40.000	0.200	2	-0.05	-0.12%	2	0.2430	0.61%
VSL	M937400	40.101	0.034	0.06015	0.06910	40.200	0.380	2	0.10	0.25%	2	0.4043	1.01%
CENAM	M937407	39.953	0.034	0.05993	0.06890	40.100	0.510	2	0.15	0.37%	2	0.5283	1.32%
SMU	M937405	40.128	0.034	0.06019	0.06913	40.110	0.190	2	-0.02	-0.04%	2	0.2350	0.59%
VNIIM	M937403	40.116	0.034	0.06017	0.06912	45.220	0.250	2	5.10	12.72%	2	0.2857	0.71%
NMISA	M937424	40.094	0.034	0.06014	0.06909	39.800	0.210	2	-0.29	-0.73%	2	0.2514	0.63%
KRISS	M937414	40.111	0.034	0.06017	0.06911	39.910	0.140	2	-0.20	-0.50%	2	0.1967	0.49%
IPQ	M937419	40.090	0.034	0.06014	0.06908	38.530	0.300	2	-1.56	-3.89%	2	0.3303	0.82%
INMETRO	M937401	40.127	0.034	0.06019	0.06913	29.495	0.369	2	-10.63	-26.50%	2	0.3941	0.98%

⁵ As defined in the MRA [9], a degree of equivalence is given by Δx and $U(\Delta x)$.

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Table 9: Results and degrees-of-equivalence for carbon dioxide

Lab	Cylinder	x_{prep} mmol/mol	u_{prep} mmol/mol	u_{ver} mmol/mol	u_{KCRV} mmol/mol	x_{lab} mmol/mol	u_{lab} mmol/mol	k_{lab}	D $\mu\text{mol/mol}$	D/x	k	$U(D)$ $\mu\text{mol/mol}$	$U(D)/x$
NIST	M937423	119.800	0.012	0.11980	0.12040	119.93	0.11	2	0.130	0.11%	2	0.265	0.22%
NIM	M937410	120.100	0.012	0.12010	0.12070	120.20	0.60	2	0.100	0.08%	2	0.647	0.54%
NPL	M937411	119.790	0.012	0.11979	0.12039	119.70	0.20	2	-0.090	-0.08%	2	0.313	0.26%
VSL	M937400	120.010	0.012	0.12001	0.12061	120.07	0.34	2	0.060	0.05%	2	0.417	0.35%
CENAM	M937407	120.330	0.012	0.12033	0.12093	120.17	0.94	2	-0.160	-0.13%	2	0.971	0.81%
SMU	M937405	120.040	0.012	0.12004	0.12064	119.98	0.12	2	-0.060	-0.05%	2	0.269	0.22%
VNIIM	M937403	120.240	0.012	0.12024	0.12084	120.00	0.57	2	-0.240	-0.20%	2	0.619	0.51%
NMISA	M937424	119.970	0.012	0.11997	0.12057	120.17	0.26	2	0.200	0.17%	2	0.355	0.30%
KRISS	M937414	119.890	0.012	0.11989	0.12049	119.88	0.12	2	-0.010	-0.01%	2	0.269	0.22%
IPQ	M937419	119.920	0.012	0.11992	0.12052	120.61	0.32	2	0.690	0.58%	2	0.401	0.33%
INMETRO	M937401	119.900	0.012	0.11990	0.12050	119.72	1.11	2	-0.180	-0.15%	2	1.136	0.95%

Table 10: Results and degrees-of-equivalence for propane

Lab	Cylinder	x_{prep} $\mu\text{mol/mol}$	u_{prep} $\mu\text{mol/mol}$	u_{ver} $\mu\text{mol/mol}$	u_{KCRV} $\mu\text{mol/mol}$	x_{lab} $\mu\text{mol/mol}$	u_{lab} $\mu\text{mol/mol}$	k_{lab}	D $\mu\text{mol/mol}$	D/x	k	$U(D)$ $\mu\text{mol/mol}$	$U(D)/x$
NIST	M937423	5.9745	0.0037	0.00597	0.00703	5.979	0.015	2	0.0045	0.08%	2	0.0206	0.34%
NIM	M937410	5.9758	0.0037	0.00598	0.00703	5.969	0.036	2	-0.0068	-0.11%	2	0.0386	0.65%
NPL	M937411	5.9692	0.0037	0.00597	0.00702	5.980	0.020	2	0.0108	0.18%	2	0.0244	0.41%
VSL	M937400	5.9770	0.0037	0.00598	0.00703	5.980	0.017	2	0.0030	0.05%	2	0.0221	0.37%
CENAM	M937407	5.9550	0.0037	0.00596	0.00701	5.934	0.034	2	-0.0210	-0.35%	2	0.0368	0.62%
SMU	M937405	5.9812	0.0037	0.00598	0.00703	6.004	0.058	2	0.0228	0.38%	2	0.0597	1.00%
VNIIM	M937403	5.9793	0.0037	0.00598	0.00703	5.901	0.043	2	-0.0783	-1.31%	2	0.0452	0.76%
NMISA	M937424	5.9760	0.0037	0.00598	0.00703	6.048	0.030	2	0.0720	1.20%	2	0.0331	0.55%
KRISS	M937414	5.9787	0.0037	0.00598	0.00703	5.98	0.06	2	0.0013	0.02%	2	0.0616	1.03%
IPQ													
INMETRO	M937401	5.9810	0.0037	0.00598	0.00703	5.620	0.172	2	-0.3610	-6.04%	2	0.1726	2.89%

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Table 11: Results and degrees-of-equivalence for nitrogen monoxide

Lab	Cylinder	x_{prep} μmol/mol	u_{prep} μmol/mol	u_{ver} μmol/mol	u_{KCRV} μmol/mol	x_{lab} μmol/mol	U_{lab} μmol/mol	k_{lab}	D μmol/mol	D/x	k	$U(D)$ μmol/mol	$U(D)/x$
NIST	M937423	80.120	0.052	0.0801	0.0955	80.14	0.29	2	0.020	0.02%	2	0.347	0.43%
NIM	M937410	80.138	0.051	0.0801	0.0950	79.65	0.80	2	-0.488	-0.61%	2	0.822	1.03%
NPL	M937411	80.049	0.051	0.0800	0.0949	80.3	0.8	2	0.251	0.31%	2	0.822	1.03%
VSL	M937400	80.156	0.052	0.0802	0.0955	80.34	0.39	2	0.184	0.23%	2	0.434	0.54%
CENAM	M937407	79.859	0.052	0.0799	0.0953	78.20	1.70	2	-1.659	-2.08%	2	1.711	2.14%
SMU	M937405	80.210	0.052	0.0802	0.0956	80.18	0.80	2	-0.030	-0.04%	2	0.823	1.03%
VNIIM	M937403	80.185	0.052	0.0802	0.0956	80.78	0.42	2	0.595	0.74%	2	0.461	0.58%
NMISA	M937424	80.142	0.052	0.0801	0.0955	79.42	0.51	2	-0.722	-0.90%	2	0.545	0.68%
KRISS	M937414	80.176	0.052	0.0802	0.0956	80.72	0.45	2	0.544	0.68%	2	0.489	0.61%
IPQ													
INMETRO	M937401	80.207	0.051	0.0802	0.0950	79.60	1.40	2	-0.607	-0.76%	2	1.413	1.76%

Table 12: Results and degrees-of-equivalence for sulphur dioxide

Lab	Cylinder	x_{prep} μmol/mol	u_{prep} μmol/mol	u_{ver} μmol/mol	u_{KCRV} μmol/mol	x_{lab} μmol/mol	U_{lab} μmol/mol	k_{lab}	D μmol/mol	D/x	k	$U(D)$ μmol/mol	$U(D)/x$
NIST	M937423	80.004	0.048	0.0800	0.0933	80.25	0.25	2	0.25	0.31%	2	0.3120	0.39%
NIM	M937410	80.022	0.048	0.0800	0.0933	79.16	0.79	2	-0.86	-1.08%	2	0.8117	1.01%
NPL	M937411	79.933	0.048	0.0799	0.0932	79.8	0.4	2	-0.13	-0.17%	2	0.4413	0.55%
VSL	M937400	80.039	0.048	0.0800	0.0933	79.85	0.21	2	-0.19	-0.24%	2	0.2810	0.35%
CENAM	M937407	79.743	0.048	0.0797	0.0931	80.5	3.3	2	0.76	0.95%	2	3.3052	4.14%
SMU	M937405	80.094	0.048	0.0801	0.0934	80.47	0.87	2	0.38	0.47%	2	0.8898	1.11%
VNIIM	M937403	80.068	0.048	0.0801	0.0934	80.77	0.47	2	0.70	0.88%	2	0.5057	0.63%
NMISA	M937424	80.026	0.048	0.0800	0.0933	80.13	0.54	2	0.10	0.13%	2	0.5713	0.71%
KRISS	M937414	80.060	0.048	0.0801	0.0933	79.84	0.44	2	-0.22	-0.27%	2	0.4780	0.60%
IPQ	M937419	80.017	0.048	0.0800	0.0933	79.64	0.44	2	-0.38	-0.47%	2	0.4779	0.60%
INMETRO	M937401	80.091	0.048	0.0801	0.0934	80.0	0.9	2	-0.09	-0.11%	2	0.9192	1.15%

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In the figures 1, 3, 5, 7, and 9 the relative deviation of the submitted data with respect to the gravimetric value is given. In these figures, the uncertainty bars represent the expanded uncertainty associated with the results submitted.

In the figures 2, 4, 6, 8, and 10 the degrees of equivalence for all participating laboratories are given in absolute relation to the gravimetric value. The uncertainties are, as required by the MRA [9], given as 95% confidence intervals. For the evaluation of uncertainty of the degrees of equivalence, the normal distribution has been assumed, and a coverage factor $k = 2$ was used. For obtaining the standard uncertainty of the laboratory results, the expanded uncertainty (stated at a confidence level of 95%) from the laboratory was divided by the reported coverage factor.

In addition, figures of the laboratory results with their reported expanded uncertainties are presented relative to the gravimetric value. The results of INMETRO, participating as a pilot study, are included in these figures.

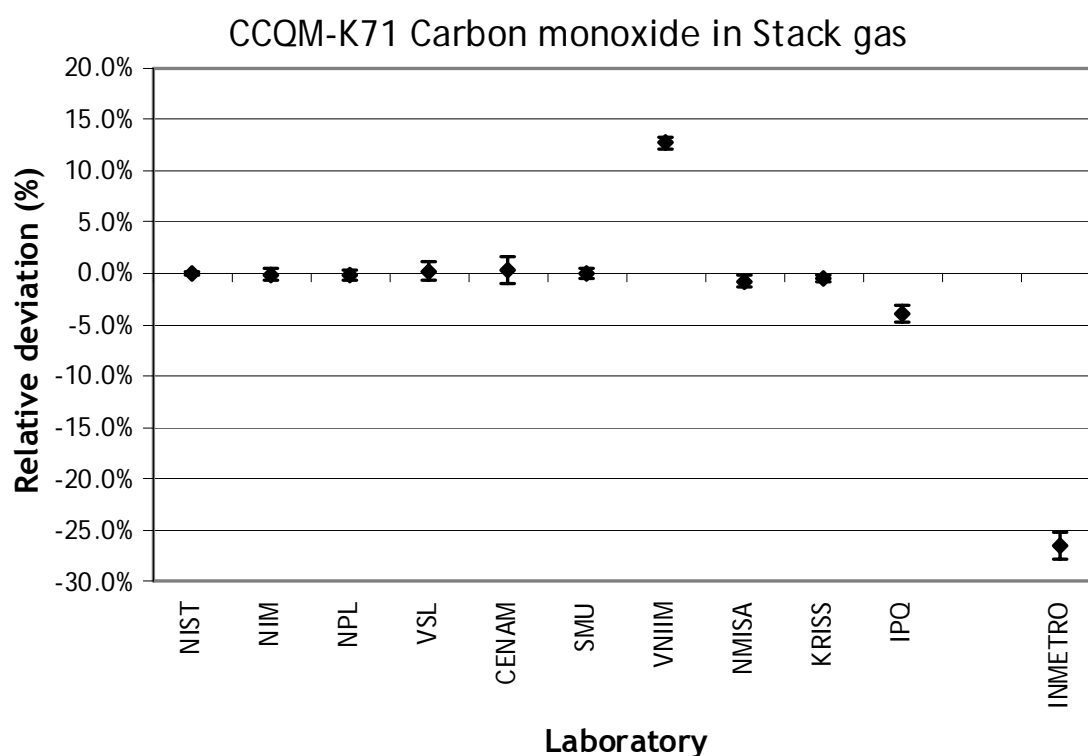


Figure 1: Relative deviation of submitted data for carbon monoxide

CCQM-K71 Carbon monoxide in Stack gas

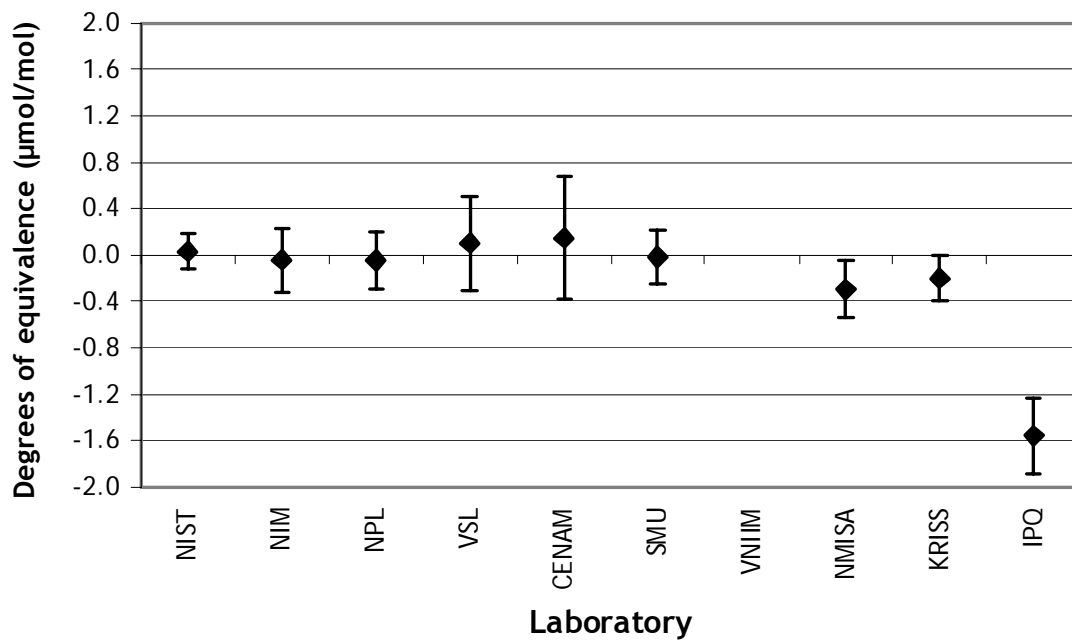


Figure 2: Degrees-of-equivalence for carbon monoxide

CCQM-K71 Carbon dioxide in Stack gas

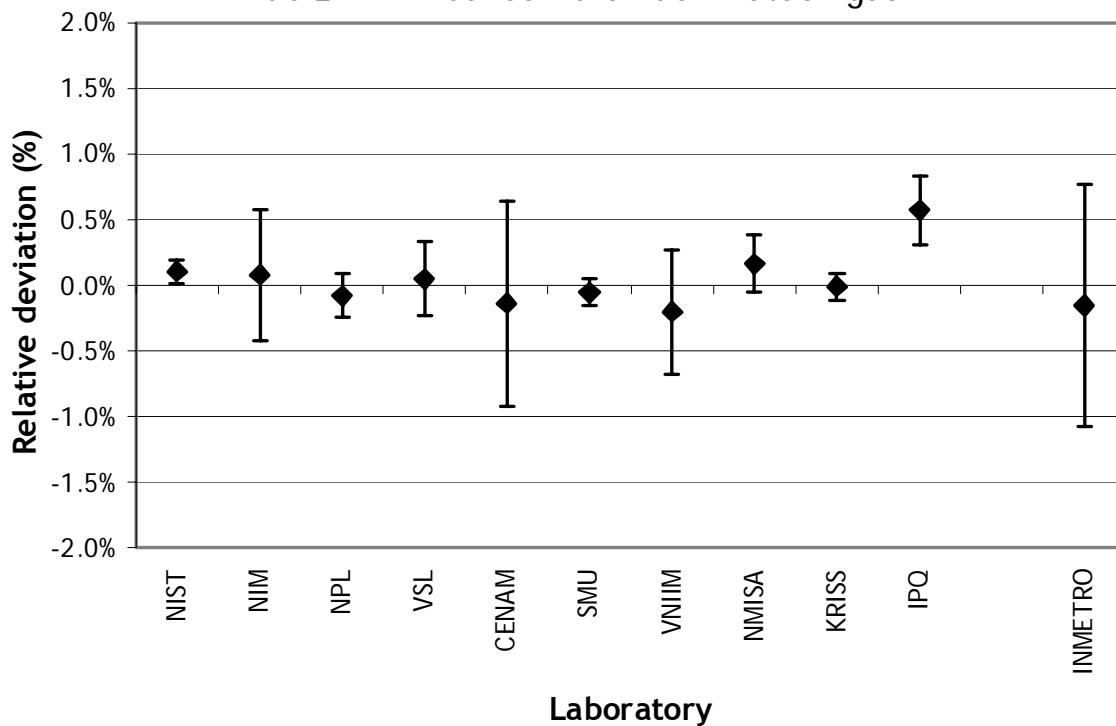


Figure 3: Relative deviation of submitted data for carbon dioxide

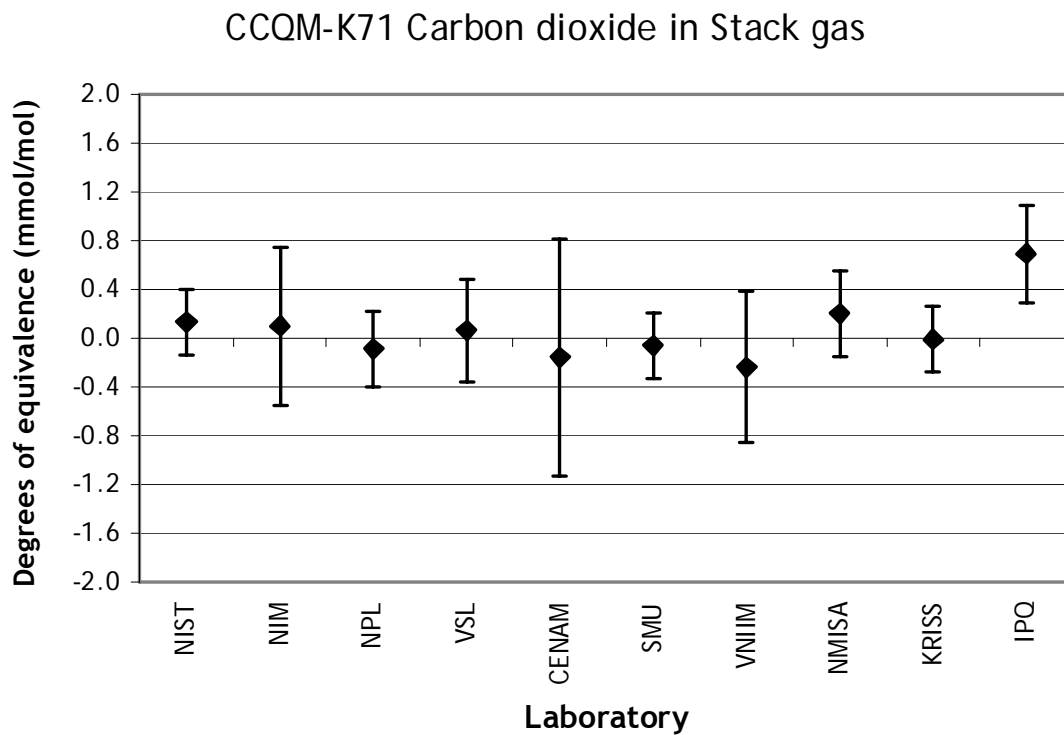


Figure 4: Degrees-of-equivalence for carbon dioxide

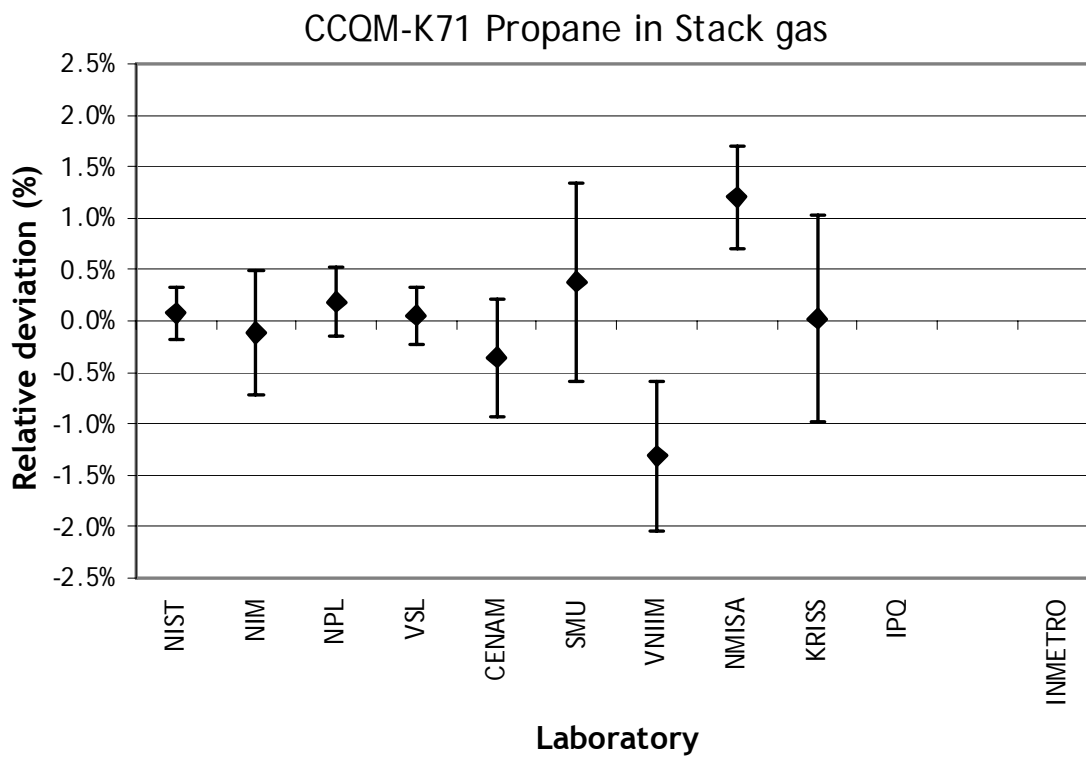


Figure 5: Relative deviation of submitted data for propane

CCQM-K71 Propane in Stack gas

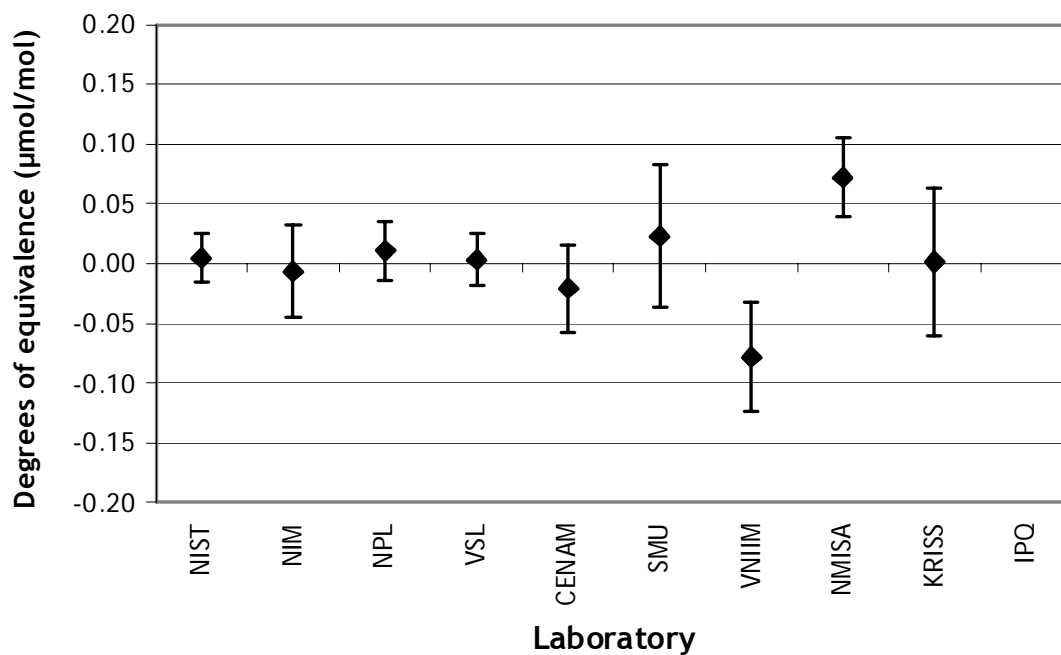


Figure 6: Degrees-of-equivalence for propane

CCQM-K71 Nitrogen monoxide in Stack gas

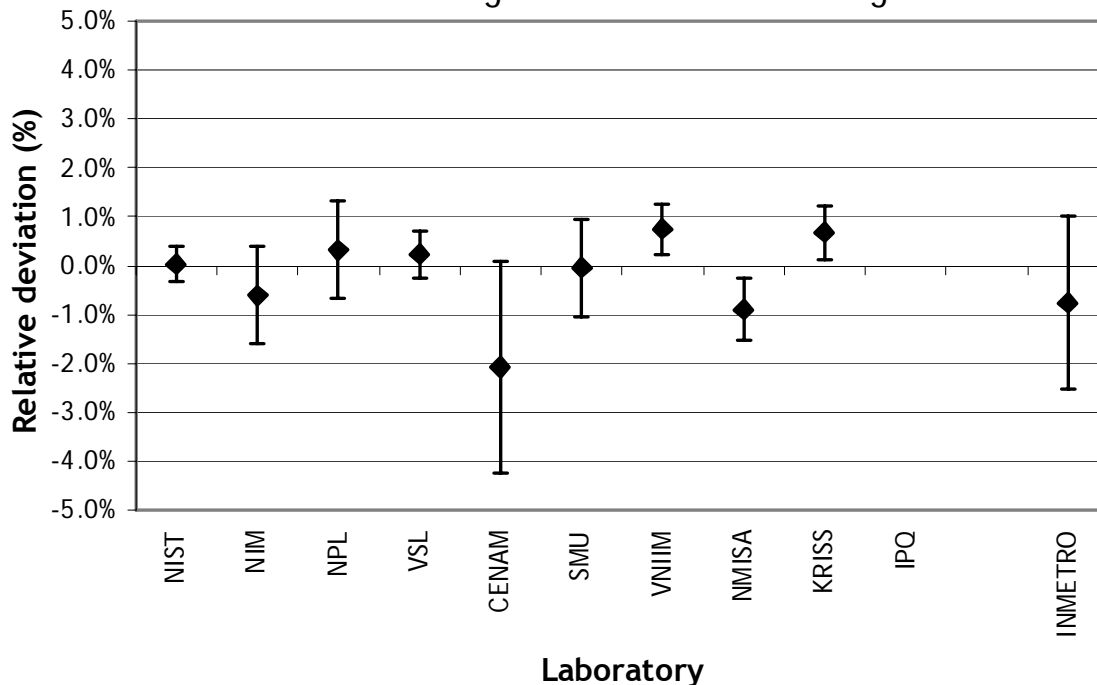


Figure 7: Relative deviation of submitted data for nitrogen monoxide

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CCQM-K71 Nitrogen monoxide in Stack gas

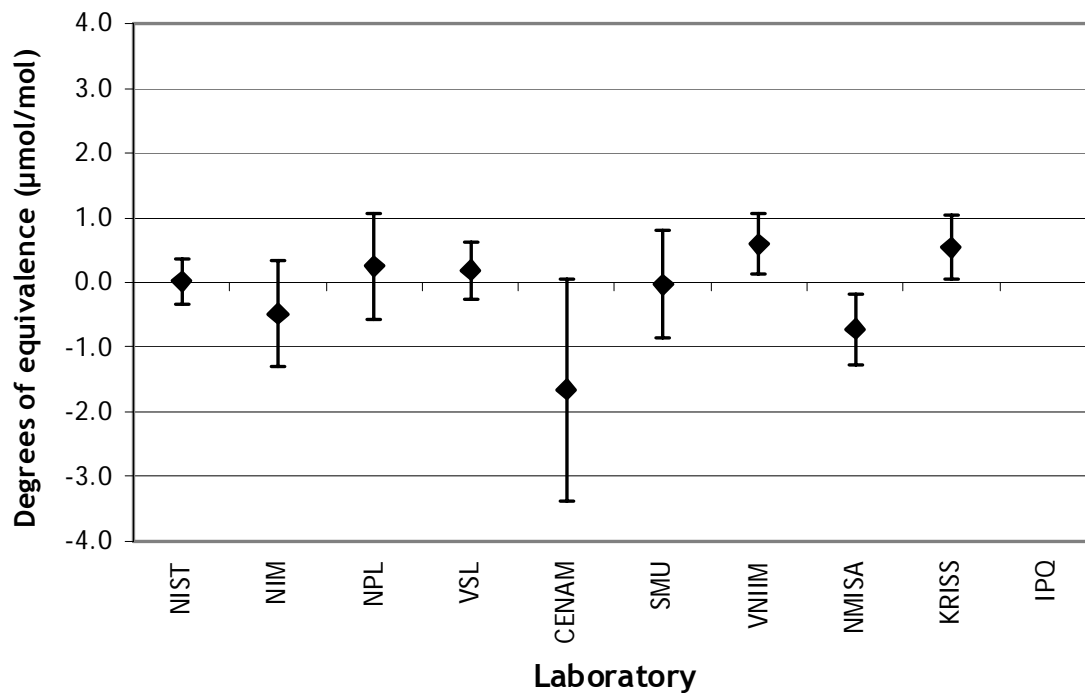


Figure 8: Degrees-of-equivalence for nitrogen monoxide

CCQM-K71 Sulphur dioxide in Stack gas

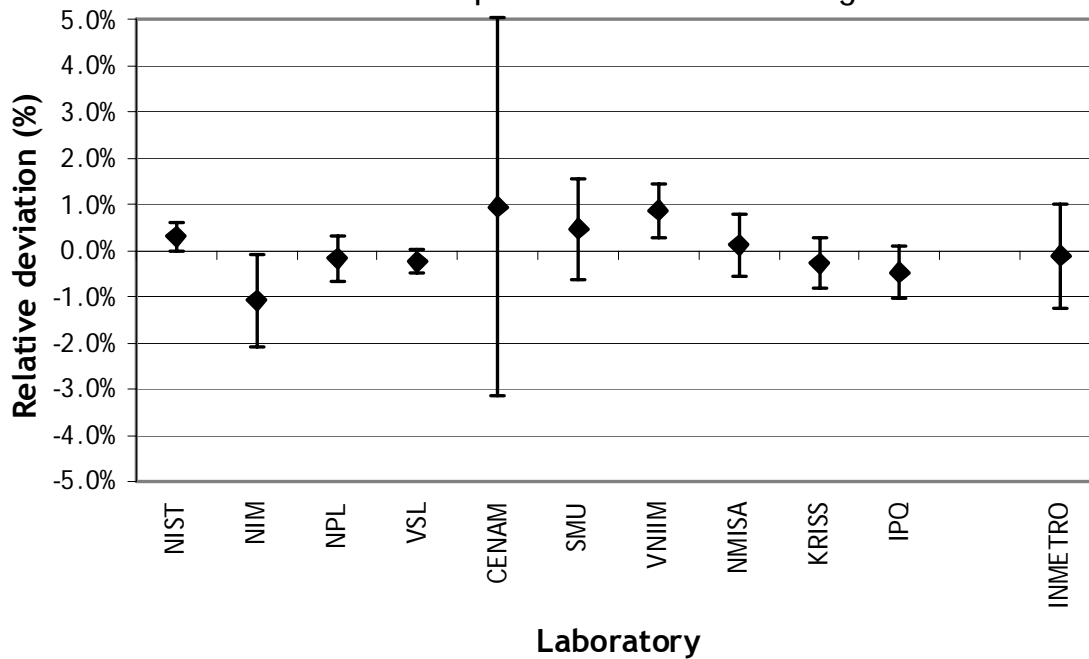


Figure 9: Relative deviation of submitted data for sulphur dioxide

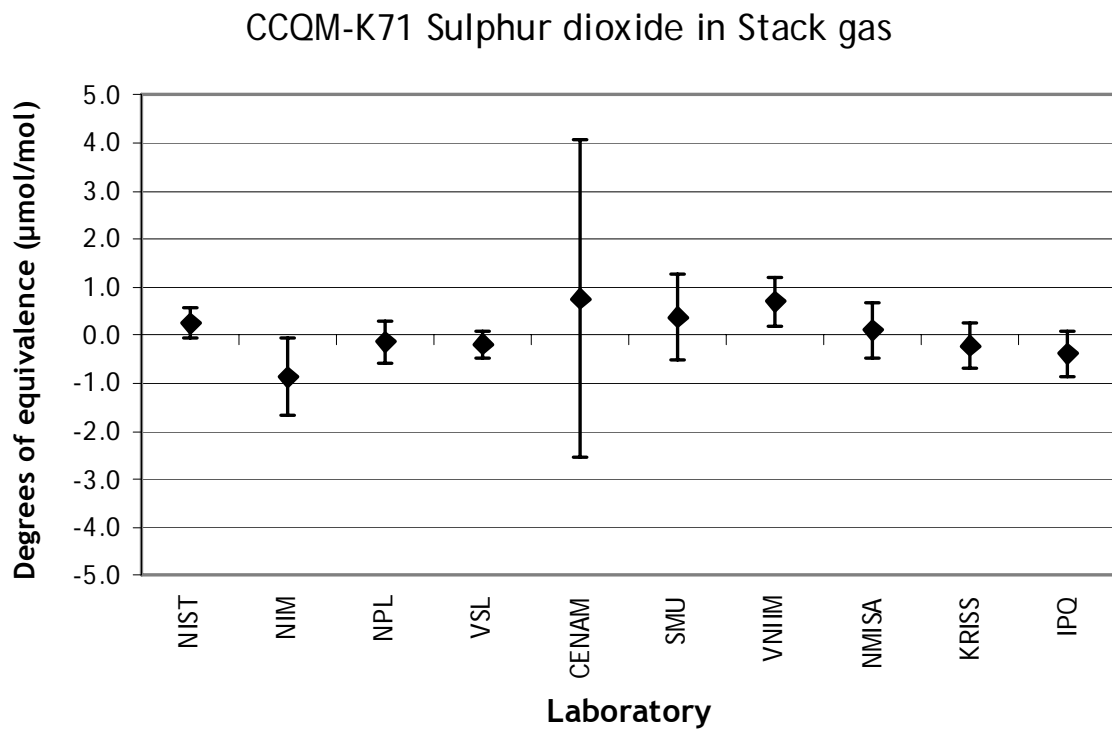


Figure 10: Degrees-of-equivalence for sulphur dioxide

4 Discussion and conclusions

Most of the participating NMI's mastered the challenges set in this key comparison well. IPQ reported results for CO, CO₂ and SO₂ only. INMETRO took part in this comparison as a pilot study.

The results for carbon monoxide showed serious deviations for INMETRO (-26.5% relative), VNIIM (+12.7% relative) and IPQ (-3.9% relative). In none of the cases was equivalence with the KCRV demonstrated. Two other results inconsistent with the KCRV were reported by NMISA and KRIS.

For carbon dioxide, all laboratories except IPQ reported results consistent with the KCRV.

For propane, INMETRO reported a seriously deviating result (-6.0% relative). NMISA and VNIIM also reported deviating results (in absolute sense more than 1% relative). None of these three results were consistent with the KCRV.

Three results for nitrogen monoxide were not consistent with the KCRV: KRIS, VNIIM and NMISA. With the exception of CENAM, none of the results differed more than 1% relative from the KCRV.

For sulphur dioxide, two results were not consistent with the KCRV: NIM and VNIIM. Only one result deviated more than 1% relative from the reference value (NIM).

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Measurement report INMETRO⁶

Laboratory name: LABAG/INMETRO

Cylinder number: M937401

Measurement #1

Component	Date (dd/mm/yy)	Result	Unit	Standard deviation (% relative)	number of replicates
NO	28/10/08	79.9	µmol/mol	2.5	8
SO ₂	28/10/08	79.9	µmol/mol	0.1	8
CO	07/11/08	29.495	µmol/mol	0.210	5
CO ₂	26/09/08	11.977	% mol/mol	0.180	8
C ₃ H ₈	17/10/08	5.499	µmol/mol	0.900	8

Measurement #2

Component	Date (dd/mm/yy)	Result	Unit	Standard deviation (% relative)	number of replicates
NO	29/10/08	77.9	µmol/mol	0.1	8
SO ₂	29/10/08	79.9	µmol/mol	0.1	8
CO	****	****	****	****	****
CO ₂	29/09/08	11.969	% mol/mol	0.160	8
C ₃ H ₈	23/10/08	5.584	µmol/mol	1.470	8

Measurement #3

Component	Date (dd/mm/yy)	Result	Unit	Standard deviation (% relative)	number of replicates
NO	30/10/08	80.9	µmol/mol	0.5	8
SO ₂	30/10/08	80.1	µmol/mol	0.1	8
CO	****	****	****	****	****
CO ₂	30/09/08	11.969	% mol/mol	0.120	8
C ₃ H ₈	28/10/08	5.811	µmol/mol	1.210	8

⁶ This laboratory participated in this comparison as a study.

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Results

Component	Result	Unit	Expanded Uncertainty	Coverage factor[1]
NO	79.6	µmol/mol	1.4	2
SO ₂	80.0	µmol/mol	0.9	2
CO	29.495	µmol/mol	0.369	2
CO ₂	11.972	% mol/mol	0.111	2
C ₃ H ₈	5.620	µmol/mol	0.172	2

[\[1\] The coverage factor shall be based on approximately 95% confidence.](#)

Details of the measurement method used

1) To analyse the components NO and SO₂, the infrared analysers (HORIBA - model VIA-510) were used.

Measuring range to analyse NO: 0-100/200/1000/2000 ppm

Measuring range to analyse SO₂: 0-100/200/1000/2000 ppm

Analysers out put: 0 – 10 V

Calibration Standards

Three standards were used to calibrate the infrared analyser model VIA-510 to analyse NO. They were prepared according International Standard ISO 6142:2001 by VSL.

PRM 289180

Component	Assigned value(x) 10 ⁻⁶ mol/mol	Standard uncertainty (u(x)) 10 ⁻⁶ mol/mol
Nitric oxide	50.06	0.13

PRM 9303 E

Component	Assigned value(x) 10 ⁻⁶ mol/mol	Standard uncertainty (u(x)) 10 ⁻⁶ mol/mol
Nitric oxide	200.3	0.4

PRM 9300 E

Component	Assigned value(x) 10 ⁻⁶ mol/mol	Standard uncertainty (u(x)) 10 ⁻⁶ mol/mol
Nitric oxide	453.0	0.9

Calibration Standards

Three standards were used to calibrate the infrared analyser model VIA-510 to analyse SO₂. They were prepared according International Standard ISO 6142:2001 by VSL.

PRM D 751937

Component	Assigned value(x) 10 ⁻⁶ mol/mol	Standard uncertainty (u(x)) 10 ⁻⁶ mol/mol
Sulfur dioxide	120.0	0.3

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PRM D 751942

Component	Assigned value(x) 10 ⁻⁶ mol/mol	Standard uncertainty (u(x)) 10 ⁻⁶ mol/mol
Sulfur dioxide	180.2	0.5

PRM D 751954

Component	Assigned value(x) 10 ⁻⁶ mol/mol	Standard uncertainty (u(x)) 10 ⁻⁶ mol/mol
Sulfur dioxide	250.6	0.5

Instrument Calibration

The standards used are listed above. The injection was done manually. The order of the injections was: first injection of the standards and then injection of the sample, and they were injected eight times. And the calibration was done according ISO 6143, the best model was determined using the software B_Least.

Sample handling

After arrival in the laboratory, the cylinder was stabilised at room temperature (21°C and humidity of 55%) before measurements. The standards and sample were transferred directly to the infrared analyser using a system composed of pressure regulator, flow meter and control valves.

2) To analyse the component CO the Gas Chromatograph (GC) with catalytic methanizer was used.

Varian CP-3800 GC equipped with thermal conductivity detector (TCD) and flame ionisation detector (FID).

The carbon monoxide was determined with column catalytic methanizer and detected using the flame ionisation detector (FID).

Carrier gas: Helium.

Column: 15 m x 0,25mm x 0,39mm Factorfour capillary column

Data collection was performed using Software Galaxie 1.X.

Calibration Standards

Three standards were used to calibrate the GC. They were prepared according International Standard ISO 6142:2001 by VSL.

PRM D247552

Component	Assigned value(x) 10 ⁻⁶ mol/mol	Standard uncertainty (u(x)) 10 ⁻⁶ mol/mol
Carbon monoxide	7.002	0.035

PRM MY 9656

Component	Assigned value(x) 10 ⁻⁶ mol/mol	Standard uncertainty (u(x)) 10 ⁻⁶ mol/mol
Carbon monoxide	10.00	0.05

PRM D247714

Component	Assigned value(x) 10 ⁻⁶ mol/mol	Standard uncertainty (u(x)) 10 ⁻⁶ mol/mol
Carbon monoxide	50.08	0.20

Instrument Calibration

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The standards used are listed above. The injection was done manually. The order of the injections was: first injection of the standards and then injection of the sample and they were injected five times. And the calibration was done according ISO 6143, the best model was determined using the software B_Least.

Sample handling

After arrival in the laboratory, the cylinder was stabilised at room temperature (21°C and humidity of 55%) before measurements. The standards and sample were transferred directly to the GC using a system composed of three valves, pressure regulator and flow meter.

3) To analyse the component CO₂ the Micro Gas Chromatography (GC – model 4900) was used.

This Micro GC has four channels and only analyse gases. The channel B was used to analyse the component CO₂, with a detector TCD and a column pora PLOT Q (0,15mmID, 10mts). The injection volume was 10uL.

Calibration Standards

Three standards were used to calibrate the GC. They were prepared according International Standard ISO 6142:2001 by VSL. PRM D523407

Component	Assigned value(x) 10 ⁻² mol/mol	Standard uncertainty (u(x)) 10 ⁻² mol/mol
Carbon dioxide	7.005	0.001

PRM D247547

Component	Assigned value(x) 10 ⁻² mol/mol	Standard uncertainty (u(x)) 10 ⁻² mol/mol
Carbon dioxide	8.993	0.005

PRM D523447

Component	Assigned value(x) 10 ⁻² mol/mol	Standard uncertainty (u(x)) 10 ⁻² mol/mol
Carbon dioxide	15.015	0.008

Instrument Calibration

The standards used are listed above. Pressure correction was take into account. The measurement was done automatically using an automatic multi selective valve. The order of injections was: first injection of the standards and then injection of the sample and they injected eight times. And the calibration was done according ISO 6143, the best model was determined using the software B_Least.

Sample handling

After arrival in the laboratory, the cylinder was stabilised at room temperature (21°C and humidity of 55%) before measurements. The standards and sample were transferred directly to the GC using a system composed of with an automatic multi selective valve, pressure regulators and flow meter.

4) And to analyse the component C₃H₈ the Gas Chromatography (GC – 3800 special) was used.

A GC specifically set up for natural gas analysis was used:

The GC model is Varian CP-3800 (ISO 6974 configuration) equipped with both TCD and FID detectors, but the component propane was determined using the FID detector.

Carrier gas: Helium.

Columns: 1.5 m x 1/8" ultimetel Molsieve 13X 80/100
0.5 m x 1/8" ultimetel Hayesep T 80/100

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0.5 m x 1/8" ultimetmetal Hayesep Q 80/100
60 m x 0.25 mm CP-Sil 5 CB

Data collection was performed using Star Chromatography Workstation 6.3

Calibration Standards

Three standards were used to calibrate the GC. They were prepared according International Standard ISO 6142:2001 by Inmetro, but the stability tests have not been done yet, so the uncertainties reported above are related to the gravimetric preparation only.

PSM 100255

Component	Assigned value(x) 10 ⁻⁶ mol/mol	Standard uncertainty (u(x)) 10 ⁻⁶ mol/mol
Propane	4.994	0.002

PSM 107518

Component	Assigned value(x) 10 ⁻⁶ mol/mol	Standard uncertainty (u(x)) 10 ⁻⁶ mol/mol
Propane	6.994	0.002

PSM 107528

Component	Assigned value(x) 10 ⁻⁶ mol/mol	Standard uncertainty (u(x)) 10 ⁻⁶ mol/mol
Propane	9.991	0.003

Instrument Calibration

The standards used are listed above. Pressure correction was take into account. The measurement was automatic with an automatic multi selective valve. The order of the injections was: first Injection of the standards and then injection of the sample and they were injected eight times. And the calibration was done according ISO 6143, the best model was determined using the software B_Least.

Sample handling

After arrival in the laboratory, the cylinder was stabilised at room temperature (21°C and humidity of 55%) before measurements. The standards and sample were transferred directly to the GC using a system composed of four valves, pressure regulator and flow meter.

Evaluation of measurement uncertainty

The uncertainty of the unknown sample was calculated according to ISO 6143, using the software B_least. The combined uncertainty was multiplied by a coverage factor of 2 with a confidence interval of 95%. Three sources of uncertainty were considered:

- Uncertainty of the standards (certificate – type B)
- Uncertainty of the area (analysis – type A)
- Calibration curve (type A)

Measurement report NIM

Measurement of NO

Group #	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (% relative)	number of replicates
1	10/12/08	79.591	0.32%	6
2	11/12/08	79.704	0.14%	7
3	11/12/08	79.664	0.05%	6

Measurement SO₂

Group #	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (% relative)	number of replicates
1	12/12/08	78.781	0.42%	6
2	12/12/08	79.542	0.22%	6
3	17/12/08	78.879	0.33%	7
4	17/12/08	79.526	0.18%	6
5	17/12/08	78.796	0.33%	7
6	17/12/08	79.442	0.18%	6

Measurement CO

Group #	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (% relative)	number of replicates
1	12/01/09	40.113	0.22%	6
2	12/01/09	40.043	0.02%	6
3	13/01/09	39.998	0.23%	6
4	13/01/09	40.063	0.16%	6

Measurement CO₂

Group #	Date (dd/mm/yy)	Result (mmol/mol)	Standard deviation (% relative)	number of replicates
1	22/12/08	120.23	0.20%	6
2	23/12/08	120.28	0.30%	9
3	24/12/08	120.27	0.32%	7
4	24/12/08	120.15	0.30%	9
5	06/01/09	120.29	0.19%	6
6	06/01/09	120.13	0.47%	15

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Measurement C₃H₈

Group #	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (% relative)	number of replicates
1	14/01/09	5.961	0.10%	6
2	15/01/09	5.981	0.19%	4
3	15/01/09	5.965	0.15%	4
4	15/01/09	5.971	0.18%	4
5	15/01/09	5.967	0.17%	6

Results

Component	Result	Expanded Uncertainty	Coverage factor
NO	79.65 μmol/mol	0.80 μmol/mol	2*
SO ₂	79.16 μmol/mol	0.79 μmol/mol	2*
CO	40.05 μmol/mol	0.24 μmol/mol	2*
CO ₂	120.2 mmol/mol	0.6 mmol/mol	2*
C ₃ H ₈	5.969 μmol/mol	0.036 μmol/mol	2*

*The coverage factor was based on approximately 95% confidence.

Reference method

NO was analyzed by 42C NO-NO₂-NO_x Analyzer from Thermo Environmental Instruments made in U.S.A. based on Chemiluminescence principle, with the range of measurement: 0-100ppm.

SO₂ was analyzed by 43C SO₂ Analyzer from Thermo Environmental Instruments made in U.S.A. based on UV fluorescence principle, with the range of measurement: 0-100ppm.

CO was analyzed by 48C CO Analyzer from Thermo Environmental Instruments made in U.S.A. based on infrared principle, with the range of measurement: 0-100ppm.

Another instrument was QGS-08B CO-Analyzer from Beijing Analyze Instrument factory based on infrared principle, with the range of measurement: 0-50ppm.

CO₂ was analyzed by AO2020 CO-CO₂ Gas Analyzers of ABB automation products made in Germany, based on infrared principle, with the range of measurement: 0-20% mol/mol.

C₃H₈ was analyzed by GC-FID (GC-2010, Shimadzu, Japan) with a column of HP-AL/KCL (30m*0.533mm*15.00um). The oven temperature was 80° C. The column flow rate was 5.82mL/min and the total flow rate was 42.0mL/min.

Calibration standards

All of the references we used were made by the gravimetric method according to ISO 6142-2001 by ourselves. The pure gases were checked before using to make sure that their purities were good enough and the impurities had no effect on the quality of reference gas mixture. The parent gases were filled into a 4-liter aluminum cylinder. At least, 10 g parent gas was filled into the cylinder. The cylinder was weighed before and after the filling using a balance with the sensitivity of 1 mg.

The concentration of reference gas was calculated according to the following equation.

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$$x_i = \frac{\sum_{A=1}^P \left(\frac{x_{i,A} \cdot m_A}{\sum_{i=1}^n x_{i,A} \cdot M_i} \right)}{\sum_{A=1}^P \left(\frac{m_A}{\sum_{i=1}^n x_{i,A} \cdot M_i} \right)}$$

The uncertainty of reference gas included the contributions from gravimetric method and from stability. The uncertainty from stability was evaluated based on short-time and long-time testing before this comparison. The uncertainty from gravimetric method was calculated according to the following equation.

$$u^2(x_i) = \sum_{r=1}^q \left(\frac{\partial f_i}{\partial f_r} \right)^2 \cdot u^2(y_r) + 2 \sum_{r=1}^{q-1} \sum_{s=r+1}^q \left(\frac{\partial f_i}{\partial f_r} \right) \left(\frac{\partial f_i}{\partial f_s} \right) \cdot u(y_r, y_s)$$

Mass of parent gas filled, molecular weight and mole fraction of compound were the main sources of the uncertainty of gravimetric method.

The reference gases used were listed in the following table:

Cylinder Number	Component and assigned value(x)	Relative standard uncertainty (u(x))
411356	NO: 79.05 µmol/mol	0.45%
	N ₂ : balance	
411221	NO: 79.45 µmol/mol	0.45%
	N ₂ : balance	
354378	SO ₂ : 76.72 µmol/mol	0.40%
	N ₂ : balance	
354741	SO ₂ : 77.80 µmol/mol	0.40%
	CO ₂ : 117.3 mmol/mol	0.20%
	N ₂ : balance	
434169	SO ₂ : 82.41 µmol/mol	0.40%
	CO ₂ : 128.9 mmol/mol	0.20%
	N ₂ : balance	
435085	CO: 39.94 µmol/mol	0.22%
	CO ₂ : 120.7 mmol/mol	0.20%
	N ₂ : balance	
435036	CO: 41.11 µmol/mol	0.22%
	CO ₂ : 121.1 mmol/mol	0.20%
	N ₂ : balance	
435140	CO: 41.60 µmol/mol	0.22%
	CO ₂ : 122.0 mmol/mol	0.20%
	C ₃ H ₈ : 6.779 µmol/mol	0.20%
	N ₂ : balance	
435142	CO: 40.37 µmol/mol	0.22%
	CO ₂ : 120.2 mmol/mol	0.20%
	C ₃ H ₈ : 7.972 µmol/mol	0.20%
	N ₂ : balance	

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435041	CO: 39.37 $\mu\text{mol/mol}$	0.22%
	CO ₂ : 120.5 mmol/mol	0.20%
	C ₃ H ₈ : 5.627 $\mu\text{mol/mol}$	0.20%
	N ₂ : balance	
410856	CO ₂ : 121.2 mmol/mol	0.20%
	N ₂ : balance	
412222	CO ₂ : 131.8 mmol/mol	0.20%
	N ₂ : balance	
435094	CO ₂ : 90.7 mmol/mol	0.20%
	N ₂ : balance	
435026	CO ₂ : 106.3 mmol/mol	0.20%
	N ₂ : balance	
434907	CO ₂ : 120.1 mmol/mol	0.20%
	C ₃ H ₈ : 6.150 $\mu\text{mol/mol}$	0.20%
	N ₂ : balance	
435111	CO ₂ : 120.4 mmol/mol	0.20%
	C ₃ H ₈ : 7.309 $\mu\text{mol/mol}$	0.20%
	N ₂ : balance	

Instrument calibration

When testing CO, CO₂, NO and SO₂, a series reference gases were introduced into the analyzer in sequence and repeated this sequence until the signal readings of the analyzer were stable. Then the sample gas was introduced into the analyzer. To make sure there was no signal drift, the reference gas was analyzed again. In all these operations, the gas flow rates into the monitor and venting should be consistent. Single point calibration was used to calculate the concentration of target compound in sample cylinder.

When analyzing C₃H₈, "A-B-A-B-A" type calibration was used. That means the sample gas and our reference gas were measured in the order of Reference – Sample – Reference – Sample – Reference. The gas pressure at the sample loop of GC was controlled at almost same value during one analysis sequence. Single point calibration was used to calculate the concentration of target compound in sample cylinder.

Sample handling

When package box including comparison cylinder arrived at the lab, it was in good state. Then the box was unpacked and the comparison cylinder was stored at room temperature. A SS regulator was connected to the cylinder.

To analyze C₃H₈, the gas mixtures in both comparison cylinder and the reference cylinder, via regulators and Teflon tube, were introduced into a 6-port valve. The 6-port valve was driven by compressed air. The size of sample loop used here was 1mL and the gas pressure before the sample loop was controlled at 0.1MPa by regulator. In case of GC-FID used, single point calibration method was used.

When testing CO, CO₂, NO and SO₂, the reference and sample gases were directly introduced into the analyzer through a "T" type tube by the pump inside the instrument used. The flow rate was about 0.5~1L/min, controlled by a flow controller. Another outlet of the "T" tube was vented to the atmosphere. There was a pressure regulator between the cylinder and the inlet of the "T" tube to control the total gas flow rate and make sure that about 100mL/min vent to the atmosphere. The venting flow rate was read from a flow meter.

Evaluation of measurement uncertainty

The contributions of measurement uncertainty were from reference gas, signal readings of the sample gas and reference gas, repeatability in one day or one group and reproducibility in different days or groups.

$$u(c_{CCQM}) = \sqrt{u^2(c_{PRM}) + u^2(H_{CCQM}) + u^2(H_{PRM}) + u^2(f_{int ra}) + u^2(f_{int er})}$$

Here, u means relative standard uncertainty.

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$u(c_{CCQM})$: Measurement uncertainty of concentration of the target component in the comparison sample gas cylinder.

$u(H_{CCQM})$: Uncertainty of signal reading of the sample gas from instrument or peak height on GC-FID.

$u(H_{PRM})$: Uncertainty of signal reading of the reference gas from instrument or peak height on GC-FID.

For the H_{CCQM} and H_{PRM} , the relative standard uncertainty could be calculated from the relative standard deviation (RSD) of the signal reading. The relative standard uncertainty is RSD/sqrt(n), where n is the number of signal reading.

$u(c_{PRM})$: Uncertainty of concentration of the reference gas, which was combined by the uncertainty from gravimetric method according to ISO 6142-2001 and the uncertainty from the stability of the reference gas.

$u(f_{int\ ra})$: Uncertainty of repeatability in one day or one group. The relative standard uncertainty of $f_{int\ ra}$ was calculated from the relative standard deviation (RSD) of repeating test in one day or one group. The relative standard uncertainty is RSD/sqrt(n), where n is the number of the repeating test.

$u(f_{int\ er})$: Uncertainty of reproducibility in different days or groups. The relative standard uncertainty $f_{int\ er}$ was calculated from the relative standard deviation (RSD) of repeating test in different days or groups. The relative standard uncertainty is RSD/sqrt(n), where n is the number of the repeating test.

Uncertainties estimation for the results is listed in following table.

Relative standard uncertainty	NO	SO ₂	CO	CO ₂	C ₃ H ₈
$u(c_{PRM})$	0.45%	0.40%	0.22%	0.20%	0.20%
$u(H_{CCQM})$	0.08%	0.04%	0.06%	0.02%	0.10%
$u(H_{PRM})$	0.08%	0.04%	0.06%	0.02%	0.10%
$u(f_{int\ ra})$	0.16%	0.21%	0.16%	0.12%	0.10%
$u(f_{int\ er})$	0.04%	0.19%	0.06%	0.03%	0.06%
$u(c_{CCQM})$	0.49%	0.49%	0.29%	0.24%	0.27%
Relative expanded uncertainty**	1.0%	1.0%	0.6%	0.5%	0.6%

**The coverage factor $k=2$ (95% confidence level)

Measurement report KRISS

Laboratory : KRISS
 Laboratory code :
 Cylinder number : M937414

Measurement #1

Component	Date	Result (mol/mol)	Standard deviation (% relative)	number of replicates
NO	2008-09-19	80.20×10^{-6}	0.48	6
SO ₂	2008-09-19	79.46×10^{-6}	0.38	6
CO	2008-09-23	39.91×10^{-6}	0.24	3
CO ₂	2008-09-22	119.87×10^{-3}	0.06	4
C ₃ H ₈	2008-09-22	5.98×10^{-6}	0.06	3

Measurement #2

Component	Date	Result (mol/mol)	Standard deviation (% relative)	number of replicates
NO	2008-09-21	81.27×10^{-6}	0.11	6
SO ₂	2008-09-21	79.48×10^{-6}	0.32	6
CO	2008-09-27	39.89×10^{-6}	0.06	4
CO ₂	2008-09-24	119.87×10^{-3}	0.06	3
C ₃ H ₈	2008-09-26	5.98×10^{-6}	0.09	3

Measurement #3

Component	Date	Result (mol/mol)	Standard deviation (% relative)	number of replicates
NO	2008-09-27	80.79×10^{-6}	0.25	6
SO ₂	2008-09-27	80.18×10^{-6}	0.18	6
CO	2008-09-29	39.94×10^{-6}	0.38	6
CO ₂	2008-09-26	119.90×10^{-3}	0.09	3
C ₃ H ₈	2008-09-29	5.97×10^{-6}	0.03	3

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Measurement #4

Component	Date	Result (mol/mol)	Standard deviation (% relative)	number of replicates
NO	2008-09-30	80.64×10^{-6}	0.15	6
SO ₂	2008-09-30	80.24×10^{-6}	0.06	6
CO	-	-	-	-
CO ₂	-	-	-	-
C ₃ H ₈	2008-09-30	5.97×10^{-6}	0.01	3

Results

Component	Result (mol/mol)	Expanded Uncertainty (mol/mol)	Coverage factor[1]
NO	80.72×10^{-6}	0.45×10^{-6}	2
SO ₂	79.84×10^{-6}	0.44×10^{-6}	2
CO	39.91×10^{-6}	0.14×10^{-6}	2
CO ₂	119.88×10^{-3}	0.12×10^{-3}	2
C ₃ H ₈	5.98×10^{-6}	0.06×10^{-6}	2

[1] The coverage factor shall be based on approximately 95% confidence.

Reference Method

NO analyzer, SO2 analyzer and GC were used in the analyses.

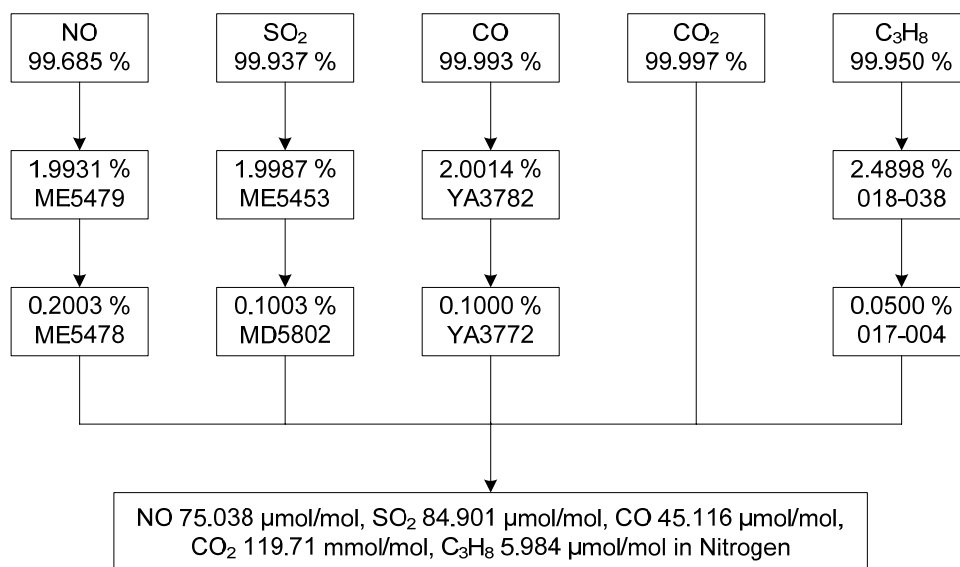
	NO	SO2
Instrument	Chemiluminescence NO/NOx Analyzer (42C, TEI)	NDIR SO2 Analyzer (Ultramat 6, Siemens)
Conditions - Sample flow rate :	300 ml/min	300 ml/min

	CO	CO2	C3H8
Instrument	GC(Agilent 6890)	GC(Agilent 6890)	GC(Agilent 6890)
Conditions Detector :	TCD	TCD	FID
Column :	MS5A, 1/8", 12 ft	CRT1, 1/8", 12 ft	Al2O3/KCl, 530 μm, 30 m
Oven temp. :	100 oC	100 oC	100 oC
Carrier gas :	He	He	He
Sample loop :	2 ml	2 ml	1 ml

Calibration Standards

All standards have been prepared by the gravimetric method according to ISO 6142. 6-component standard gas mixture was prepared for this comparison as follow, after preliminary test of sample cylinder.

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Standard gas mixture for CCQM comparison (ME 5432)

Component	Assigned value (mol/mol)	Expanded uncertainty (mol/mol, $k=2$)
NO	75.038×10^{-6}	0.075×10^{-6}
SO ₂	84.901×10^{-6}	0.085×10^{-6}
CO	45.116×10^{-6}	0.135×10^{-6}
CO ₂	119.71×10^{-3}	0.120×10^{-3}
C ₃ H ₈	5.984×10^{-6}	0.060×10^{-6}

Instrument Calibration

GC responses were obtained by A-B-A method with a calibration standard and a sample gas mixture. 3~7 samples in each cylinder were introduced into GC, and average value was used. Average value of the first and last data was used to correct the instrumental drift.

Sample Handling

The cylinder was stored to acclimatize to laboratory conditions before analysis was started. The cylinder was equipped with 2 stage-regulator set to approximately 3 bar and regulator was flushed 5 times before the first measurement. And output line from regulator and sampling line were connected with quick-connector. The flow rate of sample and standard gas was controlled by MFC constantly.

Evaluation of Measurement Uncertainty:

Concentration of the unknown gas mixture was calculated with the following equation.

Error! Objects cannot be created from editing field codes.

where:

Error! Objects cannot be created from editing field codes. = concentration of sample

Error! Objects cannot be created from editing field codes. = concentration of standard

Error! Objects cannot be created from editing field codes. = average response for sample

Error! Objects cannot be created from editing field codes. = average response for standard

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In this evaluation, the uncertainty on the gravimetric preparation, impurity, stability and homogeneity were included in the uncertainty of the standard gas mixture, but the uncertainty on the linearity was not considered.

Measurement report CENAM

Laboratory name: CENAM. Centro Nacional de Metrología. México

Cylinder number: M937407

Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Carbon dioxide	02/10/2008	119,95 mmol/mol	0,41	4
Sulfur dioxide	30/10/2008	81,77 µmol/mol	0,58	3
Carbon monoxide	07/10/2008	40,708 µmol/mol	0,032	4
Nitrogen monoxide	30/10/2008	76,5 µmol/mol	1,1	3
Propane	15/10/2008	5,927µmol/mol	0,077	4

Measurement # 2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Carbon dioxide	03/10/2008	120,49 mmol/mol	0,21	4
Sulfur dioxide	31/10/2008	79,27 µmol/mol	0,55	3
Carbon monoxide	09/10/2008	39,776 µmol/mol	0,20	4
Nitrogen monoxide	31/10/2008	78,02 µmol/mol	0,97	3
Propane	16/10/2008	5,939 µmol/mol	0,10	4

Measurement # 3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Carbon dioxide	06/10/2008	120,06 mmol/mol	0,16	4
Sulfur dioxide	03/11/2008	80,38 µmol/mol	0,35	3
Carbon monoxide	10/10/2008	39,833 µmol/mol	0,17	4
Nitrogen monoxide	03/11/2008	80,2 µmol/mol	1,4	3
Propane	20/10/2008	5,937 µmol/mol	0,11	4

Measurement # 4

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Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Carbon dioxide				
Sulfur dioxide	-	-	-	-
Carbon monoxide	14/10/2008	40,069 µmol/mol	0,71	4
Nitrogen monoxide	-	-	-	-
Propane				

Results

Component	Result (mol/mol)	Expanded Uncertainty	Coverage factor ⁷
Carbon dioxide	120,17 mmol/mol	0,94	2
Sulfur dioxide	80,5 µmol/mol	3,3	2
Carbon monoxide	40,10 µmol/mol	0,51	2
Nitrogen monoxide	78,2 µmol/mol	1,7	2
Propane	5,934 µmol/mol	0,034	2

Measurement method

Carbon dioxide

It was used an Agilent Technologies 6890 Gas Chromatograph, with TCD, split/splitless injector, gases injection valve, including Chemstation NT to collect and process data. A low pressure regulator placed in the outlet of cylinder, with SS tubing of 1/8". To control the flow of injection was used a regulator of low pressure. A HP PLOT Q capillary column 30 m, 530µm, 40 µm was used to separate CO₂ peak.

Oven program: 60 °C, 6,4 min, isothermal

He flow = 59,9 ml/min (15 cm/s) , at 14,9 kPa, constant

TCD temperature = 250 °C

Injector temperature = 150 °C

Carbon monoxide

It was used an Agilent Technologies 6890 Gas Chromatograph, with FID and Ni catalytic methanizer, split/splitless injector, a valve of injection gases, including Chemstation NT to collect and process data. A low pressure regulator placed in the outlet of cylinder, with SS tubing of 1/8. To control the flow of injection was used a regulator of low pressure. A HP PLOT Q capillary column A HP of 30 m, 530µm, and 40 µm was used to separate CO peak.

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Oven program: 60 °C, 8 min, isothermal
He flow 76,1 ml/min (59 cm/s) , at 59,6 kPa, constant
Make up N₂: 25 ml/min
FID temperature = 250 °C
Injector temperature = 150 °C
Flame gases flows: air = 300 ml/min, H₂ = 45 ml/min

Propane

Agilent Technologies 6890 Gas Chromatograph, with FID, gases auxiliary injector injection, including Chemstation NT to collect and process data. A low pressure regulator placed in the outlet of cylinder, with SS tubing of 1/8. To control the flow of injection was used a regulator of low pressure. A Haysep 80/100 packed column, ss 1/8 was used to separate C₃H₈ peak.

Oven program: 100 °C, 4,7 min, isothermal
327,8 kPa, constant pressure
Make up N₂: 25 ml/min
FID temperature = 250 °C
Injector temperature = 150 °C
Flame gases flows: air = 300 ml/min, H₂ = 45 ml/min

Nitrogen monoxide and Sulphur dioxide

For FTIR measurements a NICOLET-Magna-IR-750 was used. A variable 20 m path length gas cell from Perkin Elmer-Foxboro was fixed in the nominal optical pathlength of 9,75 m. Measurement conditions: 1 cm⁻¹ unapodized resolution, 80 scans, Happ-Genzel apodization, water correction performed by the OMNIC-Software, 2 levels of zero-filling, DTGS detector. Nominal measurement pressure for all samples: 800 hPa. The optical bench set up was continuously purged with N₂ (4.8).

Calibration standards

The calibration standards for the measurements were 5 primary standards (primary standard mixtures, PSMs) multicomponent of CO₂, CO, NO, SO₂ and C₃H₈ in N₂ balance, prepared by weigh, the cylinders were weighted after each compound addition and thermal equilibrium with the room. The method used for the preparation of PSMs was the gravimetric method following the guidelines of the ISO/DIS 6142. The procedure for weighing was a Borda weighing scheme (RTRTRTR). The parent gases were in all cases at least 3,8 of purity and 6.0 for balance. Their uncertainties were calculated by type B evaluation or/and type A evaluation.

Reference method

The calibration procedure was according to ISO 6143 using B_Least program software for multipoint Calibration. It was used 5 concentration levels in the following sequence: Std₃MStd₅MStd₂Std₄MStd₁.....

For every FTIR measurement a fresh Background of <1Pa vacuum was used. All sample replicates were sequentially measured. Cylinders were measured randomly. The quantification was performed by B_least software with the 5 multipoint calibration of the PSMs.

Evaluation of measurement uncertainty

The main sources of uncertainty considered to estimate the combined standard uncertainty are derived from the:

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Model used for evaluating measurement uncertainty:

$$C = \mu + \delta_T + \delta_s + \delta_m$$

The combined uncertainty has three contributions:

- a) Reproducibility and Repeatability.

The combined effect (δ_T) of the reproducibility and repeatability was evaluated by the statistical method of analysis of variance.

- b) Mathematical model effect (δ_m).

This component corresponds to the estimated uncertainty which come from the B_Least program software for multipoint Calibration.

Coverage factor: k=2

Expanded uncertainty: It was obtained by the product of the combined standard uncertainty and a factor of 2 and it was calculated according to the "Guide to the Expression of Uncertainty in Measurement, BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, OIML (1995)"

Uncertainty Measurement to CO₂

Quantity X_i	Estimate x_i	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$ <i>mmol/mol</i>	Sensitivity coefficient c_i	Contribution $u_i(y)$
Repeatability and Reproducibility	-----	A	Normal	0,11	1	0,11
Model	-----	A	Normal	0,46	1	0,46

Measurement Uncertainty for SO₂

Quantity X_i	Estimate x_i	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$ / ($\mu\text{mol/mol}$)	Sensitivity coefficient c_i	Contribution $u_i(y)$ / ($\mu\text{mol/mol}$)
Model + combination of repeatability and intermediate precision	-----	A	Normal	1,65	1	1,65

Uncertainty Measurement to CO

Quantity X_i	Estimate x_i	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$ ($\mu\text{mol/mol}$)	Sensitivity coefficient c_i	Contribution $u_i(y)$ ($\mu\text{mol/mol}$)
Repeatability and Reproducibility	-----	A	Normal	0,202	1	0,202
Model	-----	A	Normal	0,153	1	0,153

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Measurement Uncertainty for NO

Quantity X_i	Estimate x_i	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$ / ($\mu\text{mol/mol}$)	Sensitivity coefficient c_i	Contribution $u_i(y)$ / ($\mu\text{mol/mol}$)
Model + combination of repeatability and intermediate precision	-----	A	Normal	0,85	1	0,85

Uncertainty Measurement to C₃H₈

Quantity X_i	Estimate x_i	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$ ($\mu\text{mol/mol}$)	Sensitivity coefficient c_i	Contribution $u_i(y)$ ($\mu\text{mol/mol}$)
Repeatability and Reproducibility	-----	A	Normal	0,010	1	0,010
Model	-----	A	Normal	0,014	1	0,014

Measurement report VSL

Laboratory : VSL

Laboratory code : VSL

Cylinder number : M937400

Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
NO	2008-10-14	$80,42 \cdot 10^{-6}$	0,05	3
SO ₂	2008-09-30	$79,85 \cdot 10^{-6}$	0,06	3
CO	2009-01-29	$40,24 \cdot 10^{-6}$	0,47	5
CO ₂	2008-10-03	$11,992 \cdot 10^{-2}$	0,11	5
C ₃ H ₈	2008-10-03	$5,976 \cdot 10^{-6}$	0,06	5

Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
NO	2008-10-27	$80,42 \cdot 10^{-6}$	0,12	3
SO ₂	2008-10-21	$79,86 \cdot 10^{-6}$	0,06	3
CO	2009-02-04	$40,02 \cdot 10^{-6}$	0,28	5
CO ₂	2008-12-31	$12,004 \cdot 10^{-2}$	0,04	5
C ₃ H ₈	2008-12-31	$5,978 \cdot 10^{-6}$	0,06	5

Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
NO	2008-10-29	$80,45 \cdot 10^{-6}$	0,14	3
SO ₂	2008-11-06	$79,82 \cdot 10^{-6}$	0,02	3
CO	2009-02-20	$40,35 \cdot 10^{-6}$	0,42	5
CO ₂	2009-02-04	$12,025 \cdot 10^{-2}$	0,04	5
C ₃ H ₈	2009-02-04	$5,976 \cdot 10^{-6}$	0,10	5

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Measurement #4

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
NO	2008-12-15	$80,16 \cdot 10^{-6}$	0,03	3
SO ₂	-			
CO	-			
CO ₂	2009-02-20	$11,993 \cdot 10^{-2}$	0,07	5
C ₃ H ₈	2009-02-20	$5,991 \cdot 10^{-6}$	0,17	5

Results

Component	Result (mol/mol)	Expanded Uncertainty (mol/mol)	Coverage factor ⁸
NO	$80,34 \cdot 10^{-6}$	$0,39 \cdot 10^{-6}$	2
SO ₂	$79,85 \cdot 10^{-6}$	$0,21 \cdot 10^{-6}$	2
CO	$40,20 \cdot 10^{-6}$	$0,38 \cdot 10^{-6}$	2
CO ₂	$12,007 \cdot 10^{-2}$	$0,034 \cdot 10^{-2}$	2
C ₃ H ₈	$5,980 \cdot 10^{-6}$	$0,017 \cdot 10^{-6}$	2

Reference method and calibration

NO:

The NO was analyzed using an ND-UV monitor (ABB Limas). A suite of 7 Primary Standard gas Mixtures and the K-71 cylinder M937400 were connected to a computer operated multiposition valve box. During the night the set of standards and the K-71 mixture are analyzed in three individual sequences. For every run a 2nd order analysis function is calculated for the PSMs and the concentration in the K-71 mixture is determined from this function.

The ND-UV monitor is also sensitive for SO₂. Test measurements have been performed to assess the influence of an SO₂ concentration on the monitor response. Using a gasdivider 10 fractions of a 2000 ppm mixture of SO₂ in N₂ is added to a constant NO fraction. This results in a 2nd order cross-sensitivity function for SO₂ on this monitor. This experiment is repeated 3 times in 2008. A correction is applied on the NO result (for K-71 approx. -5.4 % rel) and the uncertainty of this correction is added to the calculation of the measurement uncertainty.

SO₂:

The SO₂ was analyzed using an ND-IR monitor (ABB Limas). A suite of 7 Primary Standard gas Mixtures and the K-71 cylinder M937400 were connected to a computer operated multiposition valve box. During the night the set of standards and the K-71 mixture are analyzed in three individual sequences. For every run a 2nd order analysis function is calculated for the PSMs and the concentration in the K-71 mixture is determined from this function.

The ND-IR monitor is also sensitive for C₃H₈. Test measurements have been performed to assess the influence of a C₃H₈ concentration on the monitor response. Using a gasdivider 4 fractions of a 80 ppm mixture of C₃H₈ in N₂ is added to a constant SO₂ fraction. This results in a 1st order cross-sensitivity function for C₃H₈ on this monitor. This experiment is repeated 2 times in 2008. A correction is applied on the SO₂ result (for K-71 approx. -0,2 % rel) and the uncertainty of this correction is added to the calculation of the measurement uncertainty.

⁸ The coverage factor shall be based on approximately 95% confidence.

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The response for SO₂ on the ND-IR monitor appears to be pressure dependent. In such a way that introducing a sample with 0,1% more pressure in the cell this results in an increased response with 0,2% relative. Due to the difference in density of the K-71 mixture in comparison to the binary standards (i.e. without CO₂), the flow and pressure in the cell is lower for the K-71 mix. A correction of +0,1% is applied to the analysis result. An uncertainty for this correction is added.

CO:

The CO fraction is analyzed on an Agilent 6890 GC equipped with a methanizer-FID combination. The CO is separated from the other components on a packed 10 ft Porapack N column in series with a 3 ft Molsieve 13x. With a Nickel Catalyst operated at 400 °C the CO is converted to CH₄ and detected on the FID. A suite of 5 PSMs together with the K-71 mixture are connected to a multiposition valve sample box. A 1 ml sample loop is flushed for 3 minutes before injection. Each mixture is injected 6 times. The average response of the final 5 injections is used for further calculation. A 2nd order analysis function is calculated from the PSMs. The flow is stopped 6 seconds before injection in order to inject under ambient pressure conditions.

No corrections for any cross-sensitivity have been applied.

CO₂ and C₃H₈:

Both components are analyzed in the same measurement cycle on an Agilent 6890 GC equipped with a TCD and an FID in paralel. The sample is injected on a 10 ft Porapack N column and both components are detected individually. Hereby CO₂ is detected with the TCD and C₃H₈ with the FID. Together with the K-71 sample cylinder also 5 PSMs of CO₂ in N₂ and 5 PSMs of C₃H₈ in N₂ are connected to a computer programmed multiposition valve gas sampling box. A sample loop of 1 ml is flushed for 3 minutes before performing 6 injections for each mixture. A 2nd order analysis function is obtained for CO₂ and a 1st order for propane.

No corrections for any cross-sensitivity are applied.

Calibration standards

All Primary Standard gas Mixtures for the measurements of NO, SO₂, CO, CO₂ and C₃H₈ are binary mixtures of the specific component in nitrogen. Preparation is performed according ISO6142:2001. The standard uncertainty is based on the uncertainty of the gravimetric preparation process and the purity analysis of the parent gases.

Composition of calibrants:

Component	Cylinder number	Assigned value(x) / mol/mol	Standard uncertainty (u(x)) / mol/mol
NO	VSL327336	$19,994 \cdot 10^{-6}$	$6,55 \cdot 10^{-9}$
	VSL327330	$30,006 \cdot 10^{-6}$	$9,76 \cdot 10^{-9}$
	VSL327333	$39,891 \cdot 10^{-6}$	$8,93 \cdot 10^{-9}$
	VSL227354	$50,094 \cdot 10^{-6}$	$15,24 \cdot 10^{-9}$
	VSL227344	$60,029 \cdot 10^{-6}$	$18,03 \cdot 10^{-9}$
	VSL289173	$79,936 \cdot 10^{-6}$	$23,70 \cdot 10^{-9}$
	VSL274496	$99,289 \cdot 10^{-6}$	$20,79 \cdot 10^{-9}$

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Component	Cylinder number	Assigned value(x) / mol/mol	Standard uncertainty (u(x)) / mol/mol
SO ₂	VSL353679	$9,995 \cdot 10^{-6}$	$2,97 \cdot 10^{-9}$
	VSL253592	$20,012 \cdot 10^{-6}$	$4,65 \cdot 10^{-9}$
	VSL353259	$29,980 \cdot 10^{-6}$	$6,56 \cdot 10^{-9}$
	VSL253604	$40,014 \cdot 10^{-6}$	$13,07 \cdot 10^{-9}$
	VSL176734	$60,028 \cdot 10^{-6}$	$18,25 \cdot 10^{-9}$
	VSL253601	$80,058 \cdot 10^{-6}$	$23,14 \cdot 10^{-9}$
	VSL305254	$100,01 \cdot 10^{-6}$	$28,75 \cdot 10^{-9}$

Component	Cylinder number	Assigned value(x) / mol/mol	Standard uncertainty (u(x)) / mol/mol
CO	VSL151921	$30,059 \cdot 10^{-6}$	$7,33 \cdot 10^{-9}$
	VSL328526	$39,931 \cdot 10^{-6}$	$10,47 \cdot 10^{-9}$
	VSL203774	$60,005 \cdot 10^{-6}$	$10,59 \cdot 10^{-9}$
	VSL303624	$79,987 \cdot 10^{-6}$	$12,96 \cdot 10^{-9}$
	VSL353602	$100,08 \cdot 10^{-6}$	$19,98 \cdot 10^{-9}$

Component	Cylinder number	Assigned value(x) / mol/mol	Standard uncertainty (u(x)) / mol/mol
CO ₂	VSL309541	$6,986 \cdot 10^{-2}$	$4,72 \cdot 10^{-6}$
	VSL209454	$8,506 \cdot 10^{-2}$	$4,81 \cdot 10^{-6}$
	VSL251950	$9,992 \cdot 10^{-2}$	$5,21 \cdot 10^{-6}$
	VSL209513	$12,511 \cdot 10^{-2}$	$5,15 \cdot 10^{-6}$
	VSL209441	$14,802 \cdot 10^{-2}$	$5,36 \cdot 10^{-6}$

Component	Cylinder number	Assigned value(x) / mol/mol	Standard uncertainty (u(x)) / mol/mol
C ₃ H ₈	VSL300675	$4,0029 \cdot 10^{-6}$	$0,83 \cdot 10^{-9}$
	VSL408734	$6,0021 \cdot 10^{-6}$	$1,14 \cdot 10^{-9}$
	VSL408747	$7,9997 \cdot 10^{-6}$	$1,40 \cdot 10^{-9}$
	VSL407265	$9,9876 \cdot 10^{-6}$	$3,96 \cdot 10^{-9}$
	VSL203723	$20,018 \cdot 10^{-6}$	$5,09 \cdot 10^{-9}$

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Sample handling

The cylinder M937400 together with the PSMs used for calibration are equipped with a pressure regulator. Sampling takes place with automated multi position valve sample boxes as described in VSL 's work instructions for routine analyses.

Evaluation of measurement uncertainty

Analyte	Relative Standard uncertainties / %				Expanded Uncertainty
	Gravimetric standards	Analysis	Correction Cross Sens.	Pressure dependence	Total
NO	0,04	0,17	0,17		0,49 %
SO ₂	0,04	0,10	0,06	0,03	0,26 %
CO	0,03	0,47			0,94 %
C ₃ H ₈	0,04	0,13			0,28 %
CO ₂	0,04	0,14			0,28 %

The standard uncertainties were added as squares and expanded with a coverage factor of $k=2$.

Measurement report IPQ

Laboratory : Instituto Português da Qualidade

Laboratory code :

Cylinder number : M937419

Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
NO	---	---	---	---
SO ₂	20/10/08	79,71 x10 ⁻⁶	0,05	3
CO	05/11/08	38,48 x10 ⁻⁶	0,07	3
CO ₂	21/10/08	12,054 x10 ⁻²	0,039	3
C ₃ H ₈	---	---	---	---

Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
NO	---	---	---	---
SO ₂	19/11/08	79,68 x10 ⁻⁶	0,06	3
CO	06/11/08	38,47 x10 ⁻⁶	0,12	3
CO ₂	18/11/08	12,065 x10 ⁻²	0,014	3
C ₃ H ₈	---	---	---	---

Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
NO	---	---	---	---
SO ₂	20/11/08	79,53 x10 ⁻⁶	0,02	3
CO	14/11/08	38,64 x10 ⁻⁶	0,07	3
CO ₂	19/11/08	12,063 x10 ⁻²	0,027	3
C ₃ H ₈	---	---	---	---

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Results

Component	Result (mol/mol)	Expanded Uncertainty	Coverage factor ⁹
NO	---	---	---
SO ₂	79,64 x10 ⁻⁶	0,44 x10 ⁻⁶	2
CO	38,53 x10 ⁻⁶	0,30 x10 ⁻⁶	2
CO ₂	12,061 x10 ⁻²	0,032 x10 ⁻²	2
C ₃ H ₈	---	---	---

Reference Method

SO₂: Non Dispersive Infrared Spectroscopy (NDIR): Analyzer: URAS 14

CO: Non Dispersive Infrared Spectroscopy (NDIR): Analyzer: Horiba Ambient CO Monitor APMA 360

CO₂: Non Dispersive Infrared Spectroscopy (NDIR): Analyzer: URAS 4

Data Collection: Auto-sampler - Software Sira version 2.0

Calibration Standards

The preparation was done according to ISO 6142:2001- Gravimetric method

The estimated uncertainty was done according ISO GUM: 1995 "Guide to the Expression of Uncertainty in Measurement".

Five primary standard mixtures, from IPQ and VSL, were used for each component.

Composition of calibrants:

Component	Assigned value(x)	Standard uncertainty (u(x))
NO	---	---
SO ₂	VSL 6729: 25,02 x10 ⁻⁶	0,13 x10 ⁻⁶
	VSL 6829: 100,10 x10 ⁻⁶	0,25 x10 ⁻⁶
	PRM 203405: 182,3 x10 ⁻⁶	0,7 x10 ⁻⁶
	PRM 208352: 319,6 x10 ⁻⁶	0,9 x10 ⁻⁶
	VSL 6836: 500,3 x10 ⁻⁶	1,0 x10 ⁻⁶
CO	PSM 118342: 7,992 x10 ⁻⁶	0,046 x10 ⁻⁶
	PSM 108331: 10,007 x10 ⁻⁶	0,041 x10 ⁻⁶
	PSM 202602: 40,00 x10 ⁻⁶	0,08 x10 ⁻⁶
	PSM 302590: 50,03 x10 ⁻⁶	0,14 x10 ⁻⁶
CO ₂	PSM 102552: 7,000 x10 ⁻²	0,013 x10 ⁻²

⁹ The coverage factor shall be based on approximately 95% confidence.

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Component	Assigned value(x)	Standard uncertainty ($u(x)$)
	PSM 202511: $7,502 \times 10^{-2}$	$0,011 \times 10^{-2}$
	PSM 202537: $9,990 \times 10^{-2}$	$0,021 \times 10^{-2}$
	PSM 102603: $15,298 \times 10^{-2}$	$0,037 \times 10^{-2}$
	PSM 102571: $17,499 \times 10^{-2}$	$0,020 \times 10^{-2}$
C ₃ H ₈	---	---

Instrument Calibration

The calibration instrument was done according to ISO 6143. We have used the B_Least program to determine the best model for data handling. All components of mixture have a goodness of fit less than 2 using a linear function.

For all components were used a set of five PSM (from IPQ and VSL). At least three repeated analyses were performed in three independent days.

Manual calibration (zero and span are calibrated separately by pressing the analyzer system display and control unit softkeys)

Sample handling

After arrival the cylinder was storage at ambient temperature in a storage room.

The cylinder was connected to a valve to reduce the pressure. The samples were transferred to the analyser through an auto-sampler.

Evaluation of measurement uncertainty

The uncertainty measurement was done according ISO GUM: 1995 "Guide to the Expression of Uncertainty in Measurement".

The uncertainty of measurement associated with the final result has been evaluated and includes three main uncertainty sources:

- Uncertainty of Primary Standard mixtures;
- Standard deviation of the mean (GC-Analysis);
- Cross interference

these uncertainties were combined and the result was multiplied by a coverage factor of 2 with a confidence interval of 95 %.

NOTE 1 : Propane was not analysed because we don't have equipment that can do measurements in the 1-10 $\mu\text{mol/mol}$ range.

NOTE 2 : We had cross interferences, mainly in NO and CO measurements. We used a NDIR-URAS14 analyser for NO measurements and we had the CO₂ as interferent, with a interference about 10 %. Because of this high interference we didn't report the results.

For CO we used a NDIR-HORIBA analyser and we had CO₂ as interferent, with a interference about 0,5 %. We report the results and we include the cross interference as uncertainty source in the estimated uncertainty.

Measurement report VNIIM

Reference method

FTIR, GC-FID, GC-ECD

Instruments: Fourier spectrometer “FSM-1201” (“Montoring”, Russia), gas chromatograph with FID “Crystal 5000.1” (“Chromatec”, Russia), gas chromatograph with ECD “Crystal 5000.2” (“Chromatec”, Russia). All instruments are in the set of equipment of National Primary Measurement Standard GET 154.

Calibration standards

Characteristics of pure substances used for preparation of the calibration standards are shown in table 1.

Table 1 - Description of pure components

Component	Mole fraction 10^{-6} mol/mol	Standard uncertainty 10^{-6} mol/mol
C ₃ H ₈	999794.4	3.4
CO	998686.6	16.3
NO	999250.0	322.8
SO ₂	999900.0	40.8
CO	999972.7	3.0
N ₂	999994.9	0.35

All standard gas mixtures were prepared in aluminum cylinders with Aculife IV treatment, V=5 L.

Weighting were performed on the balance 81-V-HCE-20kg (“hnu-Voland”, USA). Experimental standard deviation for 5 L cylinders: 8 mg.

Preparation of standard mixtures was carried out in several stages.

1st stage:

Preparation of the first gas pre-mixture C₃H₈/N₂ with C₃H₈ mole fraction of $\approx 3.3\%$.

Preparation of the first gas pre-mixture CO/N₂ with CO mole fraction of $\approx 6\%$.

Verification of mole fraction was carried out by NDIR analyzer. Relative standard deviation for each measurement series was not more than 0.06%

Preparation of the calibration gas mixtures CO₂/N₂ with CO₂ mole fraction of $\approx 12.5\%$.

There were prepared 3 standard gas mixtures.

Verification of mole fraction was carried out by FTIR analyzer. Relative standard deviation for each measurement series was not more than 0.04%.

2nd stage:

Preparation of the second gas pre-mixture C₃H₈+NO+SO₂/N₂ with C₃H₈ mole fraction of $\approx 0.17\%$, NO mole fraction of $\approx 2.2\%$, SO₂ mole fraction of $\approx 2.2\%$.

Verification of mole fraction was carried out by FTIR analyzer. Relative standard deviation for each measurement series was not more than: for C₃H₈ – 0.09%, for SO₂ – 0.1%, for NO – 0.06%

Preparation of the second gas pre-mixture CO/N₂ with CO mole fraction of $\approx 0.1\%$.

Verification of mole fraction was carried out by NDIR analyzer. Relative standard deviation for each measurement series was not more than 0.07%

3rd stage:

Preparation of the third gas pre-mixture C₃H₈+NO+SO₂ /N₂ with C₃H₈ mole fraction of ≈ 72 ppm, NO mole fraction of ≈ 950 ppm, SO₂ mole fraction of ≈ 950 ppm.

Verification of mole fraction of C₃H₈ was carried out by gas chromatograph with FID. Relative standard deviation for each measurement series was not more than C₃H₈ – 0.26%.

Verification of mole fraction of SO₂ was carried out by “Lambda 900” (Perkin Elmer, USA) spectrophotometer with gas cell. Relative standard deviation for each measurement series was not more than 0.1%.

Verification of mole fraction of NO was carried out by FTIR analyzer. Relative standard deviation for each measurement series was not more than 0.12%

4th stage:

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Preparation of the calibration gas mixtures $C_3H_8+NO+SO_2+CO/N_2$ with C_3H_8 mole fraction of ≈ 6.1 ppm, NO mole fraction of ≈ 80.1 ppm, SO_2 mole fraction of ≈ 80.4 ppm, CO mole fraction of ≈ 50.6 ppm.

There were prepared 3 standard gas mixtures.

Verification of mole fraction of C_3H_8 was carried out by gas chromatograph with FID. Relative standard deviation for each measurement series was not more than 0.32%.

Verification of mole fraction of CO was carried out by gas chromatograph with ECD. Relative standard deviation for each measurement series was not more than 0.22%.

Verification of mole fraction of NO and SO_2 was carried out by FTIR analyzer. Relative standard deviation for each measurement series was not more than: for NO – 0.11 %, for SO_2 – 0.13 %.

The characteristics of calibration standards are shown in table 2.

Table 2 – Characteristics of calibration standards

Standard gas mixture N	Component	Assigned value 10^{-6} mol/mol	Relative standard uncertainty (gravimetry)
1	CO	50.689	0,051 %
	C_3H_8	6.128	0,027 %
	SO_2	80.578	0,026 %
	NO	80.051	0,085 %
	N_2	Balance	–
2	CO	52.046	0,051 %
	C_3H_8	6.342	0,027 %
	SO_2	82.711	0,026 %
	NO	83.440	0,085 %
	N_2	Balance	–
3	CO	50.127	0,051 %
	C_3H_8	5.862	0,027 %
	SO_2	77.027	0,026 %
	NO	77.139	0,085 %
	N_2	balance	–
4	CO_2	12.1423	0,003 %
	N_2	balance	–
5	CO_2	12.9445	0,003 %
	N_2	Balance	–
6	CO_2	12.4930	0,003 %
	N_2	balance	–

Instrument calibration

Linear regression by 3 calibration point was used for instrument calibration.

Sample handling

Prior to measurement the cylinder was stabilized to room temperature.

Measurement results

Results of measurement of C_3H_8 mole fraction in cylinder № M937403 are shown in table 3

Table 3 – Results of measurements of C_3H_8 in gas mixture in cylinder № M937403

Measurement #1

Component	Date (dd/mm/yy)	Result (10^{-6} mol/mol)	Standard deviation (10^{-6} mol/mol)	Number of replicates
C_3H_8	03/12/2008	5,892	0,030	7

Measurement #2

Component	Date (dd/mm/yy)	Result (10^{-6} mol/mol)	Standard deviation (10^{-6} mol/mol)	Number of replicates
C_3H_8	15/12/2008	5,911	0,030	7

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Results of measurement of NO mole fraction in cylinder № M937403 are shown in table 4.

Table 4 – Results of measurements of NO in gas mixture in cylinder № M937403

Measurement #1

Component	Date (dd/mm/yy)	Result (10^{-6} mol/mol)	Standard deviation (10^{-6} mol/mol)	Number of replicates
NO	05/12/2008	81.07	0.28	5

Measurement #2

Component	Date (dd/mm/yy)	Result (10^{-6} mol/mol)	Standard deviation (10^{-6} mol/mol)	Number of replicates
NO	18/12/2008	80.49	0.28	5

Results of measurement of SO₂ mole fraction in cylinder № M937403 are shown in table 5.

Table 5 – Results of measurements of SO₂ in gas mixture in cylinder № M937403

Measurement #1

Component	Date (dd/mm/yy)	Result (10^{-6} mol/mol)	Standard deviation (10^{-6} mol/mol)	Number of replicates
SO ₂	05/12/2008	80.63	0.33	5

Measurement #2

Component	Date (dd/mm/yy)	Result (10^{-6} mol/mol)	Standard deviation (10^{-6} mol/mol)	Number of replicates
SO ₂	18/12/2008	80.92	0.33	5

Results of measurement of CO₂ mole fraction in cylinder № M937403 are shown in table 6.

Table 6 – Results of measurements of CO₂ in gas mixture in cylinder № M937403

Measurement #1

Component	Date (dd/mm/yy)	Result (10^{-2} mol/mol)	Standard deviation (10^{-6} mol/mol)	Number of replicates
CO ₂	8/12/2008	11.981	0.040	5

Measurement #2

Component	Date (dd/mm/yy)	Result (10^{-2} mol/mol)	Standard deviation (10^{-6} mol/mol)	Number of replicates
CO ₂	22/12/2008	12.019	0.040	5

Results of measurement of CO mole fraction in cylinder № M937403 are shown in table 7.

Table 7 – Results of measurements of CO in gas mixture in cylinder № M937403

Measurement #1

Component	Date (dd/mm/yy)	Result (10^{-6} mol/mol)	Standard deviation (10^{-6} mol/mol)	Number of replicates
CO	11/12/2008	45.34	0.18	5

Measurement #2

Component	Date (dd/mm/yy)	Result (10^{-6} mol/mol)	Standard deviation (10^{-6} mol/mol)	Number of replicates
CO	24/12/2008	45.01	0.18	5

Measurement #3

Component	Date (dd/mm/yy)	Result (10^{-6} mol/mol)	Standard deviation (10^{-6} mol/mol)	Number of replicates
CO	26/12/2008	45.31	0.18	5

Evaluation of measurement uncertainty

Total standard uncertainties of component mole fractions were calculated on the base of the following constituents:

- total standard uncertainty of component in standard gas mixture (including uncertainty of weighting, uncertainty in the purity of the parent gases);

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- standard deviation of linear regression;
- standard deviation of the measurement result of component mole fraction in investigated gas mixture in cylinder №M937403

Uncertainty budgets for components mole fractions in gas mixture in the cylinder № M937403 are shown in tables 8, 9, 10, 11, 12.

Table 8 – Uncertainty budget for C₃H₈ mole fraction in gas mixture in cylinder № M937403

№	Source of uncertainty	Type of evaluation	Standard uncertainty, % relative
1	Preparation of the calibration gas mixtures	A,B	0.027
2	Standard uncertainty of calibration	A	0.18
3	Standard deviation of measurement result	A	0.32
Combined standard uncertainty			0.36
Expanded uncertainty			0.73

Table 9 – Uncertainty budget for NO mole fraction in gas mixture n cylinder № M937403

№	Source of uncertainty	Type of evaluation	Standard uncertainty, % relative
1	Preparation of the calibration gas mixtures	A,B	0.085
2	Standard uncertainty of calibration	A	0.22
3	Standard deviation of measurement result	A	0.11
Combined standard uncertainty			0.26
Expanded uncertainty			0.52

Table 10 – Uncertainty budget for SO₂ mole fraction in gas mixture in cylinder № M937403

№	Source of uncertainty	Type of evaluation	Standard uncertainty, % relative
1	Preparation of the calibration gas mixtures	A,B	0.026
2	Standard uncertainty of calibration	A	0.26
3	Standard deviation of measurement result	A	0.13
Combined standard uncertainty			0.29
Expanded uncertainty			0.58

Table 11 – Uncertainty budget for CO mole fraction in gas mixture in cylinder № M937403

№	Source of uncertainty	Type of evaluation	Standard uncertainty, % relative
1	Preparation of the calibration gas mixtures	A,B	0.051
2	Standard uncertainty of calibration	A	0.16
3	Standard deviation of measurement result	A	0.22
Combined standard uncertainty			0.27
Expanded uncertainty			0.55

Table 12 – Uncertainty budget for CO₂ mole fraction in gas mixture in cylinder № M937403

№	Source of uncertainty	Type of evaluation	Standard uncertainty, % relative
1	Preparation of the calibration gas mixtures	A,B	0.003
2	Standard uncertainty of calibration	A	0.235
3	Standard deviation of measurement result	A	0.035
Combined standard uncertainty			0.24
Expanded uncertainty			0.48

Final results of measurements

Final result of measurements of C₃H₈, NO, SO₂, CO and CO₂ mole fractions in investigatetd gas mixture in the cylinder №M937403 are show in the table 13.

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Table 13 – Final results of measurements of components in gas mixture in cylinder № M937403

Component	Result	Expanded Uncertainty	Relative Expanded Uncertainty (%)	Coverage Factor
C ₃ H ₈	5.901 · 10 ⁻⁶ mol/mol	0.043 · 10 ⁻⁶ mol/mol	0.73	2
NO	80.78 · 10 ⁻⁶ mol/mol	0.42 · 10 ⁻⁶ mol/mol	0.52	2
SO ₂	80.77 · 10 ⁻⁶ mol/mol	0.47 · 10 ⁻⁶ mol/mol	0.58	2
CO ₂	12.000 · 10 ⁻² mol/mol	0.057 · 10 ⁻² mol/mol	0.47	2
CO	45.22 · 10 ⁻⁶ mol/mol	0.25 · 10 ⁻⁶ mol/mol	0.55	2

Substantiation of reasons for the deviation of CO measurement

VNIIM investigated the reasons for significant deviation (12.4 % rel.) of CO measurement result in multi-component gas mixture in the comparison CCQM-K71. It was determined that the deviation of the CO measurement result was caused by the use of multi-component gas mixtures for the calibration of gas chromatograph with detector ECD used in the comparison differing with regard to composition from the gas mixture of the coordinating laboratory. In particular, the multi-component gas mixtures which did not contain carbon dioxide were used for the calibration.

Repeated measurement of CO in the mixture of the coordinating laboratory was performed by the gas chromatograph with detector ECD after calibration with the multi-component gas mixtures (calibration mixture number 1 and number 2) that completely conform to the composition of the gas mixture of the coordinating laboratory. The deviation of obtained measurement results was less than 0.22 % from the reference value.

Number of calibration mixture	1	2
Assigned by the coordinating laboratory value, μmol/mol	40.230	
Result of measurement, μmol/mol	40.319	40.310
Relative deviation from assigned by the coordinating laboratory value, %	+0.22	+0.20

Measurement report NMI-SA

Measurement #1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
NO	22/12/08	79.41	0.03	3
SO ₂	14/10/08	79.81	0.04	3
CO	18/09/08	39.87	0.05	3
CO ₂	16/09/08	120.29 (mmol/mol)	0.17	3
C ₃ H ₈	26/11/08	6.0553	0.26	7

Measurement #2

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
NO	23/12/08	79.52	0.12	3
SO ₂	28/10/08	80.27	0.29	3
CO	09/12/08	39.74	0.48	3
CO ₂	10/12/08	120.19 (mmol/mol)	0.08	3
C ₃ H ₈	27/11/08	6.0490	0.24	7

Measurement #310

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
NO	06/01/09	79.56	0.12	3
SO ₂	17/12/08	80.31	0.48	3
CO	11/12/08	39.79	0.42	3
CO ₂	12/12/08	120.02 (mmol/mol)	0.04	3
C ₃ H ₈	01/12/08	6.0401	0.24	7

Results

Component	Result (µmol/mol)	Expanded Uncertainty (µmol/mol)	Coverage factor ¹¹
NO	79.42	0.51	2
SO ₂	80.13	0.54	2
CO	39.80	0.21	2
CO ₂	120.17 (mmol/mol)	0.26 (mmol/mol)	2
C ₃ H ₈	6.048	0.030	2

Measurement method

CO and CO₂:

The CO and CO₂ content of sample M937424 were analysed using a non-dispersive infrared analyser with two sets of 6 gravimetrically prepared matrix matched stack gas calibration standards using ISO 6143.

NO:

¹⁰ If more than three measurements are taken, please copy and insert a table of the appropriate format as necessary

¹¹ The coverage factor shall be based on approximately 95% confidence.

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The NO content of sample M937424 was analysed using a chemiluminescence analyser with two sets of 6 gravimetrically prepared matrix matched stack gas calibration standards using ISO 6143. The sample was also compared with gravimetrically prepared binary PSMs of NO in nitrogen.

SO₂:

The SO₂ content of sample M937424 was analysed using a UV fluorescence analyser with two sets of 6 gravimetrically prepared matrix matched stack gas calibration standards using ISO 6143. The sample was also compared with gravimetrically prepared binary PSMs of SO₂ in nitrogen.

Propane:

The C₃H₈ content of sample M937424 was analysed using a gas chromatograph equipped with a Flame Ionisation Detector (GC-FID). The components were separated using a 1.0 m x 2.2 mm ID x 3.2 mm OD column packed with Molecular Sieve 5A (40/60 mesh size) and which was operated isothermally at 130 °C with a carrier gas pressure of 260 kPa helium. A sample volume of 2 mL was injected onto the head of the column. The FID was at 300 °C. A gas sampling system (VICI Stream Selector Valve) was used to deliver the sample stream to the GC-FID at ~ 100 mL/min.

The GC-FID was calibrated with eleven gravimetrically prepared primary gas mixtures [PSM] containing [nominal] from 1 to 10 µmol/mol of C₃H₈ in a balance of nitrogen and other stack gases using ISO 6143. The concentration of sample M937424 was compared to the PSMs three times (three different days) with each day comprising 7 repeat runs for the sample M937424 and for the PSMs.

Evaluation of measurement uncertainty

All measured certification data and calculations for the component concentrations of M937424 have been reviewed for sources of systematic and random errors. The review identified three sources of uncertainty whose importance required quantification as estimated % Relative uncertainties. These uncertainties are:

Gravimetric Uncertainties (PSMs) which range from 0,03% to 0,06% relative standard uncertainty.

Repeatability uncertainty (run to run) which range from 0,1% to 1% relative standard deviation.

Reproducibility uncertainty (day to day) which gives the % relative standard deviation represented in the measurement report.

The results for each day yielded an average concentration and a standard deviation. The average concentration, ESDM, gravimetric concentration (µmol/mol) and the standard uncertainty of the concentrations for the PSMs were input into the B_LEAST software (ISO 6143) and a value predicted for concentration of the sample M937424 with a standard uncertainty.

The predicted concentrations for M937424 for three days were averaged, a standard deviation calculated for the three values. The uncertainties for the three different days were combined as shown in Equation 1:

$$u_c = \sqrt{\frac{(u_{Day1})^2 + (u_{Day2})^2 + (u_{Day3})^2}{3}} \dots\dots\dots \text{Equation 1}$$

The standard deviation for the predicted concentrations for the three days and the combined uncertainty in Equation 1 were then combined as a sum of squares as shown in Equation 2:

$$u = \sqrt{\frac{(u_c)^2 + (u_{stddev})^2}{2}} \dots\dots\dots \text{Equation 2}$$

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This standard uncertainty was converted to an expanded uncertainty by multiplying by 2 ($k = 2$).

Measurement report SMU

Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
NO	1.10.2008	0.000080068	0.10	40
SO ₂	30.9.2008	0.000080285	0.26	40
CO	11.9.2008	0.000040060	0.25	4
CO ₂	9.9.2008	0.119978	0.05	5
C ₃ H ₈	9.9.2008	0.000006004	0.50	5

Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
NO	10.10.2008	0.000080045	0.10	40
SO ₂	9.10.2008	0.00008065	0.27	40
CO	12.9.2008	0.000040112	0.20	4
CO ₂	10.9.2008	0.120010	0.04	5
C ₃ H ₈	10.9.2008	0.000006015	0.47	5

Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
NO	6.11.2008	0.000080415	0.10	40
SO ₂	4.11.2008	0.000080485	0.25	40
CO	16.9.2008	0.000040170	0.10	6
CO ₂	14.10.2008	0.119965	0.05	5
C ₃ H ₈	14.10.2008	0.000005994	0.48	5

Results

Component	Result (mol/mol)	Expanded Uncertainty (mol/mol)	Coverage factor ¹²
NO	0.00008018	0.00000080	2
SO ₂	0.00008047	0.00000087	2
CO	0.00004011	0.00000019	2
CO ₂	0.11998	0.00012	2
C ₃ H ₈	0.000006004	0.00000058	2

Reference method

Stack gas multi component mixture was analysed with several analytical techniques:

¹² The coverage factor shall be based on approximately 95% confidence.

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1. Components **CO₂** and **propane** were analysed on GC Varian using Porapack and molsieve packed columns, 2x 1mL sample loops, TCD (for CO₂) and FID (for propane) detectors, oven temperature 95 °C, method time 9 min, carrier gas Helium. All measurements were done in automatic way using selector gas valve. Before entering sample loops all gas mixtures went through a mass flow controller and pressure controller for regulation.

2. Component **CO** was analysed on GC Thermoquest Trace 2000 using Porapack and molsieve packed column (2.2m), 1 mL sample loop, FID detector, methanizer. Oven temperature was 40°C, method time 25 min with back flush, carrier gas Nitrogen. All measurements were done in automatic way using selector gas valve. Before entering sample loops all gas mixtures went through a mass flow controller and pressure controller for regulation.

3. Component **SO₂** was analysed by Fluorescence method and FT-IR analysis. The Fluorescence was analysed on Thermo electronic corporation 42C Fluorescence analyser. The temperature of chamber of analyser was over 45°C and detector over 30°C. All measurements were done in manual way with settings of flow and pressure rate, immediately. All measurements, the flow and pressure rate had been similar (p=740 mmHg, f=0,462 l/min). The integration time was 30 s. Up to 40 readings were provided.

Component SO₂ was analysed on FT-IR Varian Excalibur spectrometer equipped with 10 m multi pass gas cell. Detector type DTGS, 100 measuring scans. Several measurements were performed with the resolution of the spectrometer 0.5 cm⁻¹ and/or 1.0 cm⁻¹. The pressure in the gas cell was controlled and adjusted to the 50 KPa and/or 100 KPa, temperature=22°C (laboratory). Before measurement of the calibration standard or sample the gas cell was evacuated by turbomolecular vacuum pump and background (single beam) spectrum was collected. Absorbance units were used for spectra. The SO₂ was monitored in spectral region of 1320-1380 cm⁻¹. However, whole spectral range was 400-4000 cm⁻¹.

4. Component **NO** was analysed by Luminescence method as well as by FT-IR analysis. The Luminescence was analysed on Thermo electronic corporation 43C Luminescence analyser. The temperature of chamber of analyser was over 49°C and detector over 35°C. All measurements were done in manual way with settings of flow and pressure rate, immediately. All measurement, the flow and pressure rate had been similar (p=190 mmHg, f=0,650 l/min.). The integration time was 30s. Up to 40 readings were provided. The FT-IR analysis of NO was performed as way as mean of SO₂ concentration. The NO was monitored in spectral region of 1800-2000 cm⁻¹.

Calibration standards

All calibration standards were made gravimetrically according ISO 6142 and ISO 6143 in SMU. Impurities in parent gases - NO, CO, CO₂, SO₂, propane and nitrogen were analysed on GC and FTIR.

Except binary mixtures, 3 multi component gas mixtures in Nitrogen with following composition were prepared:

PSM MY 9775_1

Component	Assigned value(x) (mol/mol)	Standard uncertainty (u(x) _{grav+stab}) (mol/mol)
NO	0.00005006	0.00000021
SO₂	0.00009582	0.00000038
CO	0.000007219	0.000000025
CO₂	0.13092	0.00013
C₃H₈	0.000007222	0.000000031

PSM MY 9776_1

Component	Assigned value(x) (mol/mol)	Standard uncertainty (u(x) _{grav+stab}) (mol/mol)
NO	0.00009251	0.00000040
SO₂	0.00018641	0.00000068
CO	0.00006551	0.00000018
CO₂	0.15083	0.00015
C₃H₈	0.000003935	0.000000019

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PSM MY 9767_2

Component	Assigned value(x) (mol/mol)	Standard uncertainty ($u(x)_{\text{grav+stab}}$) (mol/mol)
NO	0.00007608	0.00000032
SO ₂	0.00008562	0.00000035
CO	0.000039082	0.000000085
CO ₂	0.11097	0.00011
C ₃ H ₈	0.000005921	0.000000028

In addition of multi component mixtures, several binary mixtures of measured components were used for calibration in following ranges: NO 10-100 μ mol/mol, SO₂ 10-100 μ mol/mol, CO 10-100 μ mol/mol, propane 1-10 μ mol/mol and CO₂ 0.08-0.15 mol/mol.

Instrument calibration

GC method (Varian and Trace chromatographs)

Measurement method with several automated runs was used. All runs in first, third, fifth measurement sequence had rising molar fraction, second, fourth, processed in reverse order. At least 5 calibration standards and sample were used at each automated run. From each run was made one calibration curve with sample signals. Data were subjected to the b_least program (weighted least square regression). The result of the measurement sequence was the average of molar fractions.

At b_least these models of analytical curves were used:

CO	FID methanizer area	1-polynomial
CO ₂	TCD area	1-polynomial
Propane	FID height	1-polynomial

No corrections were used.

Optical methods (Fluorescence, Luminescence, FTIR)

Calibration of the analysers was done before each day measurement (except FTIR) by one point adjustment with PSM in middle of measuring range (50 ppm). After worth, an arising the molar fraction of gas component using 5 PSMs and sample were analysed. Measuring signals of calibration standards were used for generation of calibration curve.

Sample handling

All cylinders were at SMU kept at 17 – 22 °C before measurement. Measuring cylinders were equipped with pressure reducers. Samples were transferred to the instruments in the case of GC analysis through mass-flow controller and pressure controller automatically in sequences. In the case of monitors and FT-IR, pressure and flow were adjusted to the same defined value, before each measurement, individually. No dilutions were used.

Evaluation of measurement uncertainty

GC method

Uncertainty of instrument response consisted from figure characterized roughly immediate repeatability and from signal drift estimated. From each run was made one calibration curve with sample signals. These figures together with molar fraction data were subjected to b_least program (weighted least square regression). Each run produced sample molar fraction with its standard uncertainty. From all runs results = average of molar fractions in one sequence were standard deviation found (uncertainty of type A) and from runs results uncertainties the mean (through squares) was found (uncertainty of type B). These 2 figures were combined to give result uncertainty.

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For each i^{th} day the average \bar{x}_i was calculated (1). Standard uncertainty assigned to each i^{th} day result (4) is from standard deviation of the average (2) and average from all b_{least} uncertainties that day (3).

$$\bar{x}_i = \frac{\sum_{j=1}^n x_j}{n} \quad (1)$$

$$u_1(\bar{x}_i) = \sqrt{\frac{\sum_{j=1}^n (x_j - \bar{x}_i)^2}{n * (n - 1)}} \quad (2)$$

$$u_2(\bar{x}_i) = \sqrt{\frac{\sum_{j=1}^n u(x_j)^2}{n^2}} \quad (3)$$

$$u(\bar{x}_i) = \sqrt{u_1(\bar{x}_i)^2 + u_2(\bar{x}_i)^2} \quad (4)$$

Optical methods

The sources of the uncertainty in $x_{\text{NO,anal}}$ and $x_{\text{SO}_2,\text{anal}}$ were following: statistics, instrument calibration, display resolution of the instrument and additional uncertainty source remaining cross interferences between components. These sources of standard uncertainties type A and B were combined to the standard uncertainty of the measured molar fraction.

To estimate result uncertainty from 3 days results we have kept "Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method" (Annual Book of ASTM Standards E 691-87) with some approximations.

$$s_R = \sqrt{s_{\bar{x}}^2 + s_r \frac{n-1}{n}} \quad (5)$$

$$s_r = \sqrt{\frac{\sum_{i=1}^p u(\bar{x}_i)^2}{p}} \quad (6)$$

$$s_{\bar{x}} = \frac{\max(\Delta x)}{\sqrt{3}} \quad (7)$$

$$\Delta x = \bar{x}_1 - \bar{x}_2 \quad (8)$$

p – number of days (3)

n – number of measurements in 1 day

index i represents particular day

index j represents particular result (evaluated) from one calibration curve

Final result is average from 3 day results

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$$\bar{x} = \frac{\sum_{i=1}^p \bar{x}_i}{p} \quad (9)$$

As final **standard uncertainty** we assigned to the result (9) $\max(s_R \text{ or } s_r)$

$$u(\bar{x}) = \max(s_r; s_R) \quad (10)$$

Expanded uncertainty (k=2) of final result

$$U(\bar{x}) = 2 \cdot u(\bar{x})$$

Measurement report NPL

The measurements of M937411 received from the coordinator (VSL) were made during January 2009 by direct comparison with two multi-component standards containing the same unknowns at similar concentrations. The uncertainty in the components in one of these standards is attached. The results reported all follow from a “bracketing” comparison strategy, (except for SO₂ which used a double injection method).

Analytical methods

Analyte	Method	Instrument
NO	Chemiluminescence	Rosemount NGA 2000
SO ₂	Sulphur chemiluminescence	Varian 3700 50 m, 0.53 mm polysiloxane at 30 degC Sievers SCD
SO ₂ <i>alternative method</i>	NDIR	Horiba VIA-510
CO	NDIR	ABB AO2020
CO ₂	Thermal conductivity	Agilent 7900 9m micro-packed Porapak R (TCD) 4.4m micro-packed Porapak P (FID) both isothermal at 190 degC
propane	FID	

Uncertainty of Analysis

In the cases of SO₂ and NO, measurements were also made using alternative measurement methods to identify any possible influence of chemical stability in either the travelling standard or in the NPL standards.

- In the case of SO₂, measurements were made by SCD and also by NDIR. These results differed by 0.2ppm, so we allocate an uncertainty of 0.25% due to possible chemical stability effects that would result in alternative sulphur compounds being detected by the different methods.
- In the case of NO, measurements were made by chemiluminescence of both NO and NO_x. The value from the NO_x channel was 0.5 ppm lower than that in the NO channel, so we allocate an uncertainty of 0.5% due to possible chemical stability effects that would result in alternative nitrogen compounds being present.

The standard uncertainties due to the repeatability of the analysis have been corrected for the limited number of repeats involved in the analysis of CO and NO. The other measurements involved significant numbers of repeats.

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Analyte	Standard uncertainties			Expanded Uncertainty
	Gravimetric standards	Repeatability of analysis	Chemical stability	Total
NO	0.023%	0.15%	0.5%	1%
SO ₂	0.037%	0.1%	0.25%	0.5%
CO	0.050%	0.2%	-	0.4%
propane	0.011%	0.15%	-	0.3%
CO ₂	0.008%	0.1%	-	0.2%

The standard uncertainties were added in quadrature and expanded with a coverage factor of $k=2$.

Results for M937411

Analyte	Value [μmol/mol]	Expanded Uncertainty [μmol/mol]	Relative expanded uncertainty
NO	80.3	0.8	1%
SO ₂	79.8	0.4	0.5%
CO	40.0	0.2	0.4%
propane	5.98	0.02	0.3%
	Value [mmol/mol]	Expanded Uncertainty [mmol/mol]	Relative expanded uncertainty
CO ₂	119.7	0.2	0.2%

The expanded uncertainty refers to a confidence interval of 95%.

Gravimetric Uncertainty for one of the Multi-Component Standards

Component	μmol/mol	uncertainty	% u/c
N2	881740.295	19.26354547	0.002
CO2	118050.9401	19.24858398	0.016
NO	81.05738738	0.03617610	0.045
SO2	80.19018742	0.05908993	0.074
CO	39.04345746	0.03849415	0.099
propane	6.00178832	0.00158066	0.026
Ar	2.38949083	1.08990392	45.612
H2O	0.04366054	0.02192114	50.208
O2	0.01419848	0.00424524	29.899
CxHy	0.00799187	0.00336117	42.057
NO2	0.00599127	0.00303956	50.733
N2O	0.00405328	0.00081060	19.999
methane	0.00112691	0.00247534	219.657
H2	0.00112327	0.00247534	220.370
n-butane	0.00036014	0.00006002	16.666
ethane	0.00003601	0.00012005	333.333

INPUTS
=====

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File	Mass (g)	u/c (g)
NPL1130.TXT	77.79600	0.03000
s186.txt	78.71200	0.03000
NPL939.txt	79.92700	0.03000
NPL711R.txt	196.2380	0.03000
PURECO2.txt	181.8680	0.03000
BIPLUSN2.txt	432.3060	0.03000

INPUT DATA FILES

=====

oooooooooooooooooooo NPL1130.TXT ooooooooooooooooooooo

Component	mol/mol	uncertainty
CO	0.0004920502	0.0000004493
CO2	0.0000001149	0.0000000107
CxHy	0.0000000500	0.0000000286
H2O	0.0000004998	0.0000002760
N2	0.9994821899	0.0000137363
O2	0.0000000034	0.0000000015
Ar	0.0000249877	0.0000137354
NO2	0.0000000500	0.0000000286
SO2	0.0000000500	0.0000000286

oooooooooooooooooooo s186.txt ooooooooooooooooooooo

Component	mol/mol	uncertainty
N2	0.9989990758	0.0000010252
SO2	0.0010002710	0.0000006430
Ar	0.0000004995	0.0000000453
CO2	0.0000000700	0.0000000100
O2	0.0000000550	0.0000000067
NO	0.0000000100	0.0000000091
H2O	0.0000000050	0.0000000018
CxHy	0.0000000050	0.0000000051
methane	0.0000000030	0.0000000045
H2	0.0000000030	0.0000000045
CO	0.0000000027	0.0000000023

oooooooooooooooooooo NPL939.txt ooooooooooooooooooooo

Component	mol/mol	uncertainty
N2	0.9990047881	0.0000008386
NO	0.0009945580	0.0000002682
Ar	0.0000004995	0.0000000452

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N2O	0.0000000497	0.0000000099
NO2	0.0000000249	0.0000000249
SO2	0.0000000100	0.0000000090
CxHy	0.0000000052	0.0000000045
H2O	0.0000000050	0.0000000018
O2	0.0000000050	0.0000000045
CO	0.0000000032	0.0000000023
methane	0.0000000030	0.0000000045
H2	0.0000000030	0.0000000045

***** NPL711R.txt *****

Component	mol/mol	uncertainty
N2	0.9999694844	0.0000008655
propane	0.0000299924	0.0000000067
Ar	0.0000005002	0.0000000500
H2O	0.0000000050	0.0000000020
O2	0.0000000050	0.0000000050
CxHy	0.0000000050	0.0000000050
CO	0.0000000030	0.0000000025
n-butane	0.0000000018	0.0000000003
methane	0.0000000010	0.0000000050
H2	0.0000000010	0.0000000050
NO	0.0000000005	0.0000000100
SO2	0.0000000005	0.0000000100
ethane	0.0000000002	0.0000000006
CO2	0.0000000000	0.0000000000

***** PURECO2.txt *****

Component	mol/mol	uncertainty
Ar	0.0000000500	0.0000000290
CO	0.0000000500	0.0000000290
CO2	0.9999998000	0.0000000600
N2	0.0000000500	0.0000000290
O2	0.0000000500	0.0000000290

***** BIPLUSN2.txt *****

Component	mol/mol	uncertainty
Ar	0.0000000500	0.0000000500
CO	0.0000000030	0.0000000025
O2	0.0000000050	0.0000000050
CxHy	0.0000000050	0.0000000050
H2O	0.0000000050	0.0000000020
N2	0.9999994790	0.0000008655
NO	0.0000000005	0.0000000100
SO2	0.0000000005	0.0000000100
methane	0.0000000010	0.0000000050
H2	0.0000000010	0.0000000050

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Measurement report NIST

Laboratory: NIST
Laboratory code: NIST
Cylinder number: M937423

Measurement #1:

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
NO	21/10/08	0.000080199	0.05	3
SO2	28/10/08	0.000080257	0.06	3
CO	24/09/08	0.000040102	0.06	2
CO2	6/10/08	0.11993	0.08	2
C3H8	15/10/08	0.000005979	0.03	4

Measurement #2:

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
NO	22/10/08	0.000080107	0.02	3
SO2	29/10/08	0.000080216	0.01	3
CO	29/09/08	0.000040069	0.06	2
CO2	7/10/08	0.11992	0.08	2
C3H8	16/10/08	0.000005977	0.06	2

Measurement #3:

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
NO	23/10/08	0.000080105	0.06	3
SO2	30/10/08	0.000080267	0.03	3
CO	2/10/2008	0.000040166	0.07	2
CO2	8/10/08	0.11994	0.08	2
C3H8	NA	NA		

Results:

Component	Result (mol/mol)	Expanded Uncertainty	Coverage factor
NO	0.00008014	0.00000029 ^a	2
SO2	0.00008025	0.00000025 ^b	2
CO	0.000040112	0.000000063	2
CO2	0.11993	0.00011	2
C3H8	0.000005979	0.000000015 ^b	2

^a Includes uncertainty in CO2 correction factor.

^b Includes uncertainty in possible cross interference

Reference method

Carbon Monoxide: The CO component of CCQM-K71 sample M937423 was analyzed using a gas chromatograph equipped with a flame ionization detector and a methanator (GC/FID/Meth). The components were separated using a 15' × 1/8" stainless steel column packed with Carboxen 1000, 60/80 mesh with a carrier gas flow rate of 30 mL/min helium. The column was operated with a temperature program of 100°C for 6 min, then ramped at 70 °C/min to 225 °C and held for 60 min. to let the propane (C₃H₈) component elute before the next injection. A sample volume of 0.5 mL was injected onto the head of the column. The FID was maintained at 250 °C and the methanator at 385 °C. The sample was delivered to the GC/FID/Meth using a computer operated gas sampling system (COGAS) at a sample flow of ~ 25 mL/min. Prior to injection the sample flow was switched off and turned to vent for 6 seconds in order to equalize the pressure in the loop to ambient pressure. The data was collected using the GC chromatographic software. Each sample in the sequence was injected a minimum of four times and the responses were averaged. The chromatograph for each injection was manually integrated due to peak tailing.

The GC/FID/Meth was calibrated with five gravimetrically prepared primary gas mixtures [PSM] containing nominal from 30 to 51 μmol/mol of CO in a balance of nitrogen. Sample M937423 was used as the analytical control to monitor the detector performance. It was rigorously compared to the PSMs a total of six times [twice each during three analytical periods]. The periodic sampling of M937423 during these intercomparisons allowed correction of the CO response for instrument drift throughout the day. A response ratio for each measurement was determined by dividing the CO response measured for each PSM by the drift corrected CO response for M937423. Interference of the CO₂, C₃H₈, NO and SO₂ components was investigated by sampling SRMs containing similar concentration levels of each. The only components which exhibited any response by the GC/FID/Meth were the CO₂ and C₃H₈ fractions. The GC runtime was adjusted such that these components were allowed to elute before the next injection was made.

Carbon Dioxide: The carbon dioxide (CO₂) component of CCQM-K71 sample M937423 was analyzed using a gas chromatograph equipped with a thermal conductivity detector (GC/TCD). The components were separated using an 8 m × 0.32 mm glass capillary column coated with a 10 μm loading of PLOT Q. The column was operated isothermally at 50 °C with a carrier gas head pressure of 0.17 kPa He. The TCD was operated in the high sensitivity mode at 50 °C with a data detection rate of 200 MHz. A sample flow of 120 ml/min was delivered to the GC/TCD using an automated gas sampling system (COGAS). The instrument's internal GC sample pump drew approximately 10 mL/min of sample for a period of 100 msec before injecting it onto the head of the column for a period of 50 msec. The data was collected using the GC chromatographic software. Each sample in the sequence was injected a minimum of five times and the responses were averaged.

The GC/TCD was calibrated with five gravimetrically prepared primary PSMs containing nominal from 7 to 15 % mol/mol of CO₂ in a balance of nitrogen. Sample M937423 was used as the analytical control to monitor the detector performance. It was rigorously compared to the PSMs a total of six times [twice each during three analytical periods]. The periodic sampling of M937423 during these intercomparisons allowed correction of the CO response for instrument drift throughout the day. A response ratio for each measurement was determined by dividing the CO₂ response measured for each PSM by the drift corrected CO₂ response for M937423. Interference of the CO, C₃H₈, NO and SO₂ components was investigated by sampling SRMs containing similar concentration levels of each. No response was observed for any of these components at the component concentration

Sulfur Dioxide: The sulfur dioxide (SO₂) component of CCQM-71, sample M937423, was analyzed using a Non Dispersive Ultra Violet (NDUV) analyzer (Ametek Series 900, NIST # 613059) A computer operated gas sampling system (COGAS # 14) was used to deliver the sample stream to the NDUV instrument and collect analyzer response. Sample flow (800 mL/min) to the instrument was controlled by a MKS Mass Flow Controller. Each sample was purged for three minutes followed by averaging data over 60 seconds.

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The NDUV was calibrated with six gravimetrically prepared standards (four PSMs and two Lot Standards, LS) containing nominal from 50 to 100 $\mu\text{mol/mol}$ in a balance of nitrogen. The 98.57 $\mu\text{mol/mol}$ LS was used as the analytical control. Daily, a total of six ratios (standard response divided by control response) were obtained for each of the five remaining standards and a total of three ratios (sample M937423 response divided by control response) were obtained for the unknown. This was performed for a total of three days so that three averages of three replicates of the SO_2 concentration (of M937423) were obtained. The calibration curve was linear. A test for cross interference by NO, CO, and CO_2 was performed with no interference found down to the 0.5 % relative level. This was handled as a rectangular distribution uncertainty.

Nitric Oxide: The nitric oxide (NO) component of CCQM-K71, sample M937423, was analyzed using a chemiluminescent (Chemi) NO/ NO_x continuous analyzer (Thermo Model 42C, NIST # 586629). The instrument was equipped with a thermal converter operating at 680 °C which allowed nitrogen dioxide and other oxides of nitrogen to be thermally disassociated back to nitric oxide. A computer operated gas sampling system (COGAS # 14) was used to deliver the sample stream to the chemi instrument and collect analyzer response. Sample flow (200 mL/min) to the instrument was controlled by a MKS Mass Flow Controller. Each sample was purged for three minutes followed by averaging data over 60 seconds.

The chemi. was calibrated with five gravimetrically prepared standards (three PSMs and two Lot Standards, LS) containing nominal from 50 to 100 $\mu\text{mol/mol}$ in a balance of nitrogen. The 97.62 $\mu\text{mol/mol}$ LS was used as the analytical control. Daily, a total of six ratios (standard response divided by control response) were obtained for each of the four remaining standards and a total of three ratios (sample M937423 response divided by control response) were obtained for the unknown. This was performed for a total of three days so that three averages of three replicates of the NO concentration (of M937423) were obtained. The calibration curve was linear.

Due to quenching by the CO_2 , a correction factor (CF) was employed for the chemi response of M937423. This was obtained by measuring the chemi response of a known NO concentration (40, 450 and 950 $\mu\text{mol/mol}$) with and without 5%, 10%, 15% and 20% CO_2 . It was shown that the CF was independent of NO and linear against CO_2 concentration:

$$\text{CF} = 0.005568 * \text{Conc. of } \text{CO}_2 (\% \text{mol.mol}) + 1.00004$$

Consequently, the observed chemi responses of M937423 (CO_2 concentration 11.993 %mol/mol) was multiplied by a CF of 1.06682 to obtain the actual responses.

Propane: The propane (C_3H_8) was determined using an Agilent 6890 gas chromatograph (NIST #: 632011) equipped with a flame-ionization detector (FID) operated at 250 °C. A 0.914 m by 0.32 cm stainless steel column packed with Poropak Q was operated isothermally at 80 °C. The helium column carrier flow rate was set at 40 mL/min. Samples were injected onto the column via a stainless steel 6-port gas sampling valve through a 5 mL stainless steel sample loop. The data was collected using the GC chromatographic software. Each sample in the sequence was injected a minimum of three times and the responses were averaged. Previous experiments with air balance versus nitrogen balance standards have shown that there is a potential 0.4 % bias. This was added as a rectangular distributed uncertainty.

The GC/FID was calibrated with five gravimetrically prepared PSM, nominal from 1 to 10 $\mu\text{mol/mol}$ in a balance of nitrogen. PSM X198002 was used as the analytical control to monitor the detector performance. It was rigorously compared to the PSMs a minimum of three times over a period of 2 days. The CCQM K-71 sample, M937423, was compared to X198002 six times during these intercomparisons.

Calibration standards

All PSMs used for the measurement of the CO, CO_2 , NO, SO_2 and C_3H_8 component of CCQM-K71 sample M937423 were prepared gravimetrically from the serial dilution of aliquots of existing PSMs. The standards used were:

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<u>Component</u>	<u>Assigned Value (x)</u>	<u>Standard uncertainty, u(x)</u>
Carbon Monoxide	51.023 $\mu\text{mol/mol}$	0.022 $\mu\text{mol/mol}$
	50.23 $\mu\text{mol/mol}$	0.05 $\mu\text{mol/mol}$
	43.722 $\mu\text{mol/mol}$	0.043 $\mu\text{mol/mol}$
	35.265 $\mu\text{mol/mol}$	0.035 $\mu\text{mol/mol}$
	30.252 $\mu\text{mol/mol}$	0.030 $\mu\text{mol/mol}$

<u>Component</u>	<u>Assigned Value (x)</u>	<u>Standard uncertainty, u(x)</u>
Carbon Dioxide	14.8052 % mol/mol	0.0148 % mol/mol
	14.2743 % mol/mol	0.0143 % mol/mol
	12.281 % mol/mol	0.030 % mol/mol
	9.152 % mol/mol	0.026 % mol/mol
	7.111 % mol/mol	0.023 % mol/mol

<u>Component</u>	<u>Assigned Value (x)</u>	<u>Standard uncertainty, u(x)</u>
Propane	10.240 $\mu\text{mol/mol}$	0.010 $\mu\text{mol/mol}$
	9.692 $\mu\text{mol/mol}$	0.010 $\mu\text{mol/mol}$
	8.906 $\mu\text{mol/mol}$	0.009 $\mu\text{mol/mol}$
	3.273 $\mu\text{mol/mol}$	0.003 $\mu\text{mol/mol}$
	1.005 $\mu\text{mol/mol}$	0.001 $\mu\text{mol/mol}$

<u>Component</u>	<u>Assigned Value (x)</u>	<u>Standard uncertainty, u(x)</u>
Sulfur Dioxide	98.57 $\mu\text{mol/mol}$	0.05 $\mu\text{mol/mol}$
	90.11 $\mu\text{mol/mol}$	0.13 $\mu\text{mol/mol}$
	80.15 $\mu\text{mol/mol}$	0.12 $\mu\text{mol/mol}$
	69.28 $\mu\text{mol/mol}$	0.12 $\mu\text{mol/mol}$
	60.54 $\mu\text{mol/mol}$	0.30 $\mu\text{mol/mol}$
	49.75 $\mu\text{mol/mol}$	0.12 $\mu\text{mol/mol}$

<u>Component</u>	<u>Assigned Value (x)</u>	<u>Standard uncertainty, u(x)</u>
Nitric Oxide	97.62 $\mu\text{mol/mol}$	0.04 $\mu\text{mol/mol}$
	89.989 $\mu\text{mol/mol}$	0.090 $\mu\text{mol/mol}$
	79.269 $\mu\text{mol/mol}$	0.079 $\mu\text{mol/mol}$
	65.626 $\mu\text{mol/mol}$	0.066 $\mu\text{mol/mol}$
	48.633 $\mu\text{mol/mol}$	0.019 $\mu\text{mol/mol}$

Sample handling

CCQM-K71 sample M937423 was received on September 11th, 2008. For the CO analysis the sample was allowed to equilibrate for a period of 24 hours in the laboratory before testing began. The CO₂ and C₃H₈ analyses were conducted in the same laboratory one after the other. For the CO and CO₂ analyses the sample was delivered to the respective instrument using an automated gas sampling system (COGAS). This computer controlled gas sampling system allowed random sampling of the PSMs in such a manner that the detector performance could be monitored for stability by using M937423 as the analytical control. The propane was delivered to the GC by a gas sampling valve but samples were manual changed rather than by COGAS. The NO analysis was performed next and finally the SO₂. For NO and SO₂ the samples were delivered to the appropriate instrument using COGAS where a LS was used as the control.

Evaluation of measurement uncertainty

Carbon Monoxide: All measured certification data and calculations for the CO concentration of M937423 have been reviewed for sources of systematic and random errors. The review identified two sources of uncertainty whose importance required quantification as estimated % Relative uncertainties. These uncertainties are:

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Uncertainty Source X_i	Assumed Distribution	Standard Uncertainty (% Relative), $u(x_i)$	Sensitivity Coefficient c_i	Gravimetric Standard or Analytical Component
Gravimetric Standards	Gaussian	0.04 – 0.10	1	Gravimetric
Ratio Reproducibility	Gaussian	0.14 – 0.38	1	Analytical

The data was reduced using the protocols listed in ISO6143 which pools the data collected from each analytical period yielding both a predicted concentration and uncertainty. The final concentration was calculated by averaging the data from the three analytical periods. The final uncertainty result assembles the uncertainties from the three analytical periods using the BOB a method for combining results from different measurements.

Carbon Dioxide: All measured certification data and calculations for the CO₂ concentration of M937423 have been reviewed for sources of systematic and random errors. The review identified two sources of uncertainty whose importance required quantification as estimated % Relative uncertainties. These uncertainties are:

Uncertainty Source X_i	Assumed Distribution	Standard Uncertainty (% Relative), $u(x_i)$	Sensitivity Coefficient c_i	Gravimetric Standard or Analytical Component
Gravimetric Standards	Gaussian	0.10 – 0.32	1	Gravimetric
Ratio Reproducibility	Gaussian	0.01 – 0.03	1	Analytical

The data was reduced using the protocols listed in ISO6143 which pools the data collected from each analytical period yielding both a predicted concentration and uncertainty. The final concentration was calculated by averaging the data from the three analytical periods. The final uncertainty result assembles the uncertainties from the three analytical periods using the BOB a method for combining results from different measurements.

Sulfur Dioxide: All measured certification data and calculations for the SO₂ concentration of M937423 have been reviewed for sources of systematic and random errors. The review identified two sources of uncertainty whose importance required quantification as estimated % Relative uncertainties. These uncertainties are:

Uncertainty Source X_i	Assumed Distribution	Standard Uncertainty (% Relative), $u(x_i)$	Sensitivity Coefficient c_i	Gravimetric Standard or Analytical Component
Gravimetric Standards	Gaussian	0.13 – 0.50	1	Gravimetric
Ratio Reproducibility	Gaussian	0.01 – 0.06	1	Analytical
Cross Interference	Rectangular	0.5	1	Analytical

The data was reduced using the protocols listed in ISO6143 which pools the data collected from each analytical period yielding both a predicted concentration and uncertainty. The final concentration was calculated by averaging the data from the three analytical periods. The final uncertainty result assembles the uncertainties from the three analytical periods using the BOB a method for combining results from different measurements.

Nitric Oxide: All measured certification data and calculations for the NO concentration of M937423 have been reviewed for sources of systematic and random errors. The review identified three sources of uncertainty whose importance required quantification as estimated % Relative uncertainties. These uncertainties are:

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Uncertainty Source, X_i	Assumed Distribution	Standard Uncertainty (% Relative), $u(x_i)$	Sensitivity Coefficient, c_i	Gravimetric Standard or Analytical Component
Gravimetric Standards	Gaussian	0.10	1	Gravimetric
Ratio Reproducibility	Gaussian	0.02 – 0.06	1	Analytical
Correction Factor for CO₂ Interference	Gaussian	0.17	1	Analytical

The data was reduced using the protocols listed in ISO6143 which pools the data collected from each analytical period yielding both a predicted concentration and uncertainty. The final concentration was calculated by averaging the data from the three analytical periods. The final uncertainty result assembles the uncertainties from the three analytical periods using the BOB a method for combining results from different measurements.

Propane: All measured certification data and calculations for the C₃H₈ concentration of M937423 have been reviewed for sources of systematic and random errors. The review identified two sources of uncertainty whose importance required quantification as estimated % Relative uncertainties. These uncertainties are:

Uncertainty Source X_i	Assumed Distribution	Standard Uncertainty (% Relative), $u(x_i)$	Sensitivity Coefficient c_i	Gravimetric Standard or Analytical Component
Gravimetric Standards	Gaussian	0.10	1	Gravimetric
Ratio Reproducibility	Gaussian	0.01 – 0.05	1	Analytical
Cross Interference	Rectangular	0.4	1	Analytical

The data was reduced using the protocols listed in ISO6143 which pools the data collected from each analytical period yielding both a predicted concentration and uncertainty. The final concentration was calculated by averaging the data from the two analytical periods. The final uncertainty result assembles the uncertainties from the two analytical periods using the BOB a method for combining results from different measurements.