Analysis of impurities in pure and balance gases used to prepare primary standard gas mixtures by the gravimetric method

Final report Euramet.QM-S8

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Summary

This project concerns the purity analysis of nitrogen as used in reference gas mixture preparation. This project was carried out without adding impurities to the gas used for this comparison, and is therefore more representative to evaluate the analysis of CO, CO_2, CH_4, O_2, Ar and H_2O impurities in high purity nitrogen. The analysis of the amount–of–substance fraction water was optional.

Two 50 litre high purity nitrogen cylinders were purchased from a well-qualified supplier of specialty gases. The listed components were expected to be present in the pure nitrogen at the target levels as a result of the purification of the nitrogen. From the start of this comparison it was clear that the comparison may not lead to reference values for the constituents analysed.

The results indicate that analyses of high purity gases are often limited by the limits of detection of analytical equipment used. The reports of the participating laboratories also indicate that there is no agreed method of determination of the uncertainty on a detection limit value. The results provide useful information on the performance of participants. For all analysed components there is reasonable agreement in results for LNE, VSL, Metas and NPL. For BAM only the Argon result is in agreement.

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1 Introduction

This project builds on the results of Euromet project 867 [1] on purity analysis of nitrogen. For Euromet 867 the amount fractions of the impurities in the nitrogen of interest were actually added to high purity nitrogen and were in the range from 200 – 600 nmol/mol. This project was carried out without adding gases and is therefore more representative to evaluate the analysis of CO, CO_2, CH_4, O_2, Ar and H_2O impurities in high purity nitrogen.

All participants were asked to measure the amount–of–substance fractions of CO, CO_2, CH_4, O_2 and Ar. Analysis of the amount–of–substance fraction water was optional.

Two 50 litre high purity nitrogen cylinders were purchased from a well-qualified supplier of specialty gases. The listed components were expected to be present in the pure nitrogen at the target levels as a result of the purification of the nitrogen. From the start of this comparison it was clear that the comparison may not lead to reference values for the constituents analysed.

2 Design of the comparison

2.1 Field of measurement

Amount–of–substance

2.2 Subject

Comparison on the analysis of impurities in high–purity nitrogen

2.3 Participants

Table 1 lists the participants in this supplementary comparison.

Table 1: List of participants

Acronym	Country	Institute
LNE	FR	Laboratoire National de Métrologie et d'Essais
METAS	CH	Swiss Federal Office of Metrologie
NPL	UK	National Physical Laboratory, Teddington, Middlesex, United Kingdom
VSL	NL	Van Swinden Laboratorium, Delft, the Netherlands
BAM	DE	Federal Institute for Materials Research and Testing

2.4 Measurement standards

Two cylinders of high purity nitrogen were purchased from Linde gas Benelux. Table 2 shows the specifications of the cylinders as given by the manufacturer (expressed as amount of substance fractions).

Table 2: Reported specification of the pure nitrogen by manufacturer

Component	x
Carbon dioxide + Carbon monoxide	≤ 0,2 µmol/mol
Oxygen	≤ 0,2 µmol/mol
CxHy	≤ 0,1 µmol/mol
H_2O	≤ 0,5 µmol/mol
N_2	≥ 999,999 mmol/mol

2.5 Measurement protocol

The laboratories were requested to use their normal procedure for the measurement of the impurities. For participation in this comparison, it was agreed that participants may analyse the moisture content as an option. The participants were asked to report limits of detection (and/or limits of quantification) when no impurity is analysed.

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, but the report of the evaluation of measurement uncertainty should at least allow addressing which components have been included in the evaluation and what their quantitative impact on the reported uncertainty is.

2.6 Schedule

The schedule for circulation of the travelling standard for this comparison was as follows

Cylinder 479235:	VSL → NPL → INRIM → LNE → VSL
Cylinder 2230340:	VSL → BAM → METAS → LNE →VSL

INRIM intended to participate in this comparison but decided upon receipt of the cylinder to withdraw. This cylinder was then shipped to LNE.

3 Results

3.1 Measurement methods

The measurement methods used by the participants are described in detail in the reports of participants listed in annex A of this report. A summary of the methods is given in tables 3–7.

Table 3: Summary of measurement methods and metrological traceability for CO analyses

Laboratory	Measurement technique	Calibration	Traceability
LNE	FT-IR with glass gas cell optical path 96 m	Gravimetric 4 component mixture at 350 nmol/mol level	LNE
METAS	ND-IR with external zero gas	Primary dilution set-up used to dilute commercial 5 µmol/mol mixture	Metas / Carbagas
NPL	GC- Reduction Gas Detector	Gravimetric 4 component mixture at 30 nmol/mol level	NPL
VSL	CRDS	Gravimetric 2 component mixture at 30 nmol/mol level	VSL
BAM	GC-PDID	Single point calibration multi component mixture	BAM

Table 4: Summary of calibration methods and metrological traceability for CO_2 analyses

Laboratory	Measurement technique	Calibration	Traceability
LNE	FT-IR with glass gas cell optical path 96 m	Gravimetric 4 component mixture at 350 nmol/mol level	LNE
METAS	IMR-MS with Kr ionisation	Primary dilution set-up used to dilute commercial 5 µmol/mol mixture	Metas / Carbagas
NPL	GC- FID with methaniser	Gravimetric 4 component mixture at 30 nmol/mol level	NPL
VSL	FT-IR with glass gas cell optical path 96 m	Gravimetric 2 component mixture at 30 nmol/mol level	VSL
BAM	Not analysed	-	-

Table 5: Summary of calibration methods and metrological traceability for CH_4 analyses

Laboratory	Measurement technique	Calibration	Traceability
LNE	FT-IR with glass gas cell optical path 96 m	Gravimetric 4 component mixture at 350 nmol/mol level	LNE
METAS	IMR-MS with Xe ionisation	Primary dilution set-up used to dilute commercial 5 µmol/mol	Metas / Carbagas

Laboratory	Measurement technique	Calibration	Traceability
		mixture	
NPL	GC- FID	Gravimetric 4 component mixture at 30 nmol/mol level	NPL
VSL	CRDS, wavenumber around 3086 cm^{-1}	2 Gravimetric 2 component mixture at 10 and 20 nmol/mol level	VSL
BAM	GC-PDID	Single point calibration multi component mixture	BAM

Table 6: Summary of calibration methods and metrological traceability for O_2 analyses

Laboratory	Measurement technique	Calibration	Traceability
LNE	Electrochemical analyser	Gravimetric mixture at 600 nmol/mol level	LNE
METAS	IMR-MS with Xe ionisation	Primary dilution set-up used to dilute commercial 5 µmol/mol mixture	Metas / Carbagas
NPL	Electrochemical analyser	Gravimetric 4 component mixture at 30 nmol/mol level	NPL
VSL	GC-PDHID	Gravimetrically prepared 1 µmol/mol mixture	VSL
BAM	GC-PDID	Single point calibration multi component mixture	BAM

Table 7: Summary of calibration methods and metrological traceability for Ar analyses

Laboratory	Measurement technique	Calibration	Traceability
LNE	GC-PDHID	Gravimetric mixture at 2000 nmol/mol level	LNE
METAS	IMR-MS with Xe ionisation	Primary dilution set-up used to dilute commercial 300 µmol/mol mixture	Metas / Westfalen gas
VSL	GC-PDHID	Gravimetrically prepared O_2 in N_2 mixtures (1-10 µmol/mol)	VSL
BAM	GC-PDID	Single point calibration multi component mixture	BAM

The moisture content was only analysed by VSL using a commercial Cavity Ringdown Spectrometer with traceability to the Primary Humidity Generator from VSL's Temperature & Humidity group.

3.2 Results of the comparison

In this section, the results of this comparison are summarised.

Table 8: Results for carbon monoxide (nmol mol^{-1})

Lab	Cylinder	Reported value	Reported expanded uncertainty	Limit of Detection LoD
LNE	479235	0	5.8	5
NPL	479235	0.3	0.3	0.3
VSL	479235	0	1	1
LNE	2230340	0	5.8	5
METAS	2230340	0	+6 / -2	2
BAM	2230340	130	30	
VSL	2230340	0	1	1

Table 9: Results for carbon dioxide (nmol mol^{-1})

Lab	Cylinder	Reported value	Reported expanded uncertainty	Limit of Detection LoD
LNE	479235	0	1.2	1
NPL	479235	1	1	1
VSL	479235	4.3	0.7	
LNE	2230340	0	1.2	1
METAS	2230340	1.6	1.2	1.1
BAM	2230340	NA		
VSL	2230340	2.0	0.3	

Table 10: Results for methane (nmol mol^{-1})

Lab	Cylinder	Reported value	Reported expanded uncertainty	Limit of Detection LoD
LNE	479235	0	4.6	4
NPL	479235	0.8	0.8	0.8
VSL	479235	0.3	0.3	
LNE	2230340	0	4.6	4
METAS	2230340	1.2	0.9	0.3
BAM	2230340	127	4	
VSL	2230340	0.3	0.3	

Table 11: Results for oxygen (nmol mol^{-1})

Lab	Cylinder	Reported value	Reported expanded uncertainty	Limit of Detection LoD
LNE	479235	11	10	
NPL	479235	5	3	
VSL	479235	0	30	50
LNE	2230340	18	16	
METAS	2230340	12	6	9
BAM	2230340	1530	120	
VSL	2230340	0	30	50

Table 12: Results for argon (nmol mol^{-1})

Lab	Cylinder	Reported value (nmol/mol)	Reported expanded uncertainty
LNE	479235	655	16
NPL	479235	NA	
VSL	479235	730	73
LNE	2230340	654	20
METAS	2230340	760	+850 / -760
BAM	2230340	670	50
VSL	2230340	731	73

The moisture content was only analysed by VSL. The reported values are:

Cylinder 479235 : (16 ± 4) nmol mol^{-1}

Cylinder 2230340: (4 ± 1) nmol mol^{-1}

The results are presented graphically in figures 1 - 5. A mean result is calculated if more than 1 laboratory reported a value not based on detection limits and when those results show sufficient overlap. All reported values meeting these requirements were used to calculate a mean value.

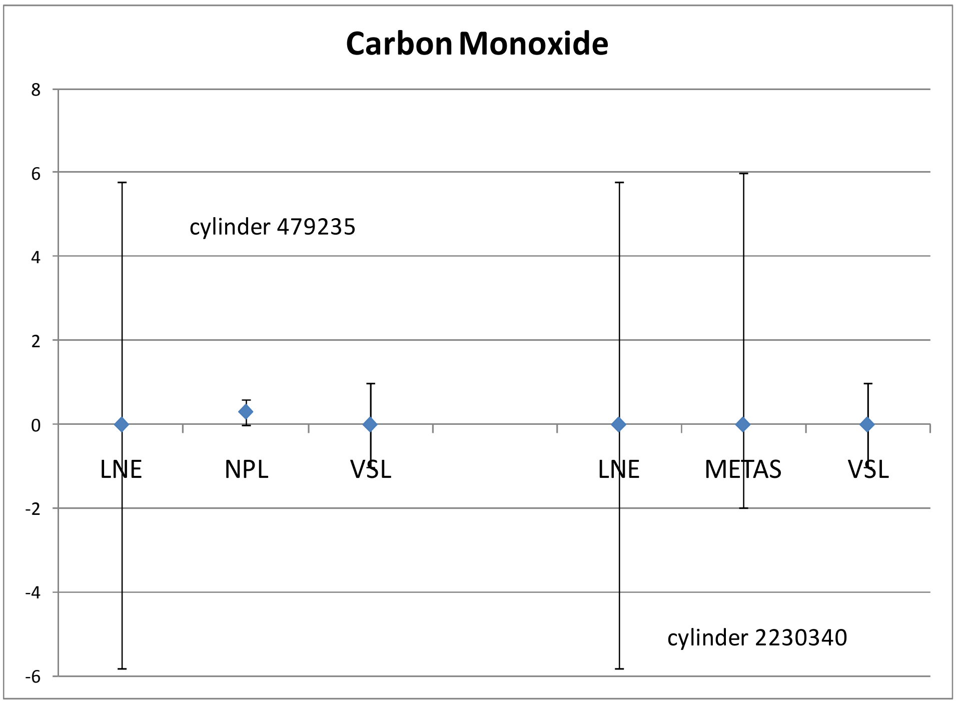

Figure 1: Reported amount—of—substance fractions and associated expanded uncertainties for carbon monoxide (nmol/mol); BAM reported for cylinder 2230340 130 ± 30 nmol/mol.

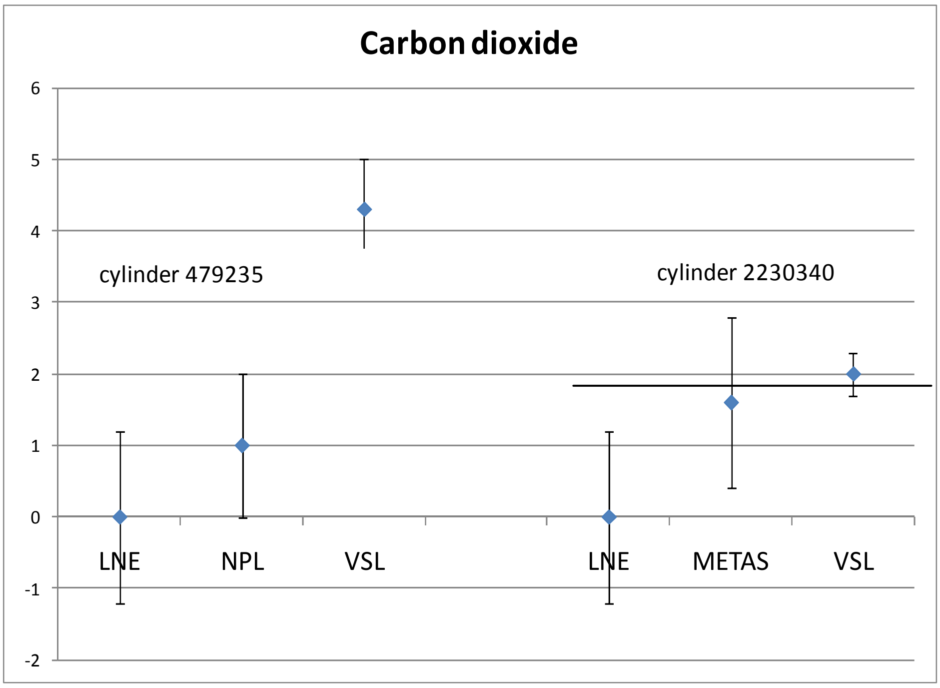

Figure 2: Reported amount—of—substance fractions and associated expanded uncertainties for carbon dioxide (nmol/mol)

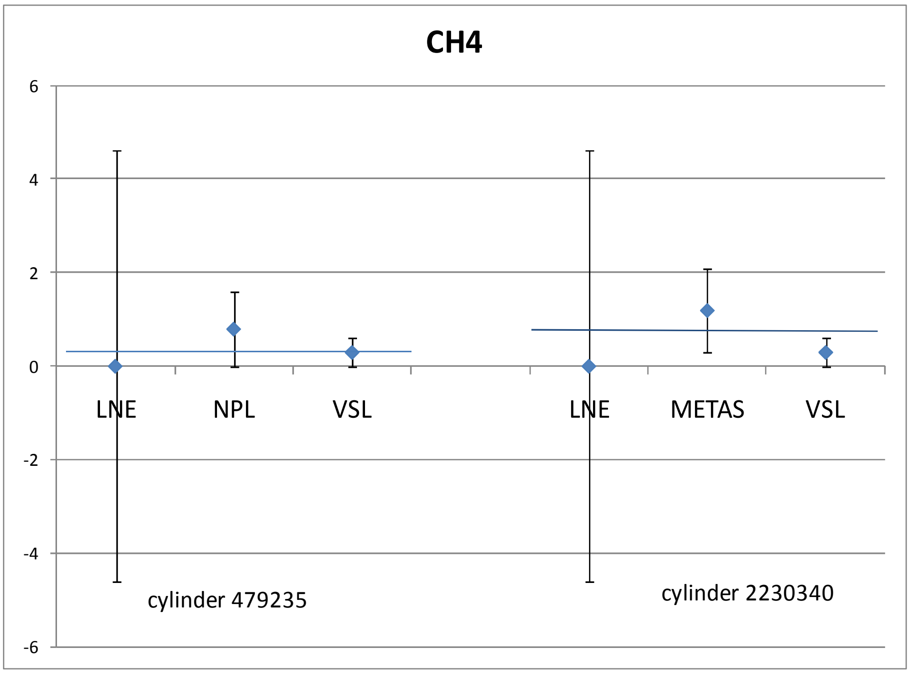

Figure 3: Reported amount—of—substance fractions and associated expanded uncertainties for methane (nmol/mol); BAM reported for cylinder 2230340 127 ± 4 nmol/mol.

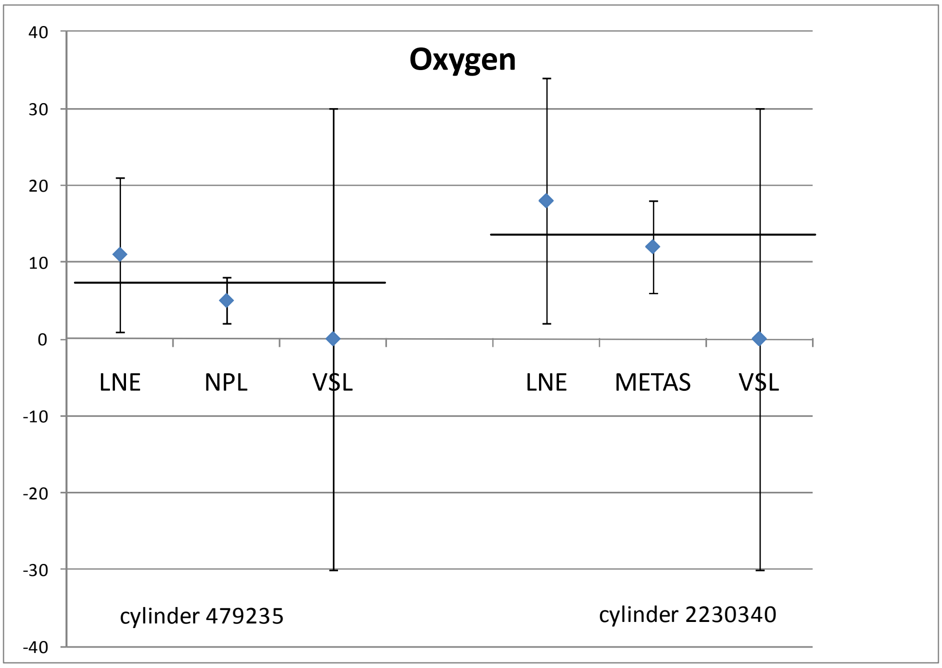

Figure 4: Reported amount—of—substance fractions and associated expanded uncertainties for oxygen (nmol/mol); BAM reported for cylinder 2230340 1530 ± 120 nmol/mol.

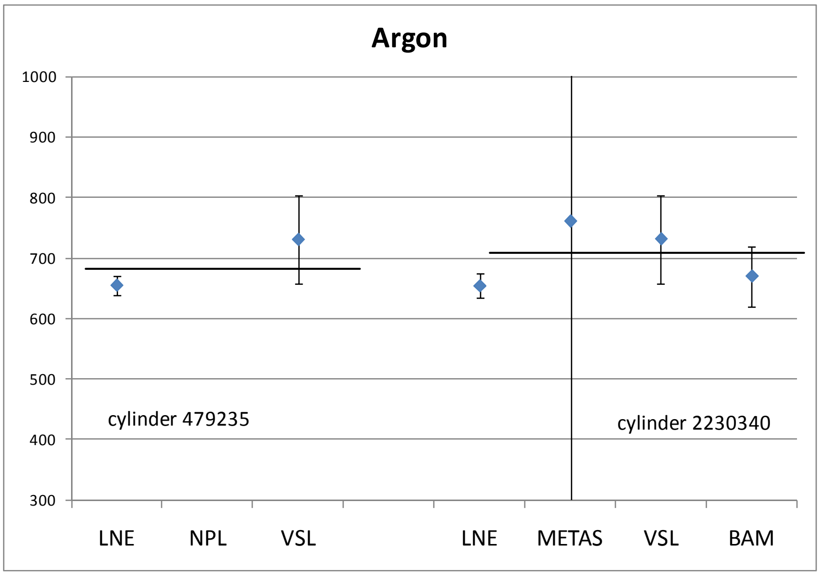

Figure 5: Reported amount—of—substance fractions and associated expanded uncertainties for argon (nmol/mol)

4 Discussion and conclusions

The results indicate that analyses of high purity gases are often limited by the limits of detection of analytical equipment used. The reports of the participating laboratories also indicate that there is no agreed method of determination of the uncertainty on a detection limit value. Due to the fact that the various participants used different analytical techniques with different limits of detection, it is not possible to calculate degrees of equivalence; this was expected from the beginning of this comparison. The results in this report however, give useful information on the performance of participants. For all analysed components there is reasonable agreement in results for LNE, VSL, Metas and NPL. For BAM only the Argon result is in agreement.

Ion-molecule mass spectrometry (IMR-MS) used by METAS is selective and sensitive for CO_2, CH_4, O_2 but is much less sensitive for Ar due to its high ionisation energy. Conventional electron impact ionisation MS (e-MS) would be much more sensitive for Ar, but is lacking the necessary ionisation energy selectivity for measuring the other components in presence of a balance gas like nitrogen.

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Measurement report LNE

Laboratory : Laboratoire National de métrologie et d'Essais
Laboratory code : LNE
Cylinder number : 479235

Carbon monoxide

Measurement	**Date (dd/mm/yy)**	**Result (mol/mol)**	**Standard deviation (% relative)**	**Number of replicates**
1	10/06/2010	< detection limit (5 nmol/mol)	-	3

Carbon dioxide

Measurement	**Date (dd/mm/yy)**	**Result (mol/mol)**	**Standard deviation (% relative)**	**Number of replicates**
1	10/06/2010	< detection limit (1 nmol/mol)	-	3

Methane

Measurement	**Date (dd/mm/yy)**	**Result (mol/mol)**	**Standard deviation (% relative)**	**Number of replicates**
1	10/06/2010	< detection limit (4 nmol/mol)	-	3

Oxygen

Measurement	**Date (dd/mm/yy)**	**Result (mol/mol)**	**Standard deviation (% relative)**	**Number of replicates**
1	26/05/2010	10.1	-	-
2	27/05/2010	6.0	-	-
3	01/06/2010	15.8	-	-
4	02/06/2010	9.0	-	-
5	03/06/2010	14.8	-	-
6	08/06/2010	9.3	-	-

Argon

Measurement	**Date (dd/mm/yy)**	**Result (mol/mol)**	**Standard deviation (% relative)**	**Number of replicates**
1	02/06/2010	652.90	0.53	36
2	03/06/2010	656.46	0.88	35
3	04/06/2010	648.24	0.68	36
4	08/06/2010	661.13	0.76	35
5	11/06/2010	654.74	0.82	38

Result

Component	**Result (nmol/mol)**	**Coverage factor**	**Assigned expanded uncertainty**
Carbon monoxide	< detection limit (5 nmol/mol)	–	–
Carbon dioxide	< detection limit (1 nmol/mol)	–	–
Methane	< detection limit (4 nmol/mol)	–	–
Oxygen	11 nmol/mol	2	10 nmol/mol
Argon	655 nmol/mol	2	16 nmol/mol

For all listed components a value and uncertainty needs to be reported even if no contamination can be found. In such case the Limit of Detection/Limit of Quantification needs to be evaluated by the laboratory and results and uncertainty associated should be reported accordingly.

Laboratory : Laboratoire National de métrologie et d'Essais
Laboratory code : LNE
Cylinder number : 2230340

Carbon monoxide

Measurement	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
1	10/06/2010	< detection limit (5 nmol/mol)	-	3

Carbon dioxide

Measurement	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
1	10/06/2010	< detection limit (1 nmol/mol)	-	3

Methane

Measurement	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
1	10/06/2010	< detection limit (4 nmol/mol)	-	3

Oxygen

Measurement	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
1	05/05/2010	23.1	-	-
2	06/05/2010	24.1	-	-
3	07/05/2010	21.0	-	-
4	03/06/2010	12.8	-	-
5	08/06/2010	8.4	-	-

Argon

Measurement	**Date (dd/mm/yy)**	**Result (mol/mol)**	**Standard deviation (% relative)**	**Number of replicates**
1	17/05/2010	652.50	0.55	40
2	19/05/2010	661.73	0.67	19
3	26/05/2010	644.11	0.74	34
4	27/05/2010	654.68	0.60	34
5	01/06/2010	657.88	0.68	43

Result

Component	**Result (nmol/mol)**	**Coverage factor**	**Assigned expanded uncertainty**
Carbon monoxide	< detection limit (5 nmol/mol)	–	–
Carbon dioxide	< detection limit (1 nmol/mol)	–	–
Methane	< detection limit (4 nmol/mol)	–	–
Oxygen	18 nmol/mol	2	16 nmol/mol
Argon	654 nmol/mol	2	20 nmol/mol

For all listed components a value and uncertainty needs to be reported even if no contamination can be found. In such case the Limit of Detection/Limit of Quantification needs to be evaluated by the laboratory and results and uncertainty associated should be reported accordingly.

Method description

1) For CO, CO_2 and CH_4

Reference Method:

A Fourier Transformed InfraRed (FTIR) has been used to analyze CO, CO_2 and CH_4. This spectrometer is a FTS 175C from BIO RAD with a spectral resolution of 0.5 cm^{-1}.

The detector is a MCT (mercury cadmium tellure) cooled with liquid nitrogen which can make measurements from 500 cm^{-1} to 4000 cm^{-1}.

The spectrometer is purged with purified air to eliminate traces of water and carbon dioxide.

The FTIR is used with a gas cell from INFRARED ANALYSIS : the cell is made in borosilicated glass and its volume is 16 liters.

The optical lengh of the cell is 96 m.

The background is made under vacuum at 10^{-6} mbars.

Calibration Standards:

LNE has prepared a gas mixture of CO, CO_2 and CH_4 at about 350 nmol/mol in nitrogen by gravimetric method.

Instrument Calibration:

The background of the FTIR has been made with the nitrogen used to prepare the gravimetric gas mixture of CO, CO_2 and CH_4 at 350 nmol/mol.

Then, an infrared spectrum has been made with the gravimetric gas mixture of CO, CO_2 and CH_4 at 350 nmol/mol and this spectrum has been used after to determine the traces of CO, CO_2 and CH_4 in the transfer cylinder of nitrogen.

Sample handling:

Cylinders were maintained inside a laboratory at a nominal temperature of (21±2) °C for all the period.

Samples were introduced into the analyser via a normal gas regulator and an overflow valve.

Evaluation of measurement uncertainty

The measurement of uncertainty has not been estimated because the CO, CO_2 and CH_4 concentrations are below the detection limits.

2) For Argon

Reference Method:

A gas chromatograph 6890 from Agilent with a HID detector (Helium Ionization Detector) has been used to analyze argon.

Calibration Standards:

LNE has prepared a gas mixture of argon at about 2000 nmol/mol in nitrogen by gravimetric method : it has been prepared in 4 steps.

The argon in pure nitrogen has been determined for each gravimetric gas mixture.

Instrument Calibration:

The gravimetric gas mixture at 2000 nmol/mol has been injected inside the gas chromatograph : the surface of the GC peak is recorded (S_1).

The nitrogen of transfer cylinder is then injected inside the GC and the surface of the GC peak (S_2) is recorded.

The argon concentration of the transfer cylinder (C_2) is equal to :

$$C_2 = \frac{C_1 \times S_2}{S_1}$$

This procedure is carried out on 5 different days.

The argon concentration is the mean of the 5 obtained values.

Sample handling:

Cylinders were maintained inside a laboratory at a nominal temperature of (21±2) °C for all the period.

Samples were introduced into the analyser via a normal gas regulator and an overflow valve.

Evaluation of measurement uncertainty

First step :

The first step consists in the estimation of the standard uncertainty on each concentration of the transfer cylinder.

An example of an uncertainty budget on one of the 5 obtained values is given in the following table.

Uncertainty source	x_I (nmol/mol)	Standard uncertainty $u(x_i)$ (nmol/mol)	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$
Concentration of the argon gravimetric gas mixture (C_1)	2174	0.0165	0.3003	$4.955\ 10^{-3}$
Surface of the GC peak for the argon gravimetric gas mixture (S_1)	384.005	1.21	1.7	2.057
Surface of the GC peak for the transfer cylinder (S_2)	115.326	0.62	5.661	3.51

Concentration of argon in the transfer cylinder (C_2)	652.9 nmol/mol
Expanded uncertainty Concentration of argon in the transfer cylinder (C_2)	8.2 nmol/mol

The standard uncertainties obtained for the 5 values are sum up in the following tables.

Cylinder number: 479235

Date	Concentrations of the unknown gas mixture (C_2) (nmol/mol)	$U(C_2)$ (nmol/mol)
02/06/2010	652.90	8.2
03/06/2010	656.46	12.8
04/06/2010	648.24	9.4
08/06/2010	661.13	11.1
11/06/2010	654.74	11.3

To maximise the uncertainties, it has been decided to take the higher uncertainty :

$$U_1 = 12.8 \text{ nmol/mol}$$

Cylinder number: 2230340

Date	Concentrations of the unknown gas mixture (C_2) (nmol/mol)	$U(C_2)$ (nmol/mol)
17/05/2010	652.50	8.0
19/05/2010	661.73	9.7
26/05/2010	644.11	13.7
27/05/2010	654.68	11.0
01/06/2010	657.88	10.3

To maximise the uncertainties, it has been decided to take the higher uncertainty :

$$U_1 = 13.7 \text{ nmol/mol}$$

Second step :

The second step consists in the calculation of the standard deviation on the mean of the 5 obtained values.

For the cylinder 479235, $\sigma = 4.73 \text{ nmol/mol}$

For the cylinder 2230340, $\sigma = 6.62 \text{ nmol/mol}$

Third step :

The third step consists in the calculation of the expanded uncertainty on the mean concentration of the unknown gas mixture as following.

For the cylinder 479235, $U(C_{argon}) = 2\times\sqrt{(U_1/2)^2+\sigma^2} = 16\,\mu\text{mol/mol}$

For the cylinder 2230340, $U(C_{argon}) = 2\times\sqrt{(U_1/2)^2+\sigma^2} = 20\,\mu\text{mol/mol}$

3) For oxygen

Reference Method:

An electrochemical analyzer DELTA F has been used to analyze oxygen.

Calibration Standards:

LNE has prepared a gas mixture of oxygen at about 600 nmol/mol in nitrogen by gravimetric method : it has been prepared in 4 steps.

The oxygen in pure nitrogen has been determined for each gravimetric gas mixture.

Instrument Calibration:

The analyzer is calibrated at 2 points : at zero with pure nitrogen and at scale point with the gravimetric gas mixture at 600 nmol/mol.

Then the nitrogen of the transfer cylinder is injected inside the analyzer.

The oxygen concentration of the transfer cylinder (C_{O2}) is equal to :

$$C_{O2} = \frac{C_{s\tan dard} \times (L_{sample} - L_O)}{(L_{s\tan dard} - L_O)}$$

With :

$C_{s\tan dard}$ the concentration of the gravimetric gas mixture

L_{sample} the reading for the transfer standard

L_O the reading at zero

$L_{s\tan dard}$ the reading for the gravimetric gas mixture

Sample handling:

Cylinders were maintained inside a laboratory at a nominal temperature of (21±2) °C for all the period.

Samples were introduced into the analyser via a normal gas regulator and an overflow valve.

Evaluation of measurement uncertainty

First step :

The first step consists in the estimation of the standard uncertainty on each concentration of the transfer cylinder.

An example of an uncertainty budget is given in the following table.

Uncertainty source	x_I (nmol/mol)	Standard uncertainty $u(x_i)$ (nmol/mol)	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$
Concentration of the oxygen gravimetric gas mixture ($C_{standard}$)	645.6	3.3000	0.01563	0.05158

Reading for the transfer standard (L_{sample})	137	2.3094	1.009	2.330
Reading at zero (L_0)	127	2.3094	0.993	2.293
Reading for the gravimetric gas mixture ($L_{standard}$)	767	2.3094	0.01576	0.0364

Concentration of oxygen in the transfer cylinder (C_{O2})	10.1 nmol/mol
Expanded uncertainty on the concentration of oxygen in the transfer cylinder (C_{O2})	6.6 nmol/mol

The standard uncertainties obtained for the different values are sum up in the following tables.

Cylinder number: 479235

Date	Concentrations of the unknown gas mixture (C_{O2}) (nmol/mol)	$U(C_{O2})$ (nmol/mol)
26/05/2010	10.1	6.6
27/05/2010	6.0	6.6
01/06/2010	15.8	6.4
02/06/2010	9.0	6.6
03/06/2010	14.8	6.4
08/06/2010	9.3	6.1

To maximise the uncertainties, it has been decided to take the higher uncertainty :

$U_1 = 6.6$ nmol/mol

Cylinder number: 2230340

Date	Concentrations of the unknown gas mixture (C_{O2}) (nmol/mol)	$U(C_{O2})$ (nmol/mol)
05/05/2010	23.1	6.5
06/05/2010	24.1	6.5
07/05/2010	21.0	6.5
03/06/2010	12.8	6.4
08/06/2010	8.4	6.1

To maximise the uncertainties, it has been decided to take the higher uncertainty :

$U_1 = 6.5$ nmol/mol

Second step :

The second step consists in the calculation of the standard deviation on the mean of the obtained values.

For the cylinder 479235, $\sigma = 3.75\ nmol/mol$

For the cylinder 2230340, $\sigma = 6.92\ nmol/mol$

Third step :

The third step consists in the calculation of the expanded uncertainty on the mean concentration of the unknown gas mixture as following.

For the cylinder 479235, $U(C_{O2}) = 2 \times \sqrt{(U_1/2)^2 + \sigma^2} = 10\,\mu\mathrm{mol/mol}$

For the cylinder 2230340, $U(C_{O2}) = 2 \times \sqrt{(U_1/2)^2 + \sigma^2} = 16\,\mu\mathrm{mol/mol}$

Measurement report NPL

Travelling standard received from coordinating laboratory

Cylinder number 479 235
Pressure on arrival = 190 bar;
Pressure after measurements at NPL = 172 bar.

Methods and Standards

Analyte	Method	Instrument	Standard gas mixture
CO	GC-RGD	Trace Analytical Ametek ta5000 Multi-Gas Monitor [1]	**NPL 255R3** CO 26.3 ppb CO_2 27.5 ppb CH_4 30.0 ppb balance N_2
CO_2	GC-FID with methaniser	Peak Performer 1	
CH_4			
O_2	Coulometry	Delta F Platinum Series NanoTraceII Oxygen analyser [2]	**D546215** O_2 9.9 ppb balance N_2
Ar	Not measured		
water vapour	Not measured		

The ta5000 Multi-Gas Monitor is a trace level gas chromatograph capable of detecting ppb concentrations of contaminants in sample gas matrices. The system consists of a microprocessor controlled gas chromatograph utilizing a Reduction Gas Detector (RGD). Species eluting from the RGD column set pass immediately into the heated bed of mercuric oxide (HgO) and the photometric detector. The resulting mercury vapour is quantified by means of an ultraviolet photometer located immediately downstream of the mercuric oxide bed.

The Delta-F sensor operates on a coulometric principle. Oxygen in the sample gas is reduced in an electrochemical reaction at the cathode to hydroxyl ions (OH^-) and the result is a measurable current flow. The electrolyte solution contains potassium hydroxide (KOH), which assists in the migration of hydroxyl ions to the anode where they are oxidized to complete the reaction.

Results

In the case of CO, CO_2 and CH_4 the measurement indicated that the analyte was only present below the detection limit of the instrument. Therefore the uncertainty has been set equal to this minimum determined level.

Analyte	Results [nmol/mol]	Expanded Uncertainty [nmol/mol]
CO	0.3	0.3
CO_2	1	1
CH_4	0.8	0.8
O_2	5	3

The uncertainty has been expended to represent a 95% confidence interval

Measurement report METAS

Laboratory: Federal Office of Metrology METAS
Laboratory code: AC-232
Cylinder number: 2
Cylinder identification: 2230340, embossed Nr

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Component	Date (yymmdd_hhmm)	LD	LQ	Result	Combined uncertainty (k=2)	Number of replicates (n_R)	Method / Comment
x_{CO} (nmol/mol)	20100217_1523	2	7	<2	+6 / -2	60	ND-IR with external zero gas
x_{CO2} (nmol/mol)	20100114_1155	1.1	1.7	1.6	1.2	150	IMR-MS with Kr ionisation
x_{CH4} (nmol/mol)	20091223_1130	0.3	1.4	1.2	0.9	300	IMR-MS with Xe ionisation
x_{O2} (nmol/mol)	20100121_0915	9	12	12	5.9	300	IMR-MS with Kr ionization.
x_{Ar} (nmol/mol)	20100215_1100	420	910	760	+850 / -760	300	IMR-MS with Xe ionisation
x_{H2O} (nmol/mol)	n.m.	n.a.	n.a.	n.a.	n.a.	n.a.	IMR-MS with Xe ionisation. Background of water too high

Table 1

n.m.: not measured, n.a.: not available

1 Limit of Detection (LD)

A definition for the limit of detection (LD) is given by IUPAC [2] with the smallest measure x_L, where x_L is defined as:

$$x_L = x_{bl} + k \cdot s_{bl}$$

where x_{bl} is the mean of the blank measures, s_{bl} is the standard deviation of the blank measures, and k is a numerical factor chosen according to the confidence level desired.

With the exemplifications given in the book by J.D.Hogan [3] it follows that *x* designates the signal input quantity (*I*) for the calculation of the amount of substance fraction with the analysis function (without its uncertainties). It further explains that the k factor of 3 requires a minimal number of 20 replicas of the blank measure. In our calculation s_{bl} is the standard deviation of the mean of 60 to 300 replica of the blank measure, see n_R.

The limit of detection (LD) is therefore calculated as follows:

$$I_L = I_{bl} + k \cdot \frac{s_{bl}}{\sqrt{n_R}}$$

With

I_L	instrument response (signal) for the limit of detection
I_{bl}	instrument response (signal) for the blank sample
k	is set = 3
s_{bl}	the standard deviation of the blank response,
n_R	number of replicates, corresponds to the number of averaged data points
$\frac{s_{bl}}{\sqrt{n_R}}$	standard deviation of the mean blank response

$$LD = I_L \cdot m_1 + b$$

with

m_1	slope of linear analysis function
b	constant of linear analysis function

The IUPAC definition does not account for the uncertainty (error) contributions from the calibration and of the repeatability (variability) of the measurement.

Other IUPAC references for the limit of detection are given in the Recommendations 1989 NOMENCLATURE FOR AUTOMATED AND MECHANISED ANALYSIS [4] and especially for mass spectrometry in the IUPAC Recommendations 1991 *RECOMMENDATIONS FOR NOMENCLATURE AND SYMBOLISM FOR MASS SPECTROSCOPY* by J. F. J. TODD [5].

1.1 Limit of Quantification (LQ)

The limit of quantification is derived from the detection decision L_C described by N.M. Faber [6]. It accounts for all known uncertainty contributions for the blank sample, Ubl. Instead of the assumed zero value for the blank the estimated residual amount of substance in the blank, x_{B_resid}, was taken and *k* was set = 2 instead of 1.65.

$$L_C = L_Q = x_{B\_resid} + U$$ (*k*=2)

$$U = 2 \cdot \sqrt{(u_I)^2 + (u_{l\_fit})^2 + (u_S)^2}$$ (*k*=2)

with

$u_I = m_1 \cdot \frac{\sigma}{\sqrt{n_R}}$ uncertainty contribution of x_B due to standard deviation of the mean blank signal response σ with n_R, the number of replicates, corresponding to the number of averaged data points

u_{l_fit} uncertainty contribution of x_B due to the uncertainties of the linear fit parameters of the analysis function

u_S standard uncertainty contribution of x_B of the nearest standard to the blank

From the analysis function

$$y = m_1 \cdot I + b$$

with

y amount of substance fraction x_B

m_1 slope of linear analysis function

I response (signal) of the measuring instrument, units: counts/s (cps) for the IMR-MS method and indicated values x_{CO} (ppb) for the ND-IR method

b constant of linear analysis function

u_{l_fit} calculated according to the GUM ISO guide [7]

$$u_{l\_fit}(y) = \sqrt{\left(\frac{\delta y}{\delta m_1}\right)^2 \cdot \delta m_1^2 + \left(\frac{\delta y}{\delta b}\right)^2 \cdot \delta b^2}$$

with the partial derivatives of the analysis function

$\left(\frac{\delta y}{\delta m_1}\right)$, $\left(\frac{\delta y}{\delta b}\right)$ and

se_1	standard uncertainty value for the coefficient m_1
se_y	standard uncertainty for the y estimate as obtained with the Excel function LINEST (German: RGP)

the uncertainty of the linear fit function becomes

$$u_{l\_fit} = \sqrt{I^2 \cdot se_1^{\ 2} + se_y^{\ 2}}$$

I is the response signal without offset at x_B=0

1.2 Number of measurements

The methods for trace analysis at METAS are used as a service to measure air pollutants. Of the five analytes of Euramet 937 comparison CO and CH_4 are considered as air pollutants. For the other analytes CO_2, O_2 and Ar, that are not measured in ordinary air pollution control programs, the methods were set-up and validated in view of this comparison. The range for CH_4 of the comparison is considerably lower than in ambient air (average level of 1.8 µmol/mol).
The original commercial ND-IR instrument is for measuring CO in air. The built-in catalytic converter oxidises CO to CO_2 for generating its own zero air. The ND-IR instrument was modified allowing measuring CO in N_2 with an external zero gas. The original validation range for ambient levels of CO was considerably extended towards the low range of this comparison.

Due to the necessary method development and additional validation work the required measurements 1 and 2 for this comparison were considered as final validation steps. The result given is from measurement 3 after the final validation steps and under optimised measurement conditions (i.e. flushing procedures, number of flushing cycles, condition times, etc.).

1.3 Decimal numbers and specifications of impurities

The number of decimals of the results are determined by the uncertainty in accordance with ref 6, section 7.2.6. For uncertainties ≤5 two significant figures are given, for uncertainties > 5 one figure is given. The numbers are rounded to the next higher significant digit.

The numerical values are given with the same number of digits as the uncertainties and are rounded according the rounding rules for decimal numbers.

The values for the limits of detection and quantification are treated the same way as the uncertainty.

Uncertainties of impurity specifications, e.g. x_B < 1 ppb for a dilution gas, are calculated with a rectangular distribution with x_B=0.5 ppb and a U (k=2) of (1/1.73) ppb =0.57 ppb according to ref 6, section 4.4.5 and ref [8].

2 Method description forms

2.1 Reference Method IMR-MS

Chemical mass spectrometry (charge exchange ionization with ion molecule reaction, IMR-MS) with a quadrupole mass separator was used to measure CO_2, CH_4, O_2 and Ar. Specific ionisation was achieved with ions of three selectable gases with their respective energies: Hg+ (10.4 eV), Xe+ (12.13 eV) and Kr+ (14 eV) [9], [10]. The instrument was a modified and extended Airsense 2000 from v+f [11] [12] with increased sensitivity and signal stability enabling to measure trace amounts of substances. The pressure of the inlet gas (first stage) is controlled and the pumping system extended and placed outside of the instrument rack to reduce background signal and minimise vibrations. All main instrument parameters were recorded using computer controlled measurement sequences allowing long sampling times and signal averaging, external calibration and data analysis [13].

For Ar with an ionisation energy of 15.76 eV the original ionisation method of the manufacturer with accelerated Hg^+ was changed to accelerated Xe^+ to increase the sensitivity and to reduce the drift of the background signal. With this new measurement setup it was possible to measure in the range of the comparison, i.e. between 1 µmol/mol and 5 µmol/mol.

For water the background signal of the N_2 ($x_{H2O} \approx 1$ µmol/mol) flushed IMR-MS on mass 20.02 was about 500 cps and decreased not significantly after flushing with N2 BIP Plus ($x_{H2O} \leq 20$ nmol/mol) for 30 min. No significant signal differences were observed in repeated long measurement cycles between N_2 BIP Plus, purified and dried N_2 BIP Plus ($x_{H2O} \leq 1$ nmol/mol) and the N_2 Euramet 937. The sensitivity with the main isotope 18 instead of 20 would be approximately 500 times higher, but the expected background signal is 250 000 cps, a signal that is far beyond the linear limit of $\approx 50\,000$ cps and the damage limit of $\approx 100\,000$ cps of the channeltron detector. It was therefore concluded that water cannot be measured with the IMR-MS method in the expected range under the experimental conditions at the time of the comparison.

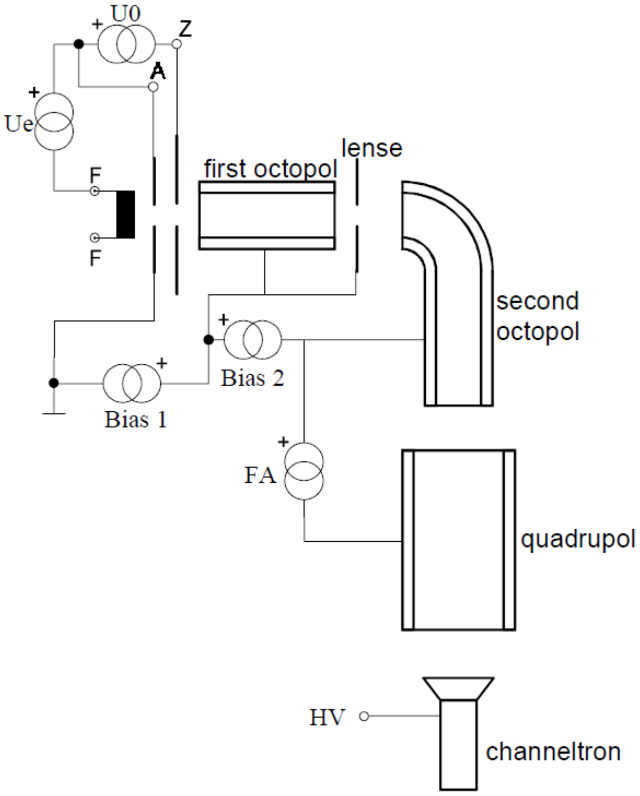


Fig.1 Scheme of IMR-MS Airsense 2000 with ion path, F: filament, A: anode, Z: extracting lens. The sample gas is fed with a capillary tubing into the reaction chamber where the charge exchange for the ionisation takes place. It is located between the second octopole and the quadrupole mass separator.

Main measurement parameters of IMR-MS method

Analyte	CO_2	CH_4	O_2	Ar	H_2O
Ionisation energy (eV)	13.77	12.51	12.07	15.76	12.61
Ionising gas	Kr	Xe	Xe	Xe	Xe
Mass of isotope for analysis	43.99	16.03	31.99	39.96	20.02
Natural abundance (%)[14]	98.426	98.831	99.521	99.600	0.199
Integration time (s)	1	1	1	1	1
Averaging time (s) / mass	150	300	300	300	300
Number of recorded masses	2	1	1	1	1
Mass resolution (a.u., max. 100)	96	96	98	96	96
Gas pressure 1 st stage (mbar)	1000	1000	1000	1000	1000
Gas pressure 2nd stage (mbar)	60	60	60	60	60
Octopole 1 (V p-p)	180	180	180	180	180
Bias Octopole 1 (V)	-4.5	-4.5	-4.5	-4.5	-4.5
Octopole 2 (V p-p)	150.1	150.1	150.1	150.1	150.1
Bias Octopole 2 (V)	0.5	0.5	0.5	0.5	0.5
Ue set (V)	-21	-23	-23	-29.1	-23
Flushing cycles between samples	3	3	3	3	3
Flushing time (min)1)	2	2	2	2	n.a.2)
Conditioning time (min)1)	1	1	1	1	n.a.2)

Table 2

1) between samples during the automated measuring sequence
2) n.a. not applicable, no automated measurement sequence recorded

2.2 Reference Method ND-IR Absorption

A non-dispersive infrared (ND-IR) photometer, the Ambient CO monitor APMA-370 from Horiba was used [15]. It was operated in the following modified and extended configuration:

1) The original mist catcher was left out for the measurement of dry gases.

2) The sample gas path was extended. A second commutating valve was put in the inlet line to reduce pressure changes of the inlet

3) A bypass for the built-in CO catalytic converter was added to operate it alternatively also with an external zero gas.

These modifications allowed to measure gases like N_2 without the necessary oxygen for the built-in catalytic converter.

The measurement sequence, the data analysis and calculations were the same as for the IMR-MS method. The refreshing interval of the data of 5 s corresponded to the sampling interval, resulting in averaging 60 data points in five minutes for each sub-sequence. The lower detectable limit was calculated as for the IMR-MS method.

Calibration Standards

Component	Cylinder Nr.	Amount of substance (mol/mol)	Uncertainty (% relative, k=2), (mol/mol), k=2	Certificate Nr.	Manufacturer
Carbon monoxide	**9212**	**$5.0*10^{-6}$**	**4.8 %**	**5980**	**Carbagas[16]**
Zero Gas: N_2 BIP Plus	**S 661294**	**$0.50*10^{-9}$**	**$0.57*10^{-9}$**	**46.28/03/2006 10387 (Lot)**	**Multigas Air Products**
Carbon dioxide	**5641**	**$5.0*10^{-6}$**	**4.7 %**	**5979**	**Carbagas**
Zero Gas: N_2 BIP Plus	**S 661294**	**$0.50*10^{-9}$**	**$0.57*10^{-9}$**	**46.28/03/2006 10387 (Lot)**	**Multigas Air Products**
Methane	**4453**	**$5.0*10^{-6}$**	**4.8 %**	**5971**	**Carbagas**
Zero Gas: N_2 BIP Plus	**S 661294**	**$0.50*10^{-9}$**	**$0.57*10^{-9}$**	**46.28/03/2006 10387 (Lot)**	**Multigas Air Products**
Oxygen	**5151**	**$5.0*10^{-6}$**	**4.8 %**	**5972**	**Carbagas**
Zero Gas: N_2 BIP Plus	**S 661294**	**$3.6*10^{-9}$**	**$0.57*10^{-9}$**	**46.28/03/2006 10387 (Lot)**	**Multigas Air Products**
Argon	**1479128**	**$307*10^{-6}$**	**2.00 %**	**3923079**	**Westfalen Gas**
Zero Gas: N_2	**27600500 858158**	**$0.050 *10^{-6}$**	**$0.057 *10^{-6}$**	**3923078**	**Westfalen Gas**

Table 3

The standard gas mixtures of CO, CO_2, CH_4 and O_2 were the second best quality of the supplier. They were the same standards that are routinely used for the services of the laboratory to measure zero air generators. Since the amount of substance fractions of the standards are at the lower limit of the certified range as specified by the supplier their uncertainties are relatively high.

2.3 Evaluation of residual amounts of analytes in the dilution gas

The purity of the N_2 BIP Plus was checked with the instrument response signals of each analyte without and with a MonoTorr PS3 purifier from SAES Pure Gas [17]. The nitrogen with the lower signal for the specific analyte, i.e. the cleaner gas, was taken as zero and dilution gas. The specifications of the MonoTorr for the maximum residual amount of analyte fractions, x_B_Matrix, were taken for the calculation of the x_B the diluted standards in either case. No further evidence for the residual amounts of analyte in zero nitrogen can possibly be given.

O_2 with a substantial background signal on mass 31.99 due to residual air in the MS, the slightly lower signal with the MonoTorr PS3 purified N_2 BIP Plus was only seen from the calculated values after the measurement. Therefore unpurified N_2 BIP Plus had been used for diluting the standard. The first analysis function was calculated by arbitrarily setting x_{O2}=0, U=0, for the dilution gas and was used to determine the x_{O2} of the MonoTorr PS3 purified N_2 from its response signal. This result tells how much less oxygen MonoTorr PS3 purified N_2 contains than unpurified N_2, it was x_{O2}=- 3.12 ppb O_2. From the specification given for the MonoTorr PS3 purified N_2 of $x_{O2} < 1$ ppb and with a rectangular probability density function with a=0.5 ppb, the residual O_2 fraction of unpurified N_2 BIP Plus is therefore 3.62 ppb with a=0.5 ppb. This value was then used to calculate the x_{O2} of the diluted standards (see Table 4) for the second analysis function used to determine the oxygen amount of the N_2 Euramet 937 sample from its response signal.

2.4 Standard handling

The 10 l cylinders were stored horizontally and rotated before use for at least 24 h in alternate sense. Prior to mounting the pressure regulating valve the inside of the connector and the sealing surface of the cylinder valve were cleaned with methanol dipped cotton tips. Then the main valve was shortly opened to rinse the connector piece. After connecting the pressure regulating valve and tubings they were flushed and evacuated back to the high pressure valve, initially three times and then once before each use. The connecting lines to the gas selecting system (made of integrated gas components, IGC, from Swagelok) and to the mass flow controller for the gas standards were electro polished 1/8” SST tubings.

2.5 Dilution and zero gas handling

The same procedure for the connection and flushing of the pressure regulator as for the standards were applied. The connecting line consisted of metal bellow hoses and 1/4” SST tubings.
A SST gas mixing nozzle from Bronkhorst was used for the gas dilution.

2.6 Amount of substance fraction x_{Bi} of diluted standards

The method of diluting standard gas mixtures of higher amount of substance with inert gases by using thermal mass flow controllers was used according to the norm ISO 6145-7 [18]. Provided the validity of the ideal gas law the amount of substance fraction x_{Bi} of the mixture i of two gases 1 and 2 is calculated as follows:

$$x_{Bi} = \frac{x_{B1} \cdot q_{V1} + x_{B2} \cdot q_{V2}}{q_{V1} + q_{V2}}$$

with x_{B1} amount of substance fraction of analyte B in gas 1

q_{V1} volume flow of gas 1

x_{B2} amount of substance fraction of analyte B in gas 2

q_{V2} volume flow of gas 2

The volume flows of the standard and dilution gas respectively were generated by two thermal digital mass flow controllers from Bronkhorst. From the averaged indicated volume flows the calibrated flows were calculated from the interpolated values of the certificate (METAS Z-23210474, 2009).

The uncertainties of the diluted standards are calculated with the given formula and GUM Workbench Pro [19] and include the uncertainties of the two thermal digital mass flow controllers.

3 Instrument Calibration

3.1 Number and concentrations of standards

Three dilutions of each analyte were made with x_{Bi} close to and within the indicated target range of the comparison, if possible. x_{B4} is the estimated residual amount of analyte in the zero and dilution gas used. For Ar the lowest amount of analyte was twice the upper target limit, since the enhanced sensitivity with Xe ionisation was developed for the last measurement. The four calibration points correspond to the requirement in the norm DIN EN ISO 6143 [20] of minimal three points for linear calibration functions, since an appropriate zero gas is considered a valid calibration point.

Component	X_{B1}	*U (k=2)*	X_{B2}	*U (k=2)*	X_{B3}	*U (k=2)*	X_{B4}	*U (k=2)*
x_{CO} (nmol/mol)	80.6	3.9	40.9	2.0	20.9	1.1	0.50	0.57
x_{CO2} (nmol/mol)	52.3	2.5	26.7	1.4	13.5	0.9	0.50	0.57
x_{CH4} (nmol/mol)	52.3	2.6	26.7	1.4	13.5	0.9	0.50	0.57
x_{O2} (nmol/mol)	106.4	5.0	80.9	3.8	55.4	2.6	3.6	0.57
x_{Ar} (µmol/mol)	30.0	0.7	19.47	0.40	10.10	0.21	0.050	0.057

Table 4

3.2 Measurement sequence

The measurement procedure consists of measuring the blanks, the standards and the sample in a temporal sequence (mass spectrometry with selected ion monitoring). Fig. 2 shows the example for the ion signal of the main isotope of CH_4 at the relative mass of 16.03. In the first sub-sequence (sample 1) nitrogen with a purity of 99.999 % used for the instrument flushing, then N_2 BIP Plus (sample 2) used for diluting the standard gas mixture and in the third sub-sequence (3) the calibration gas mixture with an amount of substance fraction of 52.3 nmol/mol was measured. Each calibration gas mixture (3, 5, 7) is followed by a sub-sequence with N_2 BIP Plus (4, 6, 8) to allow additional flushing of the gas system. Sub-sequence 9 is the unknown sample, N_2 Euramet 937. Each sub-sequence lasts ten minutes to get a time interval of the last five minutes with stable conditions (i.e. for the thermal mass flow controllers) for signal averaging and statistical analysis. The entire measurement sequence, like switching gases with the integrated gas components (IGC), setting the gas flows and data acquisition from peripheral instruments like flow, pressure and temperature readings are automated with a TestStand/LabView software [21].

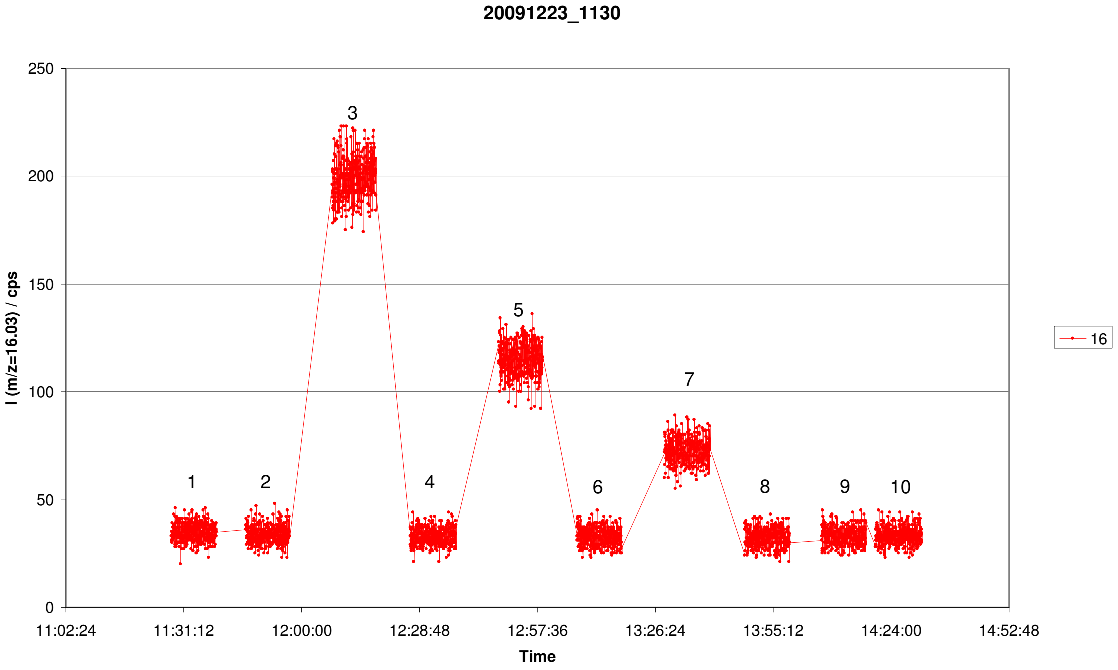


Fig 2 Raw data of the measurement sequence for methane. The ion signal of CH_4^+ at the relative mass of 16.03 is shown for the ten measured sub-sequences (1 to 10) of ten minutes each. Sub-sequences 3, 5, and 7 are the standards, 9 is the N_2 Euramet 937, for further details see text.

3.3 Baseline correction of the raw signals

The inherent background signal of the mass spectrometer was repeatedly recorded in sub-sequences with zero gas, N_2 BIP Plus, either unpurified or purified. Supposed temporal drifts of the signals (even after extended conditioning times of the MS) were corrected with a linear or quadratic fit of the signals from the repeated sub-sequences with zero gas. The calculated data from the fit function were subtracted from the entire raw data and a constant value (offset) was added to avoid negative values.

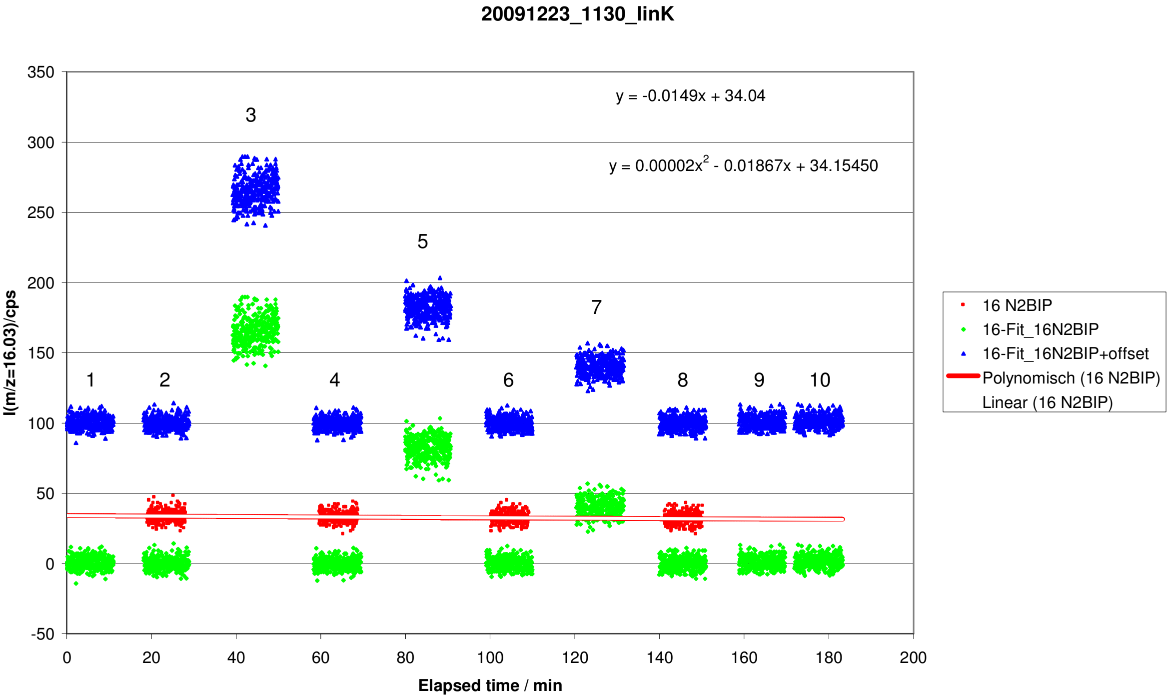
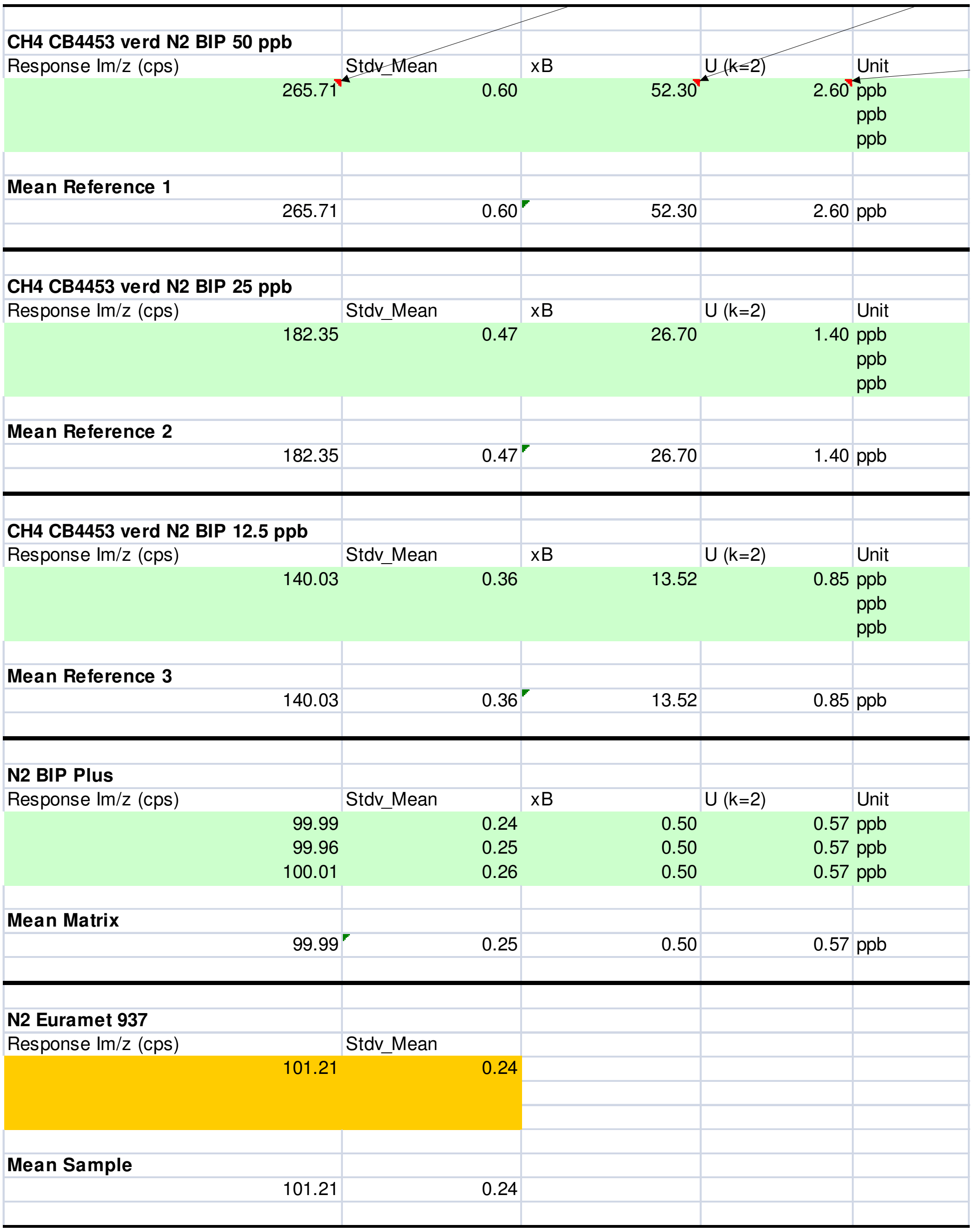


Fig. 3 Baseline correction of raw data of Fig. 2 with a quadratic fit of the sub-sequences with zero gas (red data and line), trend data after subtraction of fitted baseline (green) and upper data points trend data with added offset (blue).

3.4 Calibration procedure (mathematical model/calibration curve)

The data points of the last five minutes of each sub-sequence of the diluted standards are averaged, the standard deviation calculated and divided by the square root of the number of data points to get the standard deviation of the mean. The calculated x_{Bi} of the diluted standards are plotted against the mean signals and fitted with the Excel function LINEST to get the linear fit parameters of the analysis function with their respective standard deviations.



CH4 CB4453 verd N2 BIP 50 ppb				
Response Im/z (cps)	Stdv_Mean	xB	U (k=2)	Unit
265.71	0.60	52.30	2.60	ppb
				ppb
				ppb
Mean Reference 1				
265.71	0.60	52.30	2.60	ppb
CH4 CB4453 verd N2 BIP 25 ppb				
Response Im/z (cps)	Stdv_Mean	xB	U (k=2)	Unit
182.35	0.47	26.70	1.40	ppb
				ppb
				ppb
Mean Reference 2				
182.35	0.47	26.70	1.40	ppb
CH4 CB4453 verd N2 BIP 12.5 ppb				
Response Im/z (cps)	Stdv_Mean	xB	U (k=2)	Unit
140.03	0.36	13.52	0.85	ppb
				ppb
				ppb
Mean Reference 3				
140.03	0.36	13.52	0.85	ppb
N2 BIP Plus				
Response Im/z (cps)	Stdv_Mean	xB	U (k=2)	Unit
99.99	0.24	0.50	0.57	ppb
99.96	0.25	0.50	0.57	ppb
100.01	0.26	0.50	0.57	ppb
Mean Matrix				
99.99	0.25	0.50	0.57	ppb
N2 Euramet 937				
Response Im/z (cps)	Stdv_Mean			
101.21	0.24			
Mean Sample				
101.21	0.24			

Fig 4 Input data for the calculation of the analysis function from the mean response signals, the standard deviation of the mean and the reference values x_{Bi} for three standards and the matrix for the above example with CH_4. On the bottom is the signal of the unknown sample N_2 Euramet 937. Stdv_Mean denotes the standard deviation of the mean.

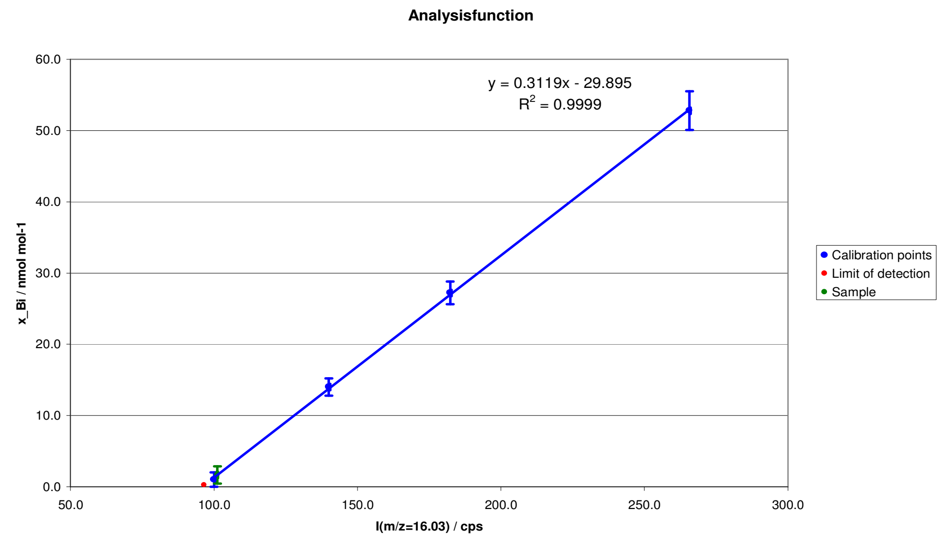
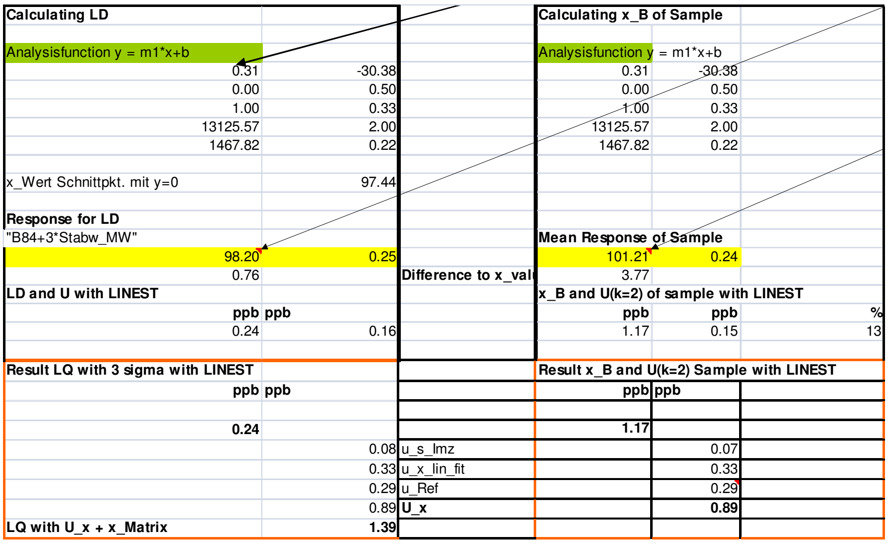


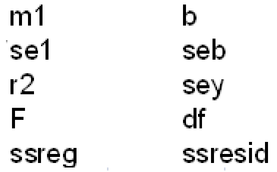
Fig. 5 Analysis function for CH_4 with error bars for the uncertainties of the standards (blue), the value for the sample (green) and the limit of detection (red).



Calculating LD			**Calculating x_B of Sample**		
Analysisfunction y = m1*x+b			Analysisfunction y = m1*x+b		
0.31	-30.38		0.31	-30.38	
0.00	0.50		0.00	0.50	
1.00	0.33		1.00	0.33	
13125.57	2.00		13125.57	2.00	
1467.82	0.22		1467.82	0.22	
x_Wert Schnittpkt. mit y=0	97.44				
Response for LD					
"B84+3*Stabw_MW"			**Mean Response of Sample**		
98.20	0.25		101.21	0.24	
0.76		**Difference to x_val**	3.77		
LD and U with LINEST			**x_B and U(k=2) of sample with LINEST**		
ppb	**ppb**		**ppb**	**ppb**	**%**
0.24	0.16		1.17	0.15	13
Result LQ with 3 sigma with LINEST			**Result x_B and U(k=2) Sample with LINEST**		
ppb	**ppb**		**ppb**	**ppb**	
0.24			**1.17**		
	0.08	u_s_lmz		0.07	
	0.33	u_x_lin_fit		0.33	
	0.29	u_Ref		0.29	
	0.89	**U_x**		**0.89**	
LQ with U_x + x_Matrix	**1.39**				

Fig.6 Calculations of the LD and LQ (left column) and analyte amount of substance fraction (right column). The analysis function is derived from LINEST (matrix under Analysis function in green), the response signals for LD and for the mean sample signal are marked in yellow. In the red frame are the values for LD (0.24 ppb), LQ (1.39 ppb) and x_B of the sample (1.17 ppb, *U*=0.89 ppb). For details of the uncertainty calculation see below.

The analyte amount of substance fraction is calculated with the analysis function and the signal of the sample. The regression parameters of the EXCEL function LINEST (RGP) in the matrix, see arrow in Fig.6, are read as follows:



m1	b
se1	seb
r2	sey
F	df
ssreg	ssresid

m_1	slope of linear analysis function
b	intercept of linear analysis function with y axes (amount of substance fraction)
se_1	standard uncertainty value of the slope
se_b	standard uncertainty value of the intercept
r^2	coefficient of determination
se_y	standard uncertainty of the y estimate
F	F-satistic or F-observed value
df	degree of freedom
ss_{reg}	regression sum of squares
ss_{resid}	residual sum of squares

3.5 Warm-up time and conditioning of the MS

The MS was pumped in a basic stand-by operation at least for two days prior to use and flushed permanently with an N_2 flow of about 150 ml/min (purity of $N_2 \geq 99.999$ %). The conditioning with the filament and analyser turned on and Kr ionisation was for two hours, followed by at least one hour under full measuring conditions. For the Ar measurements the Ar amount of the 99.999 % N_2 was too high ($x_{Ar} \approx$ 300 µmol/mol), N_2 BIP Plus ($x_{Ar} \approx$ 10 µmol/mol) was used instead for the conditioning of the MS prior to starting the measurement sequence. During operation of the MS and for trace measurements a permanent flow of 150 ml/min of a pure gas with sufficient low analyte amount is required.

For analytes with important background signal due to residual amounts, like air components, i.e. O_2, even after 1.5 h the background signal was still decreasing, Fig. 7

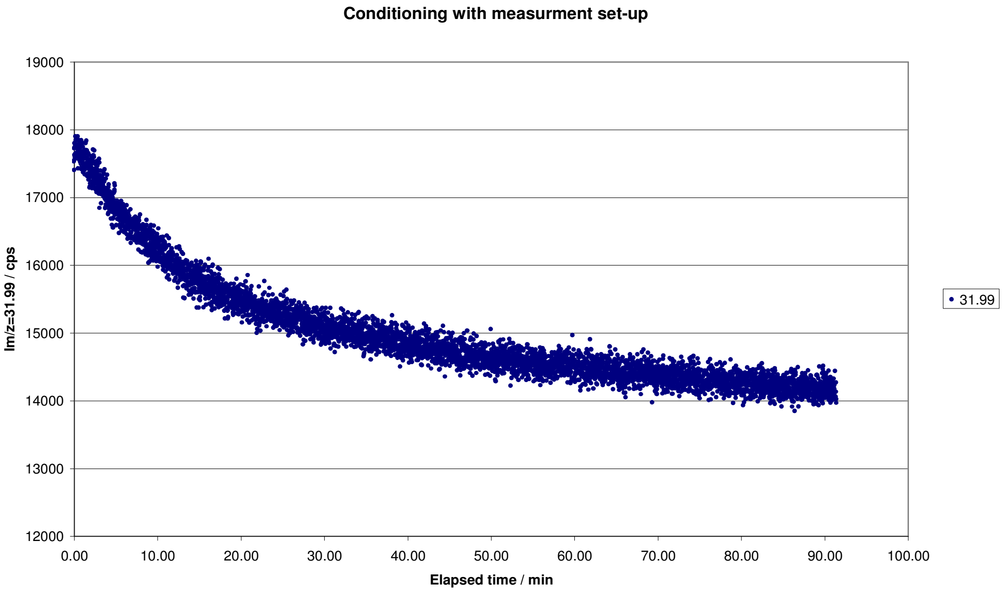


Fig. 7 Stabilisation period for O_2 with mass 31.99 under measuring conditions of the IMR-MS.

3.6 Sample handling, N_2 Euramet 937 cylinder # 2

The cylinder temperature at arrival was about 10 °C, the temperature was stabilised for 24 h at 21 °C. The remaining cylinder pressure before use was 60 bar, at the end 52 bar. The 50 l cylinder was not rotated.
The same procedure for connection and flushing as for the standards was applied.

The pressure regulating valve was a two stage regulator DLRS No.7 T0993 from Air Liquide, the connecting line to the IGC electro polished 1/8” SST tubing. An additional membrane shut-off valve for ultrapure gases was connected at the outlet that was only opened just before the start of the subsequence to prevent possible loss and contamination of the sample gas. From the IGC the sample was directly fed to the inlet of the MS through inertised (SiO_2 coated) 1/8” SST tubings.

Traceability scheme

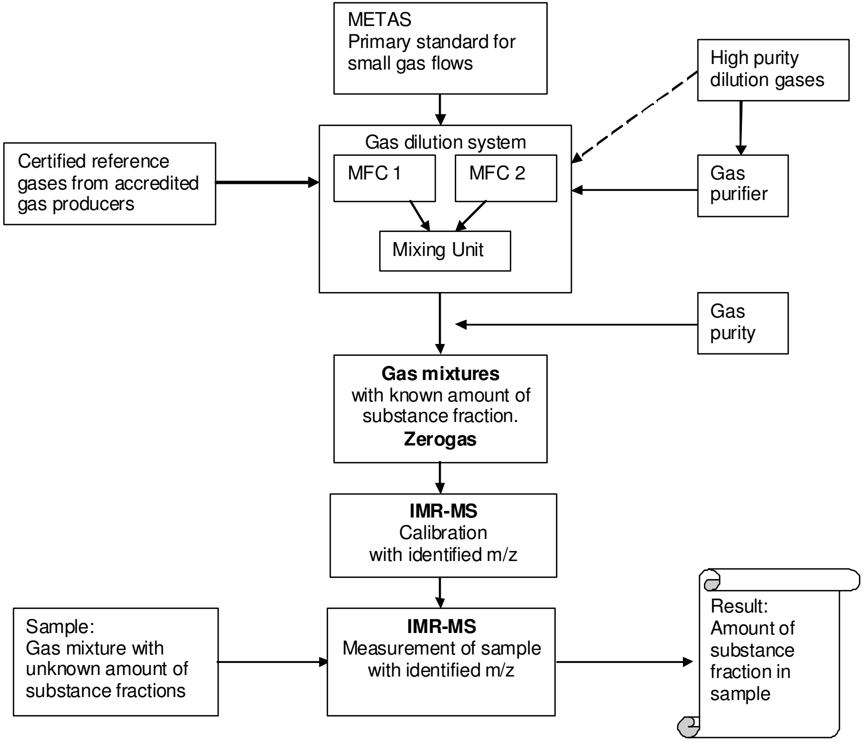


Fig. 8 Traceability scheme for the measurement results with gravimetrically produced gas mixtures in cylinders from accredited gas producers (IMR-MS method)

The central element in the chain is the dilution unit to produce the standards with the low amount of substance fractions of the analytes. The response of the IMR-MS is the ion signal (counting rate) of a specific analyte ion at a given mass to charge ratio (m/z) with z=1.

The identical scheme is used for the ND-IR method for the CO. The response is the infrared absorption at the CO stretching band centred at 2140 cm^{-1} (λ=4.673 µm).

4 Evaluation of measurement uncertainty

The uncertainty contributions for the sample are calculated the same way as for the limit of quantification with the corresponding values of the sample instead of the blank.

	Result x_B and U(k=2) Sample with LINEST	
	ppb	**ppb**
xB	**1.17**	
u_s_lmz		0.07
u_x_lin_fit		0.33
u_Ref		0.29
U_x		**0.89**

Fig. 9 Excerpt of right columns of Fig. 6 with the result and the uncertainty contribution.

The symbols given in the Excel table correspond to the following uncertainty components:

u_s_lmz $u_I = m_1 \cdot \frac{\sigma}{\sqrt{n_R}}$ uncertainty contribution of x_B due to standard deviation of the mean sample signal response σ with n_R, the number of replicates, corresponding to the number of averaged data points

u_x_lin_fit u_{l_fit} uncertainty contribution to x_B due to the uncertainties of the linear fit parameters of the analysis function

u_Ref u_S standard uncertainty of the nearest standard to the sample

For the ND-IR method an additional uncertainty component of $3/\sqrt{3}$ was added to account for the digital resolution of 3 ppb of the instrument.

$$U\_x = U = 2 \cdot \sqrt{(u_I)^2 + (u_{l\_fit})^2 + (u_s)^2}$$

U combined expanded (k=2) uncertainty of the sample

Remark:

For the evaluation of the limit of quantification and calculation of trace amount of substances for uncertainties beyond the calibration interval, the Monte Carlo simulation of the uncertainty would deliver more realistic results [22]. The implementation of the method for the present comparison, however, was beyond the scope.

4.1 Decision for results above or below the limit of quantification

In analogy to Ref. 5 the decision, if a result is above or below the limit of quantification is made according to:

$x_B \geq LQ + U$ (result is above the limit of quantification) and

$x_B \leq LQ + U$ (result is below the limit of quantification)

where *U* is the combined expanded uncertainty *(k=2)* of the sample.

For CH_4, the result for the N_2 Euramet 937 (<1.4 nmol/mol, *U*= 0.9 nmol/mol) is below the limit of quantification (1.4 nmol/mol).

If the limit of detection is used instead with the above criteria, the value of <1.4 nmol/mol is above (0.3 nmol/mol + 0.9 nmol/mol) = 1.2 nmol/mol.

Measurement report BAM

Cylinder number: 2230340

Methods and Standards:

A (customized) UNICAM Pro gas chromatograph equipped with a pulsed discharge ionization detector (PDID) and a system of columns and valves. The gas chromatograph is adapted in a way that the analysis is restricted to specified compounds in specified matrices. For an analysis, a preset intrinsic routine is to be executed. The methods have been implemented and verified by the manufacturer.

Oven temperature 0 to 80 °C (0 °C during the separation of argon and oxygen); carrier gas: helium (Alphagaz 2, Air Liquide, getter gas purifier GC 5 Purifier PS2-GC50-R/N-1/2-V, Saes Pure Gas, for helium); sampling volume: 0.5 ml. Detection oven temperature: 100 °C.

Sequence of measurement: calibration standard (BAM primary standard) – sample – calibration standard (BAM primary standard)

“Method no. 6” was applied during all measurements. Method no. 6 can analyze hydrogen, (argon plus oxygen), carbon monoxide, and methane in a matrix of nitrogen. The peaks are recorded in that sequence (increasing retention times). The balance gas is bypassed to avoid detector overflow.

Carbon dioxide cannot be analyzed by that particular method.

To analyze carbon dioxide, “method no. 3” was applied. Method no. 3 can analyze ethane, methane, carbon dioxide, and carbon monoxide in a matrix of air.

Both methods employ three columns: C1, C2, and C3. C1 (Stripper System A): Silica Gel, length 0.5 m, outside diameter 1/8”, mesh size 80–100. C2 (Heart Cut System A): Molecular Sieve 5A CP, length 1 m, outside diameter 1/8”, mesh size 80–100. C3 (Analysis System A): Molecular Sieve 5A CP, length 2 m, outside diameter 1/8”, mesh size 80–100. Gas flow of the sample gas: 60 mL min^{-1}

Sequence of method no. 6:

Time / min	Description
0.05	Valve CV1 ON. Injection of sample. Sample injection for hydrogen.
0.50	CV 1 OFF.
2.05	Valve CV1 ON. Injection of sample. Sample injection for argon/oxygen and carbon monoxide.
3.00	CV 1 OFF.
12.05	Valve CV1 ON. Injection of sample. Sample injection for methane.
13.00	CV 1 OFF.
0.25	CV 3 ON. Heart-Cut A columns in line with Analysis A columns for hydrogen.
0.85	CV 3 OFF.
2.80	CV 3 ON. Heart-Cut A columns in line

	with Analysis A columns for argon/oxygen.
3.10	CV 3 OFF.
4.8	CV 3 ON. Heart-Cut A columns in line with Analysis A columns for carbon monoxide.
5.8	CV 3 OFF.
13.70	CV 3 ON. Heart-Cut A columns in line with Analysis A columns for methane.
14.20	CV 3 OFF.
–	Switches CV 4 ON, selecting sample to the sample injection valves CV 1, CV 2.
–	Switches CV 4 OFF, selecting sample to the sample injection valves CV 1, CV 2.

Sequence of method no. 3:

Time / min	Description
0.05	Valve CV1 ON. Injection of sample for argon/oxygen, nitrogen, methane, and carbon monoxide.
1.00	CV 1 OFF.
0.01	CV 3 ON. Heart-Cut A columns in line with Analysis A columns for argon/oxygen, nitrogen, methane, and carbon monoxide.
10.00	CV 3 OFF.
–	Switches CV 4 ON, selecting sample to the sample injection valves CV 1, CV 2.
–	Switches CV 4 OFF, selecting sample to the sample injection valves CV 1, CV 2.

“Method no. 6” was modified for the separation of argon and oxygen. In those experiments, the oven temperature was stepwise reduced by intervals of 10 ℃ to finally 0 ℃. At 0 ℃, two distinct peaks were observed. Argon was eluted first.

Calibration standards:

All calibration standards were prepared gravimetrically according to ISO 6142. Prior to the preparation, all pure compounds were analyzed for impurities.

Standard BAM 5043-040524 for the determination of CO and CH_4. The matrix gas was helium. (There was no risk of detector overflow during the analysis applying method no. 6.)

Component	mole fraction [%]	relative uncertainty [%]
hydrogen	0.000028	0.129
argon	0.000027	0.109
oxygen	0.000028	0.117
nitrogen	0.000027	0.109
carbon dioxide	0.000027	0.109
methane	0.000027	0.110
carbon monoxide	0.000027	0.109
helium	99.999810	0.008

Standard BAM 5088-040429 for the determination of Ar and O_2. The matrix gas was helium. (There was no risk of detector overflow during the analysis applying method no. 6.)

Component	mole fraction [%]	relative uncertainty [%]
hydrogen	0.000268	0.116
argon	0.000262	0.094
oxygen	0.000275	0.103
nitrogen	0.000261	0.094
carbon dioxide	0.000261	0.094
methane	0.000261	0.095
carbon monoxide	0.000260	0.094
helium	99.998153	0.008

Sample handling:
The cylinders were maintained at room temperature during the entire period. The samples were connected to the GC via tubes made of stainless steel. All fittings were VCR® fittings. No pressure valves were coupled between sample cylinder and gas inlet.
Prior to the analysis, tubes and valves were evacuated to remove all traces of air. The measurements of the calibration samples (using the same GC method as for the sample) showed no additional impurities and both retention time and area of the signals were consistent with measurements recorded before. So, any leakage that could contribute to a higher result for oxygen (contamination by laboratory air) is considered to be unlikely.
All samples were processed in the same way.
A special zero gas was not administered as the balance of the calibration standards was helium.

Results

Component	mole fraction / µmol/mol	U / µmol/mol (with k = 2)
argon	0.67	0.05
oxygen	1.53	0.12
carbon monoxide	0.13	0.03
methane	0.127	0.004
carbon dioxide	no analyzable signal	

The measurements were done on 2009-09-10 and 2009-09-11. The measurements for the separation of argon and oxygen were done on 2009-09-28. The cylinder had a pressure of 62 bar after finishing the investigations.

Data reduction: Single point calibration using the abovementioned calibration standards. Number of replicates for each sample (i.e., calibration samples, sample to be analyzed): 5

Uncertainty budget:
Three terms go with the calculation of the uncertainty U: u(meas) = standard deviation from the measurement of the sample; u(cal) = standard deviation from the measurement of the calibration gases; u(intrinsic) = an intrinsic uncertainty of the calibration gas of (considers stability as well)
$U = [u(\mathrm{meas})^2 + u(\mathrm{cal})^2 + u(\mathrm{intrinsic})^2]^{0.5}$

The limit of detection (LoD) is estimated to be 0.1 ppm for all compounds which is in accordance with the manufacturer's recommendation. All methods operate intrinsic and preset peak evaluation routines which have been implemented by the manufacturer, particularly regarding peak threshold and baseline drawing, respectively.
However, several test runs with respective calibration gases of concentrations < 1 ppm sometimes did not give satisfactory and reproducible results. This was attributed to the intrinsic peak analysis routine.

For example, if the peak areas were too small (as observed during test runs), it was observed that they were either analyzed with a biased baseline or not analyzed at all.

In this study, no specific experiments were done to establish a limit of quantification (LoQ).

Measurement report VSL

Laboratory : Van Swinden Laboratory
Laboratory code : VSL
Cylinder number : 479235

Carbon monoxide

Measurement	**Result (nmol/mol)**	**Uncertainty (nmol/mol)**
FT-IR measurement	< 4	3
CRDS measurement	<1	1

Carbon dioxide

Measurement	**Result (nmol/mol)**	**Uncertainty (nmol/mol)**
FT-IR measurement	4,3	0,7

Methane

Measurement	**Result (nmol/mol)**	**Uncertainty (nmol/mol)**
CRDS measurement	0.5	0.5

Oxygen

Measurement	**Result (nmol/mol)**	**Uncertainty (nmol/mol)**
GC-PDHID	< 50	30

Argon

Measurement	**Result (nmol/mol)**	**Uncertainty (nmol/mol)**
GC-PDHID	731	73

Water

Measurement	**Result (nmol/mol)**	**Uncertainty (nmol/mol)**
CRDS	16	4

Laboratory : Van Swinden Laboratory
Laboratory code : VSL
Cylinder number : 2230340

Carbon monoxide

Measurement	**Result (nmol/mol)**	**Uncertainty (nmol/mol)**
FT-IR measurement	< 4	3
CRDS measurement	< 1	1

Carbon dioxide

Measurement	**Result (nmol/mol)**	**Uncertainty (nmol/mol)**
FT-IR measurement	2.0	0,3

Methane

Measurement	**Result (nmol/mol)**	**Uncertainty (nmol/mol)**
CRDS measurement	0.5	0.5

Oxygen

Measurement	**Result (nmol/mol)**	**Uncertainty (nmol/mol)**
GC-PDHID	< 50	30

Argon

Measurement	**Result (nmol/mol)**	**Uncertainty (nmol/mol)**
GC-PDHID	730	73

Water

Measurement	**Result (nmol/mol)**	**Uncertainty (nmol/mol)**
CRDS	4	1

Method description forms

1) For CO and CO_2

Reference Method:

A Bomem DA8 Fourier Transformed Infra Red (FTIR) has been used to analyze CO and CO_2. A Spectral resolution of 0.5 cm^{-1} is used to record the spectra
The spectrometer is operated under vacuum conditions to eliminate traces of water and carbon dioxide.
The optical length of the gas cuvet is 96 m.

Calibration Standards:

Using gravimetric techniques a series of dilutions was made for both CO in N_2 and CO_2 in N_2. At first a series of pure nitrogen cylinders were analysed to select the cylinder with lowest spectra for CO and CO_2. This nitrogen was used to make the dilutions. The actual amount of CO and CO_2 was then calculated using standard addition methods.

Instrument Calibration:

The background was taken with an evacuated FTIR. Two 10 nmol/mol CO in N_2 PSMs were used to determine the detection limit for CO. The detection limit was found to be 4 nmol/mol. For CO_2 a mixture of 9 nmol/mol was used to calibrate the signal. The detection limit for CO_2 is 0.5 nmol/mol.

Sample handling:

Cylinders were stored inside a laboratory at for a sufficient period to assurace temperature stability. During analyis pressure and temperature were recorded in the gas cuvet. Proper corrections for drift of temperature and pressure were made.

Samples were introduced into the analyser via a normal pressure regulator and an overflow valve.

Evaluation of measurement uncertainty

For CO the uncertainty was set to 75% of the limit of detection. For CO_2 also the dominating factor in the uncertainty is the limit of detection.

The CO impurity was also determined by CRDS. For the measurement of CO a continuous wave QC-laser (tuning range 2186-2195 cm^{-1}) in combination with a home-built cavity ringdown spectrometer is used with an effective absorption path length of 7 kilometres (Figure 1). The CO absorption peak centred at 2190 cm^{-1} has been selected as it shows only minor spectral interferences by compounds which might be present (H_2O and N_2O). Measurements are performed at a pressure of 1000 mbar.

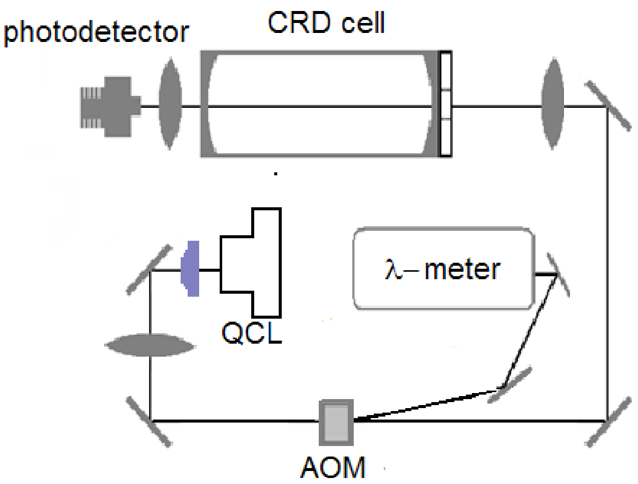


Figure 1, Experimental set-up for QCL-based CRDS measurements of carbon monoxide.

The result of the measurements of two gravimetric standards of VSL and of the two nitrogen cylinders is shown in Figure 2. The peaks are fitted with a Lorentzian profile and the area is taken as a measure for the amount of substance.

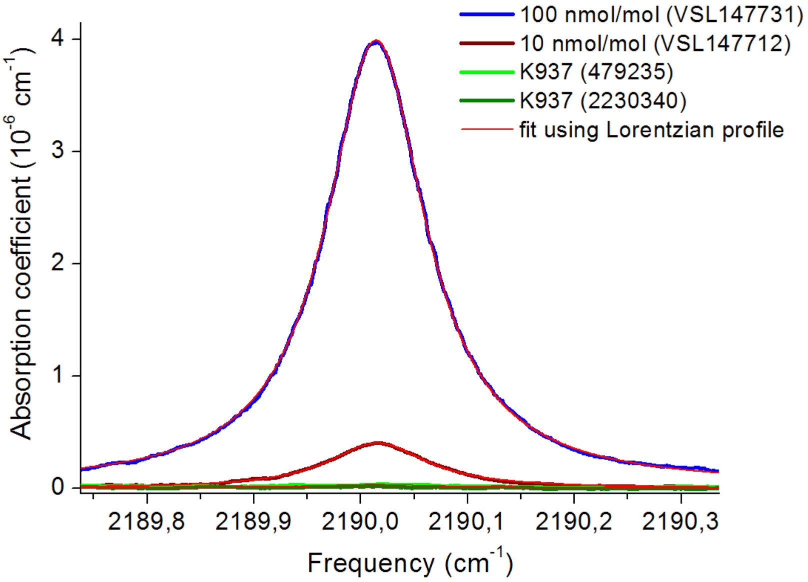


Figure 2, Measured absorption coefficients for the two standards and the two cylinders from the K937. Red lines are fits using a Lorentzian profile.

2) For methane

The instrument that has been used for the experiments is a home-built cavity ringdown spectrometer based on an mid-infrared optical parametric oscillator (2.7-3.5 µm) as light source. The wavelength is tuned over the absorption feature in 1000 steps and the average of several of such scans is taken.

<u>First experiment (before shipment):</u>

The absorption feature centered at 3086 cm^{-1} was chosen as there are only minor spectral interferences by other compounds which might be present (mainly water, partly due to leakages in the measurement cell). Next to the two nitrogen cylinders a 10 nmol/mol and a 20 nmol/mol CH_4 in nitrogen mixture (PSM) were measured.

Second experiment (after shipment)

The CRD cell has been replaced by a slightly longer cell which is better leak tight. An intracavity diaphragm is used to enhance the stability of the acquired decay times. These improvements in combination with using the methane absorption feature centered at 3057.7 cm^{-1} (about 25% stronger than the feature used in the first experiment) have resulted in a better detection limit for methane than in the first experiment. Next to the two nitrogen cylinders a 10 nmol/mol CH_4 in nitrogen standard (PSM) was measured.

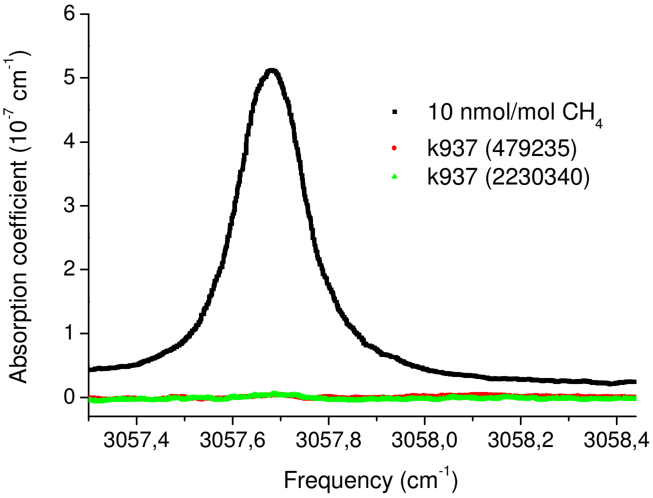


Figure 3, *Measurement result for the second experiment in which the two nitrogen cylinders and a 10.0 nmol/mol CH_4 mixture were measured.*

Additional info: a simulation using Hitran of 10 nmol/mol methane shows a good correspondence with the measurement of the standard.

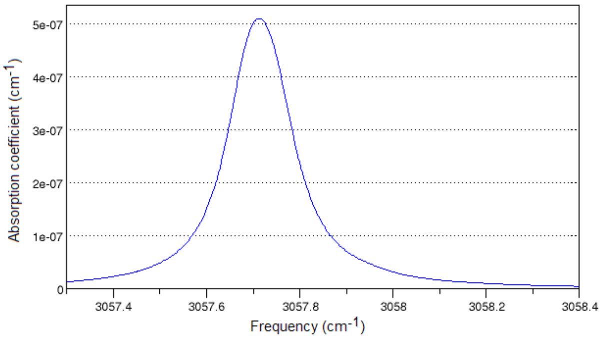


Figure 4, *Simulation using Hitran 2004 of 10 nmol/mol methane.*

Evaluation of measurement uncertainty

The limit of detection was calculated to be 1 nmol/mol for the first series of measurements and after improvement this detection limit was lowered to 0.2 nmol/mol. The reported values indicate that the amounts of methane found were close to this limit of detection. The uncertainty on this limit of detection was set to 100%.

3) For Argon

Reference Method:

An Agilent 6890 gas chromatograph with a VICI Pulsed discharge HID detector (Helium Ionization ***Detector***) has been used to analyze argon.

Calibration Standards:

As no PSM with argon in nitrogen were available, oxygen in nitrogen standards are used to calculate the argon content in the cylinders. Argon and oxygen are just separated from each other and from previous experience we know that the peak are for 5 µmol/mol O_2 is similar to the peak area for 5 µmol/mol Ar.

Instrument Calibration:

A calibration curve was made from 5 PSM of 1, 2, 3, 4 and 5 µmol/mol O_2 in N_2 standards. The argon amount was calculated from an extrapolation down to 0,7 µmol/mol.

Evaluation of measurement uncertainty

The dominant source of uncertainly in the argon determination comes from the uncertainty in the oxygen in nitrogen PSM. As the detection limit for O_2 in N_2 is around 50 nmol/mol, the uncertainty in gravimetry for the 5 PSM of oxygen is nitrogen ranges from 6% relative on the 1 µmol/mol mixture to 1.2 % relative.
In addition due to the extrapolation, the regression function also adds to the reported uncertainty.

4) For oxygen

Reference Method:
An Agilent 6890 gas chromatograph with a VICI Pulsed discharge HID detector (Helium Ionization ***Detector***) has been used to analyze oxygen.

Calibration Standards:

A 1 µmol/mol O_2 in N_2 PSM was used to determine the limit of detection.

Evaluation of measurement uncertainty

The limit of detection for the GC-PDHID is, based on the noise level, around 5 nmol/mol. However the Limit of Quantification is found to be higher due to the fact that a small oxygen peak always appears in the chromatogram most likely due to problems with the instrument integrity. Based on the rather repetitive height of this peak, the LoQ is set to 50 ppb for oxygen.

5) For moisture

Reference Method:
A commercially available CRDS has been used to analyze moisture. The laser is tuned at 1392 nm and the measurement range is 0,5 – 3000 nmol/mol.

Calibration Standards:

The CRDS for moisture is traceable to the primary humidity standard of VSL Temperature & Humidity Laboratory.

Instrument Calibration:

Gas mixtures that are calibrated against the primary humidity standard are used to check the correct working of the analyser. The read-out of the CRDS was also directly compared to the primary humidity generator and no significant differences in the assigned moisture fractions were found.

Sample handling:

Cylinders were stored inside a laboratory at for a sufficient period to assurace temperature stability. Cylinders were connected via electropolished tubing. High vacuum was used to remove moisture in the tubing.

Evaluation of measurement uncertainty

The limit of detection for the CRDS is around 1 nmol/mol. The dominant contribution to the uncertainty comes from the calibration of the analyser and is rather large at LoQ levels.