



Comparison EURO.QM-S1 (EUROMET 883)

FINAL REPORT

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Field

Amount of substance

Subject

Comparison in the field automotive exhaust gas

Table of contents

Field

Subject

Table of contents

Introduction

Participants

Measurements standards

Measurement protocol

Schedule

Measurement equation

Measurement methods

Degrees of equivalence

Results

Discussions of results and "How far the light shines?"



Introduction

Automotive gas mixtures of CO, CO₂, O₂, and C₃H₈ in nitrogen are used for the calibration of measurement equipment for automotive exhaust gases. This comparison involved four laboratories two of them have used their own gravimetric primary standards, one of them used standards prepared by an accredited laboratory and the other used their own gravimetric primary standards together with gravimetric primary standards prepared by other national laboratories.

CEM operated as the coordinating laboratory in this comparison. The selected primary gas mixtures for this comparison were individually prepared using gravimetry and thoroughly studied for their chemical composition and stability.

Participants

Table 1: List of participants in this comparison

Acronym	Country	Institute
IPQ	PT	Instituto Português da Qualidade. Monte de Caparica. Portugal
INRIM	IT	Istituto Nazionale di Ricerca Metrologica. Torino. Italy
NMi VSL	NL	NMi Van Swiden Laboratorium B.V. Delft. The Netherlands
CEM	ES	Centro Español de Metrología. Madrid. Spain

Sample Mixture

One mixture was submitted to each participating laboratory. The nominal composition was the same for all the mixtures. **Table 2** shows the nominal composition of the mixtures used (expressed as amount of substance fractions).

Table 2: Nominal composition of the mixture

Component	Composition (mol.mol ⁻¹)
Carbon monoxide	0,5 x 10 ⁻²
Carbon dioxide	14 x 10 ⁻²
Oxygen	0,5 x 10 ⁻²
Propane	100 x 10 ⁻⁶
Nitrogen	Balance

The individual mixtures was prepared gravimetrically and subsequently verified at the coordinating laboratory (CEM).



The following source gases were used: carbon monoxide (CO) 4.85 from PRAXAIR, carbon dioxide (CO₂) C-45 from Carburos Metálicos, propane (C₃H₈) N40 from Praxair, oxygen (O₂) 6.0 from PRAXAIR and nitrogen (N₂) 5.5 from Carburos Metálicos. The final mixtures had a pressure of approximately 11 MPa.

All pre-mixtures were prepared in the same matrix (nitrogen) as that of the final mixtures. The target composition of all mixtures was identical (see **table 2**).

After preparation, the mixtures were verified by comparing the comparison mixtures with the PRMs. The mixtures were verified using GC-TCD (carbon monoxide, carbon dioxide), GC-FID (propane) and a paramagnetic analyzer (oxygen).

Measurement Protocol

The laboratories were requested to use their normal procedure for measurement of the composition of the gas mixture. The participants were asked to perform at least three measurements, on different days with independent calibrations. They 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. It was not required to reproduce all numerical data underlying the results reported and the uncertainties thereof. However, the report of the evaluation of the measurement uncertainty should at least have allowed for the identification of the components which were included in the evaluation, and their quantitative impact on the uncertainty of the results reported.

Schedule

The schedule of this comparison was as follows:

November 4, 2005 – Shipment of cylinders to participating laboratories

November 14, 2005 – Start of comparison

March, 17, 2006 – Reports due to pilot laboratory

March, 17, 2006 – Cylinders due to pilot laboratory

October, 2006 – Draft A report

February, 2007 – Draft B report

Measurement equation



The reference values used in this comparison are based on gravimetry. All mixtures underwent verification prior to shipment to the participants. After return of the cylinders, they were verified once more to confirm the stability of the mixtures.

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

- gravimetric preparation (weighing process) ($x_{i,grav}$)
- purity of the parent gases ($\Delta x_{i,purity}$)

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

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

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

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

Measurement methods

The measurement methods used by the participants are described in **table 3**:

Table 3: Summary of measurement methods

Laboratory	Method
IPQ	GC (TCD) for CO and C ₃ H ₈ NDIR Analyser for CO ₂
NMi	GC (TCD) for CO, CO ₂ and O ₂ GC (FID) for C ₃ H ₈
CEM	GC (TCD) for CO and CO ₂ GC (FID) for C ₃ H ₈ Paramagnetic analyser for O ₂
INRIM	NDIR Analyser for CO and CO ₂ GC (FID) for C ₃ H ₈

A summary of the calibration methods, dates of measurement and reporting, and the way in which metrological traceability is established is given in **table 4**.



Table 4: Summary of calibration methods and metrological traceability

Laboratory	Measurements	Report	Calibration	Traceability
IPQ	02-12-2005	20-01-2006	ISO 6143	Own mixtures/NMi/NPL
NMi	15-11-2005	23-03-2006	ISO 6143	Own mixtures
CEM	21-11-2005	02-02-2006	ISO 6143	Own mixtures
INRIM	23-02-2006	24-05-2006	weighted least squares	Commercial mixtures

Degrees of equivalence

The difference between gravimetric and reported value is given as degree of equivalence, which is the difference between the value measured by the laboratory (x_{lab}) and the gravimetric value (x_{igrav}).

The degree of equivalence of each laboratory with respect to the reference value is given by a pair of numbers for each cylinder:

$$D_i = (x_{lab} - x_{igrav}) \quad (3)$$

and U_i , its expanded uncertainty ($k = 2$),

$$U_i^2 = k^2 (u_{lab}^2 + u_{igrav}^2) \quad (4)$$

A compatibility index is defined as:

$$CI_i = \frac{D_i}{U_i} \quad (5)$$

Results

In **figures 1- 5**, the degrees of equivalence for all participating laboratories are given relative to the gravimetric value. The uncertainties are given as 95 % confidence intervals. For the evaluation of uncertainty of the degrees of equivalence, the normal distribution was assumed, and a coverage factor $k = 2$ was used. For obtaining the standard uncertainty of the laboratory results, in order to obtain U_i , the expanded uncertainty (stated at a confidence level of 95 %) from the laboratory was divided by the reported coverage factor.

It is necessary to say that not all laboratories analysed all the components, laboratories IPQ and INRIM did not analyse oxygen and propane was only analysed

on one day (not three days as required by the protocol) so this result is shown in the tables and in the figures but not taken into account.

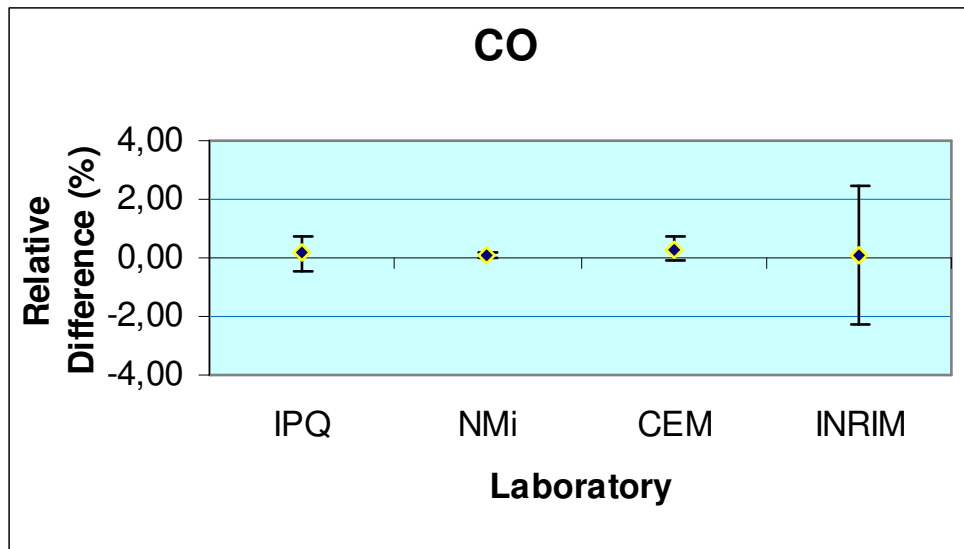


Figure 1: Degrees of equivalence for CO

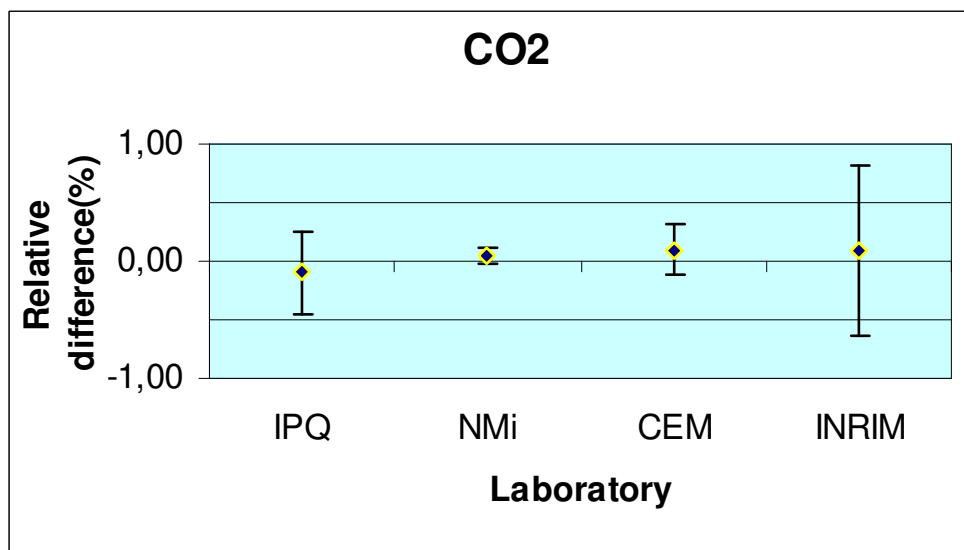


Figure 2: Degrees of equivalence for CO₂

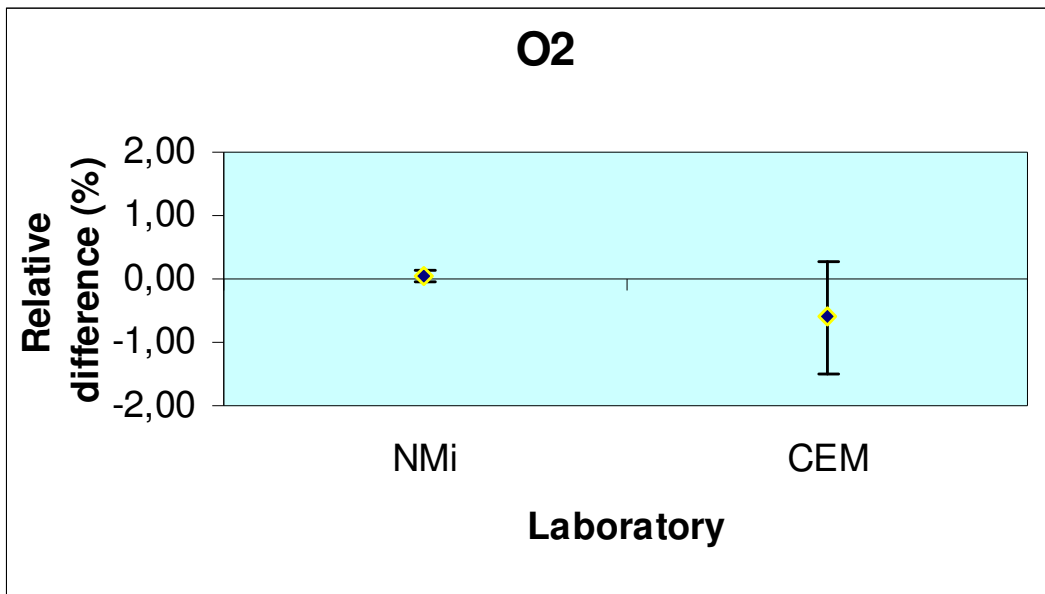


Figure 3: Degrees of equivalence for O₂

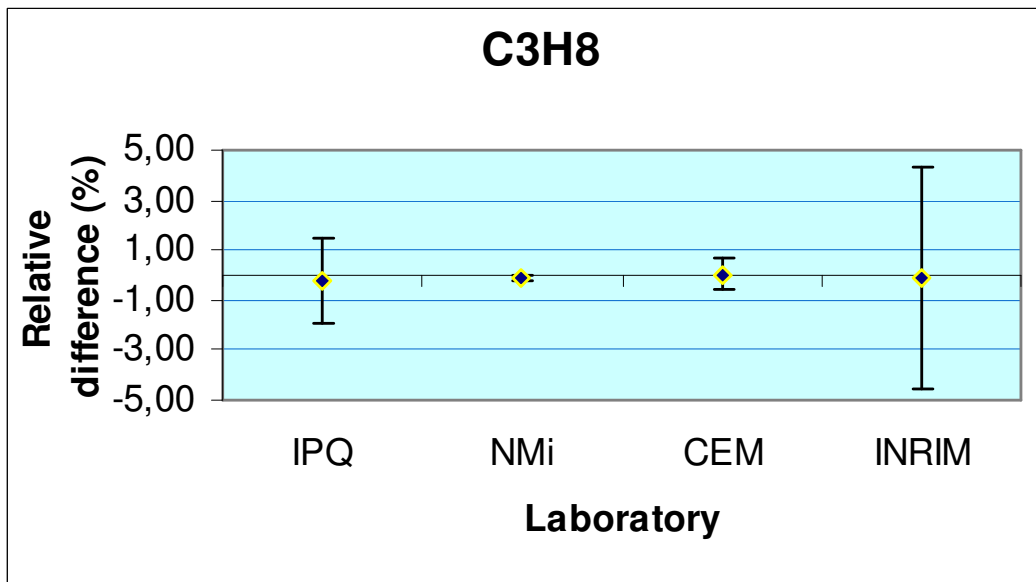


Figure 4: Degrees of equivalence for C₃H₈ (Considering results of all laboratories)

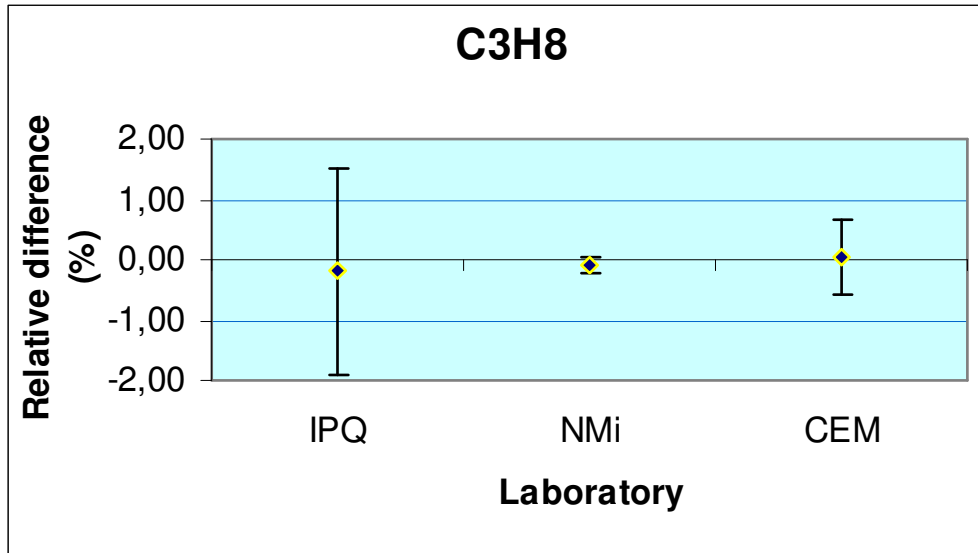


Figure 5: Degrees of equivalence for C₃H₈ (Considering results of laboratories IPQ, NMi and CEM)

On the following pages, all results of this comparison are presented. The **tables 5, 6, 7 and 8** contain the following information:

Cylinder	Identification code of the cylinder
X_{lab}	Result of measurement carried out by laboratory i
U_{lab}	Combined standard expanded uncertainty of X_{lab}
X_{igrav}	Gravimetric value of the amount of substance fraction in the cylinder
U_{igrav}	Combined standard expanded uncertainty in X_{igrav}
D_i	Degree of equivalence of laboratory i with respect to the reference value
U_i	Expanded uncertainty in D_i ($k = 2$)
D_{irel}	Relative degree of equivalence of laboratory i with respect to the reference value
U_{irel}	Relative expanded uncertainty in D_i ($k = 2$)
CI	Compatibility index



Table 5: Results for CO

Lab	Cylinder	<i>x_{grav}</i>	<i>U_{grav}</i>	<i>x_{lab}</i>	<i>U_{lab}</i>	<i>D_i</i>	<i>U_i</i>	<i>Direl (%)</i>	<i>U rel(%)</i>	<i>CI</i>
IPQ	06321	5,089	0,0006	5,0970	0,029	0,01	0,03	0,16	0,57	0,28
NMi	06313	5,011	0,0007	5,0156	0,004	0,00	0,00	0,09	0,08	1,13
CEM	06292	5,043	0,0010	5,0586	0,020	0,02	0,020	0,31	0,40	0,78
INRIM	06310	5,056	0,0010	5,0600	0,120	0,00	0,12	0,08	2,37	0,03

Units of the figures in the table mmol/mol
 Uncertainty with $k = 2$

Table 6: Results for CO₂

Lab	Cylinder	<i>x_{grav}</i>	<i>U_{grav}</i>	<i>x_{lab}</i>	<i>U_{lab}</i>	<i>D_i</i>	<i>U_i</i>	<i>Direl (%)</i>	<i>U rel(%)</i>	<i>CI</i>
IPQ	06321	138,131	0,007	137,99	0,48	-0,14	0,48	-0,10	0,35	0,29
NMi	06313	139,567	0,007	139,63	0,10	0,06	0,10	0,05	0,07	0,63
CEM	06292	138,406	0,006	138,54	0,30	0,13	0,300	0,10	0,22	0,45
INRIM	06310	136,963	0,006	137,10	1,00	0,14	1,00	0,10	0,73	0,14

Units of the figures in the table mmol/mol
 Uncertainty with $k = 2$



Table 7: Results for O₂

Lab	Cylinder	<i>x_{grav}</i>	<i>U_{grav}</i>	<i>x_{lab}</i>	<i>U_{lab}</i>	<i>D_i</i>	<i>U_i</i>	<i>Direl (%)</i>	<i>U rel(%)</i>	<i>CI</i>
NMi	06313	5,028	0,001	5,0304	0,004	0,00	0,00	0,05	0,08	0,58
CEM	06292	5,060	0,001	5,0290	0,045	-0,03	0,05	-0,61	0,90	0,68

Units of the figures in the table mmol/mol
Uncertainty with $k = 2$

Table 8: Results for C₃H₈

Lab	Cylinder	<i>x_{grav}</i>	<i>U_{grav}</i>	<i>x_{lab}</i>	<i>U_{lab}</i>	<i>D_i</i>	<i>U_i</i>	<i>Direl (%)</i>	<i>U rel(%)</i>	<i>CI</i>
IPQ	06321	100,90	0,13	100,70	1,70	-0,20	1,70	-0,20	1,69	0,12
NMi	06313	100,40	0,12	100,30	0,06	-0,10	0,13	-0,10	0,13	0,75
CEM	06292	100,00	0,12	100,05	0,61	0,05	0,62	0,05	0,62	0,08
INRIM	06310	100,10	0,12	100,01	4,40	-0,09	4,40	-0,09	4,40	0,02

Units of the figures in the table $\mu\text{mol/mol}$
Uncertainty with $k = 2$



Discussion of results and “How far the light shines?”

For CO and CO₂ the relative differences of every laboratory are smaller than 1 % (for CO even smaller than 0,5 % and for CO₂ even smaller than 0,1%). There are clear differences in the uncertainties provided by the four laboratories especially between laboratories NMI and INRIM.

For O₂ the relative differences for laboratories NMI and CEM are also smaller than 1 %, laboratories IPQ and INRIM did not analyse this component.

For C₃H₈ the results of every laboratory present relative differences smaller than 0,5%. The value of the laboratory INRIM can not be considered due to the fact that the result has been obtained from a single day analysis.

The compatibility index is less than 1 for all components and all laboratories except for CO for laboratory NMI.

Results from this comparison may be used as supporting evidence for CMC claims (calibration and measurement capabilities). As the stability of the mixtures is good, and the analytical techniques have wider applicability than this comparison, the range to which this comparison gives a suitable demonstration of measurement capabilities are:

CO: (1 – 100) mmol/mol
CO₂: (10 – 800) mmol/mol
C₃H₈: (0,02 - 3) mmol/mol
O₂: (1 – 210) mmol/mol

Completion date

March 2006



ANNEX
INDIVIDUAL REPORT OF THE PARTICIPANTS



Report forms

Laboratory : Centro Español de Metrología (CEM)

Cylinder number : 06292

Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
Carbon monoxide	06/12/05	$0,5048 \times 10^{-2}$	0,2	7
Carbon dioxide	01/02/06	$13,842 \times 10^{-2}$	0,1	7
Oxygen	20/01/06	$0,5014 \times 10^{-2}$	0,4	90
Propane	17/01/06	$100,11 \times 10^{-6}$	0,3	7
Nitrogen		matrix		

Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
Carbon monoxide	14/12/05	$0,5070 \times 10^{-2}$	0,2	7
Carbon dioxide	02/02/06	$13,846 \times 10^{-2}$	0,1	7
Oxygen	23/01/06	$0,5029 \times 10^{-2}$	0,3	90
Propane	19/01/06	$100,11 \times 10^{-6}$	0,3	7
Nitrogen		matrix		



Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
Carbon monoxide	19/12/05	$0,5058 \times 10^{-2}$	0,2	7
Carbon dioxide	07/02/06	$13,874 \times 10^{-2}$	0,1	7
Oxygen	27/01/06	$0,5043 \times 10^{-2}$	0,3	90
Propane	26/01/06	$99,92 \times 10^{-6}$	0,2	7
Nitrogen		matrix		

Results:

Component	Assigned value (x) (mmol/mol)	Expanded Uncertainty (U(x)) (mmol/mol)
Carbon monoxide	5,0586	0,02
Carbon dioxide	138,54	0,30
Oxygen	5,0290	0,045
Component	Assigned value (x) (μ mol/mol)	Expanded Uncertainty (U(x)) (μ mol/mol)
Propane	100,05	0,62
Nitrogen	matrix	---

Method description forms

Reference Method:

The certification was done according to ISO 6143:2001.



CO

Gas Chromatograph HP 6890

Columns: Porapak Q, 80/100 Mesh, 6 ft, Molecular Sieve 45/60 Mesh, 10 ft

Detector: Thermal Conductivity Detector (TCD)

Valves: System of two valves

Sample introduction: Multi position gas sampling valves.

Oven Temperature: Initial 90 °C final 155 °C (rate 15°C/min)

Carrier: He

Data Collection: Agilent Chemstation.

CO₂

Gas Chromatograph Agilent 6890 N

Columns: Porapak and Molecular Sieve

Detector: Thermal Conductivity Detector (TCD)

Valves: System of two valves

Sample introduction: Multi position gas sampling valves.

Detector Temperature: 150 °C

Carrier: He

Data Collection: Agilent Chemstation.

O₂

Paramagnetic Analyser Servomex XENTRA 4100

Sample introduction: Multi position gas sampling valves.

Data Collection: Software IR sampler.

C₃H₈

Gas Chromatograph HP 6890

Columns: Porapak Q, 80/100 Mesh, 6 ft, Molecular Sieve 45/60 Mesh, 10 ft

Detector: Flame Ionization Detector (FID)

Valves: System of two valves

Sample introduction: Multi position gas sampling valves.

Oven Temperature: Initial 90 °C final 155 °C (rate 15°C/min)

Carrier: He

Data Collection: Agilent Chemstation.



Calibration Standards:

The Calibration Standards were prepared according to ISO 6142:2001 - Gravimetric Method and certified according to ISO 6143:2001.

PSM for CO

Cylinder	Component	Assigned value (x) (mol/mol)	Expanded Uncertainty (U(x)) (mol/mol)
1004000	CO	$0,4014 \times 10^{-2}$	$0,51 \times 10^{-6}$
1005000(1)	CO	$0,500 \times 10^{-2}$	$1,56 \times 10^{-6}$
1006000	CO	$0,6058 \times 10^{-2}$	$0,72 \times 10^{-6}$

PSM for CO₂

Cylinder	Component	Assigned value (x) (mol/mol)	Expanded Uncertainty (U(x)) (mol/mol)
2130000	CO ₂	$13,0429 \times 10^{-2}$	$6,90 \times 10^{-6}$
2140000(2)	CO ₂	$14,0173 \times 10^{-2}$	$6,23 \times 10^{-6}$
2150000	CO ₂	$15,0452 \times 10^{-2}$	$6,18 \times 10^{-6}$

PSM for O₂

Cylinder	Component	Assigned value (x) (mol/mol)	Expanded Uncertainty (U(x)) (mol/mol)
3004000	O ₂	$0,4007 \times 10^{-2}$	$0,68 \times 10^{-6}$
3005000	O ₂	$0,5015 \times 10^{-2}$	$0,67 \times 10^{-6}$
3006000	O ₂	$0,6017 \times 10^{-2}$	$0,92 \times 10^{-6}$

PSM for C₃H₈

Cylinder	Component	Assigned value (x) (mol/mol)	Expanded Uncertainty (U(x)) (mol/mol)
4000900	C ₃ H ₈	$99,1 \times 10^{-6}$	$0,05 \times 10^{-6}$
4001000	C ₃ H ₈	$100,1 \times 10^{-6}$	$0,05 \times 10^{-6}$
4001100	C ₃ H ₈	$110,2 \times 10^{-6}$	$0,13 \times 10^{-6}$



Instrument Calibration:

Linear regression with 3 standards (calibration curve), using B_LEAST program, according to ISO 6143.

For GC:

7 times each cylinder

The temperature was controlled and $20,5\text{ °C} \pm 0,5\text{ °C}$

The injection was at ambient pressure

We reject always the first measurement of each cylinder for each component.

The integration parameters are different for each component

For Paramagnetic analyser:

90 readings of each cylinder

30 pressure readings

Corrections were made for zero and analysis pressure

Sample handling:

The cylinder were rolled before each analysis and kept under laboratory reference conditions (pressure, temperature and humidity conditions) during the analysis period.

We use an automatic sampler to transfer the mixtures to the GC.

The gas outlet was 2 bar

Evaluation of measurement uncertainty

The uncertainty evaluation was performed using B_LEAST program.

We use the linear fit regression

The uncertainty sources were:

- Standard uncertainty
- Instrument deviation
- Uncertainty fit regression

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

Belén Martín

Centro Español de Metrología

Tres Cantos, 25 February 2006



Report forms

Laboratory : Istituto Nazionale di Ricerca Metrologica (I.N.RI.M.)
Cylinder number : 06310

Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Carbon monoxide	23/02/06	$0,505 \cdot 10^{-2}$	0,87 %	9
Carbon dioxide	23/02/06	$13,70 \cdot 10^{-2}$	0,18 %	9
Oxygen	-	-	-	-
Propane	01/03/06	$100,01 \cdot 10^{-6}$	1,13 %	9
Nitrogen	-	-	-	-

Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Carbon monoxide	24/02/06	$0,506 \cdot 10^{-2}$	0,56 %	9
Carbon dioxide	24/02/06	$13,73 \cdot 10^{-2}$	0,22 %	9
Oxygen	-	-	-	-
Propane	-	-	-	-
Nitrogen	-	-	-	-



Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Carbon monoxide	27/02/06	$0,507 \cdot 10^{-2}$	0,60 %	9
Carbon dioxide	27/02/06	$13,72 \cdot 10^{-2}$	0,18 %	9
Oxygen	-	-	-	-
Propane	-	-	-	-
Nitrogen	-	-	-	-

Final results

Component	Result (mol/mol)	Expanded uncertainty	Coverage factor
Carbon monoxide	$0,506 \cdot 10^{-2}$	2,4 %	2
Carbon dioxide	$13,71 \cdot 10^{-2}$	0,73 %	2
Oxygen	-	-	-
Propane	$100,01 \cdot 10^{-6}$	4,4 %	2
Nitrogen	-	-	-



Method description forms

Please complete the following data regarding the description of the methods, and the uncertainty evaluation.

Reference Method:

Describe your instrument(s) (principles, make, type, configuration, data collection etc.)¹:

The instrument used for CO and CO₂ determination is a NDIR analyser ABB URAS 14, with measurement range from 0 to 8 % mol mol⁻¹ and resolution of 0,01 % mol mol⁻¹ for CO and with measurement range from 0 to 14 % mol mol⁻¹ and resolution of 0,1 % mol mol⁻¹ for CO₂. The data are visualized on the instrument display and manually recorded.

The instrument used for propane determination is a gaschromatograph CE INSTRUMENTS GC 8000 Top equipped with a flame ionisation detector. The data are recorded and collected by means of the software ChromCard (CE INSTRUMENTS).

Calibration Standards:

Describe your Calibration Standards for the measurements (preparation method, purity analyses, estimated uncertainty etc.):

The Calibration Standards used are Certified Reference Gas Mixtures of CO, CO₂, C₃H₈ and O₂ in a matrix of N₂ purchased from an accredited laboratory. They were gravimetrically prepared and their composition with the standard uncertainty for each assigned value, are reported in table 1.

¹ Please try to compile the information as short and concise as possible, for example like the description of instrumental techniques in scientific papers

Component	Assigned value (x)	Standard uncertainty (u(x))
Standard N. 1		
Carbon monoxide	0,4058 % mol mol ⁻¹	0,0014 % mol mol ⁻¹ (k = 2,28)
Carbon dioxide	13,146 % mol mol ⁻¹	0,018 % mol mol ⁻¹ (k = 2)
Propane	95,18 μmol mol ⁻¹	0,33 μmol mol ⁻¹ (k = 2)
Oxygen	0,4024 % mol mol ⁻¹	
Nitrogen	Matrix gas	
(any relevant impurities)	-	-
Standard N. 2		
Carbon monoxide	0,5040 % mol mol ⁻¹	0,0013 % mol mol ⁻¹ (k = 2)
Carbon dioxide	14,123 % mol mol ⁻¹	0,020 % mol mol ⁻¹ (k = 2)
Propane	100,50 μmol mol ⁻¹	0,35 μmol mol ⁻¹ (k = 2)
Oxygen	0,5017 % mol mol ⁻¹	
Nitrogen	Matrix gas	
(any relevant impurities)	-	-
Standard N. 3		
Carbon monoxide	0,6011 % mol mol ⁻¹	0,0016 % mol mol ⁻¹ (k = 2,28)
Carbon dioxide	15,179 % mol mol ⁻¹	0,021 % mol mol ⁻¹ (k = 2)
Propane	105,53 μmol mol ⁻¹	0,37 μmol mol ⁻¹ (k = 2)
Oxygen	0,5984 % mol mol ⁻¹	
Nitrogen	Matrix gas	
(any relevant impurities)	-	-

Tab. 1: composition of the calibration standards with the standard uncertainty for each assigned value

Instrument Calibration:

Describe your Calibration procedure (mathematical model/calibration curve, number and concentrations of standards, measurement sequence, temperature/pressure correction etc.)²:

1) Carbon dioxide

Three standards were used at the concentrations showed in the table above.

The measurements were carried out at a flow of 30 L h⁻¹. The instrument readings were collected after the signal stabilization, i.e. 2 minutes.

No correction for ambient pressure was made because the instrument had been calibrated every day in which measurements were carried out according to the following measurement protocol:

² Please state in particular the calibration model, its coefficients, and the uncertainty data (if necessary, as covariance matrix)



Standard n. 1, Sample, Standard N. 2, Sample, Standard N. 3, Sample, (repeated 3 times).
A control standard was analysed at the beginning and at the end of the entire sequence.
No correction for ambient temperature was made.
Three different calibration curves were determined, one for each measurement day and they were used to estimate the final result for CO₂.

2) Carbon monoxide

Three standards were used at the concentrations showed in the table above.

The measurements were carried out at a flow of 30 L h⁻¹. The instrument readings were collected after the signal stabilization, i.e. 2 minutes.

No correction for ambient pressure was made because the instrument had been calibrated every day in which measurements were carried out according to the following measurement protocol:

Standard n. 1, Sample, Standard N. 2, Sample, Standard N. 3, Sample, (repeated 3 times).
A control standard was analysed at the beginning and at the end of the entire sequence.

No correction for ambient temperature was made.

Three different calibration curves were determined, one for each measurement day and they were used to estimate the final result for CO.

3) Propane

Three standards were used at the concentrations showed in the table above.

As for propane, gas-chromatographic injections were made by means of a sampling valve, maintained at a temperature of 30°C. No correction for ambient temperature was made.

The ambient pressure was recorded at each injection and the measured response was corrected to standard pressure using the following equation:

$$R_{c, st} = R_c \cdot (p_{st}/p_c) \quad (1)$$

where:

$R_{c, st}$ is the response corrected to standard pressure

R_c is the measured response

p_c is the ambient pressure, [kPa]

p_{st} is the standard atmospheric pressure (101,325 kPa)

Measurements were carried out according to the following measurement protocol:

Standard n. 1, Sample, Standard N. 2, Sample, Standard N. 3, Sample, (repeated 3 times).
A control standard was analysed at the beginning and at the end of the entire sequence.

Just one calibration curve was determined and it was used to estimate the final result for propane.



4) Determination of calibration curves

For each analyte the calibration curves were determined by means of an Excel worksheet, developed at I.N.RI.M., based on the Weighted Least Squares method, which calculates a linear correction to be applied to the instrument readings according to the following equation:

$$x = y + d(y) = y + \alpha_0 + \alpha_1 y \quad (2)$$

where x is the concentration of the analyte in the reference gas mixtures, y is the instrument output and $d(y) = \alpha_0 + \alpha_1 y$ is the correction. The measurands are the polynomial coefficients α_0 and α_1 . The estimation algorithm takes care of different sources of uncertainty: the reference gas mixtures uncertainty, the repeatability of the instrument, the lack of fit, the instrument resolution. Being the reference gas mixtures purchased by the same producer, a correlation coefficient of 0,9 was adopted in the calculation.

For detailed information see the reference: Plassa M., Mosca M., Segal M. "Carbon Dioxide Determination for High Accuracy Weighings" in: *Proceedings of the 16th International Conference IMEKO TC3/APMF '98*, Myung Sai Chung Ed.; Taejon, Korea, 1998, pp. 183-191.

Calibration curves data for CO₂ are summarized in the following tables (tab. 2-4):

	α	$u_c(\alpha)$	ψ_α	
α_0	5,0E-01	2,8E-01	7,62E-02	-5,39E-03
α_1	-3,2E-02	2,0E-02	-5,39E-03	3,82E-04

Tab. 2: CO₂ calibration curve parameters of 23/02/06

	α	$u_c(\alpha)$	ψ_α	
α_0	7,1E-01	1,6E-01	2,62E-02	-1,73E-03
α_1	-4,8E-02	1,1E-02	-1,73E-03	1,15E-04

Tab. 3: CO₂ calibration curve parameters of 24/02/06

	α	$u_c(\alpha)$	ψ_α	
α_0	5,4E-01	1,9E-01	3,50E-02	-2,31E-03
α_1	-3,7E-02	1,2E-02	-2,31E-03	1,53E-04

Tab. 4: CO₂ calibration curve parameters of 27/02/06



Calibration curves data for CO are summarized in the following tables (tab. 5-7):

	α	$u_c(\alpha)$	ψ_α	
α_0	2,9E-02	1,1E-02	1,24E-04	-2,16E-04
α_1	-4,5E-03	2,0E-02	-2,16E-04	3,79E-04

Tab. 5: CO calibration curve parameters of 23/02/06

	α	$u_c(\alpha)$	ψ_α	
α_0	2,7E-02	5,5E-03	3,03E-05	-5,77E-05
α_1	-1,1E-04	1,1E-02	-5,77E-05	1,15E-04

Tab. 6: CO calibration curve parameters of 24/02/06

	α	$u_c(\alpha)$	ψ_α	
α_0	2,8E-02	4,9E-03	2,44E-05	-4,23E-05
α_1	-2,9E-03	8,7E-03	-4,23E-05	7,55E-05

Tab. 7: CO calibration curve parameters of 27/02/06

Calibration curve data for propane are summarized in table 8:

	α	$u_c(\alpha)$	ψ_α	
α_0	-3,1	14,7	216,55	-2,11
α_1	2,9E-02	1,4E-01	-2,11	2,06E-02

Tab. 8: propane calibration curve parameters of 01/03/06

Sample handling:

How were the cylinders treated after arrival (e.g. stabilized) and how were samples transferred to the instrument? (automatic, high pressure, mass-flow controller, dilution etc).:

The cylinder was kept indoor and in a horizontal position.

For CO and CO₂ analyses, samples were transferred into the NDIR analyser by means of a needle valve and a sample line of stainless steel at a flow of 30 L h⁻¹.

For propane analyses, samples were transferred to the gaschromatograph by means of a needle valve and a sample line of stainless steel. In the same way of the calibration standards, the injections were made at ambient pressure by means of a sampling valve, maintained at a temperature of 30°C.



Evaluation of measurement uncertainty

Please describe briefly how the uncertainty of measurement associated with the final result has been evaluated. Please address only the main components of uncertainty addressed in the uncertainty of the calibrants, sample handling, calibration of the equipment, and the measurement. If deemed useful, raw measurement data can be given as well in this section.

The contributions to the combined standard uncertainty of the results are due to the calibration curve and to repeatability of readings of sample measurements. From each of the three calibration curves a CO₂ and a CO concentration value with its combined standard uncertainty was estimated. The final result is the mean of these three values and its combined standard uncertainty is the largest one among the obtained uncertainties, as they were very close. As for propane, a single determination was carried out.

The contribution of calibration curve takes into account different sources: the reference gas mixtures uncertainty, the repeatability of the instrument, the lack of fit, the instrument resolution. These sources are merged together in the Excel worksheet for calibration curves calculation, hence it is very difficult to separate each contribution.

After the calibration process α_0 and α_1 being known, if a set of n_r instrument readings, arranged in a vector r , are to be corrected by the calibration algorithm, the matrix R can be defined, whose columns are the first two powers of r :

$$R = (r^0 \ r)$$

The correction vector $d(r)$ can be computed from $d(r) = R \alpha$, where α is the vector of the coefficients α_0 and α_1 . The corrected readings are:

$$q = d(r) + r \tag{3}$$

The covariance matrix of the readings is $\psi_r = s^2 I$, where s is the repeatability standard uncertainty of the instrument and I an identity matrix. The covariance matrix ψ_d of d can be estimated starting from the law of propagation of uncertainty:

$$\psi_d = \nabla_{\alpha}(d) \psi_{\alpha} \nabla_{\alpha}(d)^T + \nabla_r(d) \psi_r \nabla_r(d)^T$$

where the symbol $\nabla_z(w)$ means the Jacobian matrix, i.e. the matrix derivative, of the vector w with respect to the vector z and ψ_{α} is the variance-covariance matrix of the coefficients α_0 and α_1 .

From eq. 3 it follows that the combined standard uncertainty of a result derives from a term due to the correction obtained by the calibration curve and from a term due to instrument repeatability:

$$u_c^2(q) = u^2(d(r)) + u^2(r)$$



As an example, a typical case for CO₂ is the following one:

$$u(d(r)) = 0,042 * 10^{-2} \text{ mol/mol}$$

$$u(r) = 0,025 * 10^{-2} \text{ mol/mol}$$

$$u_c(q) = 0,049 * 10^{-2} \text{ mol/mol}$$

A typical case for CO is:

$$u(d(r)) = 0,0048 * 10^{-2} \text{ mol/mol}$$

$$u(r) = 0,0042 * 10^{-2} \text{ mol/mol}$$

$$u_c(q) = 0,0063 * 10^{-2} \text{ mol/mol}$$

The values for propane are:

$$u(d(r)) = 1,9 * 10^{-6} \text{ mol/mol}$$

$$u(r) = 1,1 * 10^{-6} \text{ mol/mol}$$

$$u_c(q) = 2,2 * 10^{-2} \text{ mol/mol}$$

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Report forms

Laboratory : IPQ - Portuguese Institute for Quality
Cylinder number : D506321

Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
Carbon monoxide	21/12/05	$0,5095 \times 10^{-2}$	0,1	6
Carbon dioxide	09/12/05	$13,791 \times 10^{-2}$	0,02	90
Oxygen				90
Propane	02/12/05	$100,9 \times 10^{-6}$	0,6	6
Nitrogen		matrix		

Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
Carbon monoxide	21/12/05	$0,5096 \times 10^{-2}$	0,2	6
Carbon dioxide	09/12/05	$13,806 \times 10^{-2}$	0,02	90
Oxygen				90
Propane	02/12/05	$100,3 \times 10^{-6}$	0,4	6
Nitrogen		matrix		



Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
Carbon monoxide	21/12/05	$0,5099 \times 10^{-2}$	0,2	6
Carbon dioxide	09/12/05	$13,801 \times 10^{-2}$	0,02	90
Oxygen				90
Propane	02/12/05	$100,9 \times 10^{-6}$	0,6	6
Nitrogen		matrix		

Results:

Component	Assigned value (x) (mol/mol)	Expanded Uncertainty (U(x)) (mol/mol)
Carbon monoxide	$0,5097 \times 10^{-2}$	$0,0029 \times 10^{-2}$
Carbon dioxide	$13,799 \times 10^{-2}$	$0,048 \times 10^{-2}$
Oxygen		
Propane	$100,7 \times 10^{-6}$	$1,7 \times 10^{-6}$
Nitrogen	matrix	---



Method description forms

Reference Method:

The certification was done according to ISO 6143:2001.

A Gas Chromatograph was used for carbon monoxide and propane analyses.

GC: HP 5890

Columns: Porapak Q, 80/100 Mesh, 10 ft, 0,125 inch OD Stainless
Molecular Sieve 5A, 45/60 Mesh, 10 ft, 0,125 inch OD Stainless

Detector: 1 Thermal Conductivity Detector (TCD)

Valves: System of two valves

Sample introduction: Multi position gas sampling valves.

Oven Temperature: 160 °C (propane) and 150 °C (carbon monoxide)

Carrier: He

Data Collection: Agilent Chemstation Plus program.

A Non Dispersive Infrared Analyser (NDIR - Uras 4) was used for carbon dioxide analyses.

Sample introduction: Multi position gas sampling valves.

Data Collection: Software Sira version 1.0.

Calibration Standards:

The Calibration Standards were prepared according to ISO 6142:2001 - Gravimetric Method and certified according to ISO 6143:2001.

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



Cylinder	Component	Assigned value (x) (mol/mol)	Expanded Uncertainty (U(x)) (mol/mol)
PSM102519	CO	$4,001 \times 10^{-3}$	$1,5 \times 10^{-5}$
PSM102585 (auto)	CO	$9,990 \times 10^{-3}$	$6,5 \times 10^{-5}$
PSM102547	CO	$3,502 \times 10^{-2}$	$2,4 \times 10^{-4}$
NPL879	CO	$4,730 \times 10^{-2}$	$2,7 \times 10^{-4}$
PSM102520	C ₃ H ₈	$5,0040 \times 10^{-5}$	$1,3 \times 10^{-6}$
PSM102554	C ₃ H ₈	$9,980 \times 10^{-5}$	$1,7 \times 10^{-6}$
PRM106412	C ₃ H ₈	$2,930 \times 10^{-4}$	$1,6 \times 10^{-6}$
PSM102585 (auto)	C ₃ H ₈	$6,005 \times 10^{-4}$	$5,5 \times 10^{-6}$
NMI2714	C ₃ H ₈	$2,001 \times 10^{-4}$	$1,6 \times 10^{-6}$
PSM102525	CO ₂	$5,5020 \times 10^{-2}$	$1,4 \times 10^{-4}$
PSM102552	CO ₂	$7,0000 \times 10^{-2}$	$2,0 \times 10^{-4}$
PSM102535	CO ₂	$1,0008 \times 10^{-1}$	$3,3 \times 10^{-4}$
PSM102541	CO ₂	$1,2495 \times 10^{-1}$	$3,7 \times 10^{-4}$
PSM102603	CO ₂	$1,5298 \times 10^{-1}$	$4,5 \times 10^{-4}$

Instrument Calibration:

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

For Carbon Monoxide (CO) was used a set of four PSM (from IPQ and NPL).

For Propane (C₃H₈) was used a set of five PSM (from IPQ and NMI).

For Carbon Dioxide (CO₂) was used a set of five PSM (from IPQ).



Sample handling:

After arrival the cylinder was stored at ambient temperature in a storage room.
The sample was transferred to the instrument through an auto-sampler.

Evaluation of measurement uncertainty

The measurement uncertainty evaluation was done according GUM: 1995 “Guide to the Expression of Uncertainty in Measurement”.

The measurement uncertainty associated with the final result was evaluated and includes two uncertainty sources:

- Uncertainty of the Primary Standard mixtures;
- Standard deviation of the mean (GC-Analysis / NDIR analysis)

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

Florbela Dias

Gonçalo Baptista

Portuguese Institute for Quality

Reference Gas Laboratory

Caparica, 20 January 2006



Report forms

Laboratory :NMI-VSL
Cylinder number : D50 6313

Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
Carbon monoxide	15-11-05	0.0050197	0.10	5
Carbon dioxide	15-11-05	0.13982	0.03	5
Oxygen	15-11-05	0.0050308	0.06	5
Propane	15-11-05	0.0001003	0.05	5
Nitrogen	N.A.			

Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Carbon monoxide	16-11-05	0.0050124	0.08	5
Carbon dioxide	16-11-05	0.13958	0.04	5
Oxygen	16-11-05	0.0050316	0.05	5
Propane	16-11-05	0.0001003	0.03	5
Nitrogen	N.A.			

Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Carbon monoxide	17-11-05	0.0050121	0.04	
Carbon dioxide	17-11-05	0.13957	0.04	
Oxygen	17-11-05	0.0050341	0.04	
Propane	17-11-05	0.0001002	0.03	
Nitrogen	N.A.			



Measurement #4

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Carbon monoxide	21-11-05	0.0050176	0.09	5
Carbon dioxide	21-11-05	0.13962	0.04	5
Oxygen	21-11-05	0.0050305	0.05	5
Propane	21-11-05	0.0001002	0.03	5
Nitrogen	N.A.			

Measurement #5

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Carbon monoxide	09-02-06	0.0050160	0.05	5
Carbon dioxide	09-02-06	0.13955	0.01	5
Oxygen	09-02-06	0.0050252	0.03	5
Propane	09-02-06	0.0001003	0.03	5
Nitrogen	N.A.			

Result

Component	Assigned value(x) (mol/mol)	Standard uncertainty ($u(x)$)
Carbon monoxide	0.0050156	2e-06 (0.000002)
Carbon dioxide	0.13963	5e-05 (0.00005)
Propane	0.0001003	3e-08 (0.00000003)
Oxygen	0.0050304	2e-06 (0.000002)
<i>Nitrogen</i>	N.A.	
(any relevant impurities)	N.A.	



Method description forms

Please complete the following data regarding the description of the methods, and the uncertainty evaluation.

Reference Method:

Describe your instrument(s) (principles, make, type, configuration, data collection etc.)³:

Mixture was analysed with GC-TCD-FID techniques. An Agilent 6890N GC with a 10 ft Porapak T column and a 10 ft Molsieve 5A column (80-100 mesh) was used for separation. The sample was injected using 0.5 mL sample loop. Propane was analysed using a flame ionisation detector and the other components were analysed using a thermal conductivity detector.

A suite of multicomponents PSM and the sample cylinder were connected to a multi-position valve and each sample was injected 5 times. Data was collected with the Agilent Chemstation software.

The barometer drift was compensated for.

Calibration Standards:

Describe your Calibration Standards for the measurements (preparation method, purity analyses, estimated uncertainty etc.):

A set of multicomponent PSM's in nitrogen matrix was used with compositions as given in the below tables.

³ Please try to compile the information as short and concise as possible, for example like the description of instrumental techniques in scientific papers



(mol/mol)	VSL203612	VSL207389	VSL209568
Carbon monoxide	0.004955 ± 0.0000009	0.049612 ± 0.000009	0.020046 ± 0.0000019
Carbon dioxide	0.040481 ± 0.000006	0.15827 ± 0.000008	0.080043 ± 0.000006
Propane	0.0001977 ± 0.00000005	0.002967 ± 0.0000005	0.000598 ± 0.0000002
Oxygen	0.005036 ± 0.0000013	0.010332 ± 0.0000018	0.019979 ± 0.0000019

(mol/mol)	VSL309610	VSL509428	VSL304135
Carbon monoxide	0.040049 ± 0.000009	0.009875 ± 0.000002	0.034983 ± 0.000009
Carbon dioxide	0.100341 ± 0.000007	0.060181 ± 0.000006	0.140001 ± 0.000007
Propane	0.0009866 ± 0.0000003	0.0003991 ± 0.00000007	0.002007 ± 0.0000005
Oxygen	0.050575 ± 0.000008	0.09968 ± 0.000008	0.20882 ± 0.000010

In addition two propane in nitrogen mixtures were used with the following composition:

VSL202781: 0.0000802 ± 0.00000006

VSL204642: 0.0000990 ± 0.00000003



All mixtures were prepared in accordance with International Standard ISO 6142: 2001 (Gas analysis - Preparation of calibration gas mixtures - Gravimetric method). Purity analysis was performed on the pure CO, CO₂, propane, oxygen and nitrogen. For each pure component a purity table was prepared listing the composition and uncertainties. These tables were used in calculating the final mixture composition. The uncertainty resulting from gravimetric preparation is listed in the above tables.

Instrument Calibration:

Describe your Calibration procedure (mathematical model/calibration curve, number and concentrations of standards, measurement sequence, temperature/pressure correction etc.)⁴:

International Standard ISO 6143:2001 (Gas analysis - Comparison methods for determining and checking the composition of calibration gas mixtures) was used to certify the sample cylinders. For the four constituents of interest a calibration curve was constructed using the mean value for the peak area's (corrected for barometric drift) and the standard deviation as standard uncertainty. The TLS method was used resulting in a calculated mole fraction and standard uncertainty for the sample cylinder. In all cases a Quadratic function was used.

Sample handling:

How were the cylinders treated after arrival (e.g. stabilized) and how were samples transferred to the instrument? (automatic, high pressure, mass-flow controller, dilution etc.):

Upon arrival the sample cylinder was stored in the laboratory at 20 °C. The sample was analysed on three consecutive days, 1 week later and a final analyses was performed 3 months later just before preparation of the report. No significant differences were found in this last measurement (#5) compared to the earlier measurements.

⁴ Please state in particular the calibration model, its coefficients, and the uncertainty data (if necessary, as covariance matrix)



A Concoa all Stainless Steel two port pressure reducer was connected to the sample cylinder. The reducer was carefully flushed as prescribed in International Standard ISO 16664:2004 (Gas analysis - Handling of calibration gases and gas mixtures - Guidelines).

Evaluation of measurement uncertainty

Please describe briefly how the uncertainty of measurement associated with the final result has been evaluated. Please address only the main components of uncertainty addressed in the uncertainty of the calibrants, sample handling, calibration of the equipment, and the measurement. If deemed useful, raw measurement data can be given as well in this section.

The uncertainty on the used PSM's was evaluated as prescribed in Alink A., Van der Veen A.M.H., "Uncertainty calculations for the preparation of primary gas mixtures. 1. Gravimetry", Metrologia 37 (2000), pp 641-650.

In performing the TLS evaluation the methods as prescribed in ISO 6143 were applied using the uncertainties in both the gravimetric value of the calibrants and the standard uncertainty in the measurements. This resulted in calculated mole fractions and uncertainties for each of the 5 measurements.

To calculate the final result the mean value for the composition was calculated and the standard uncertainty for the 5 measurements was combined in quadrature to calculate the final uncertainty.

Rob Wessel

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