Final report of

Key Comparison CCQM-K1

CO in N_2 :	CCQM-K1a
CO_2 in N_2 :	CCQM-K1b
NO in N_2 :	CCQM-K1c
SO_2 in N_2 :	CCQM-K1d
Natural gas I :	CCQM-K1e
Natural gas II :	CCQM-K1f
Natural gas III :	CCQM-K1g

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1 Summary

This report describes the results of the first key comparison on Primary Standard gas Mixtures (PSM) under the auspices of The Comité Consultatif pour la Quantité de Matière (CCQM). This key comparison is also known as Study II. The Consultative Committee adopted the task, to design a programme for co-operative work among leading national (chemical) metrology laboratories, with the objective to test the hypothesis that co-ordinated activity on the analysis of a few key reference materials, using a selected set of analytical reference methods of wide application, will provide such laboratories with a base from which international comparability to a wider range of methods and reference materials can be extended. At the start of the comparison in 1993 the target level for agreement between results was set at ≤ 1%. Progress was reported in separate reports to the CCQM and its working group on Gas analysis.

This report follows the guidelines for key comparisons carried out by the Consultative Committees of the CIPM; these guidelines were drafted in May 1998.
This final report was approved by the CCQM during the meeting in February 1999 and will be submitted to the JCRB (Joint Committee of the Regional Metrology Organizations and the BIMP) after approval of CCQMs working group on key comparisons.

The final report has been published as “The first key comparison of primary standard gas mixtures” in Metrologia, 2000, **37**, 35-49.

After approval by the CCQM and publication in Metrologia, a transcription error was found for the values of the gravimetric fraction for BNM-LNE in CCQM-K1g. The tables and graphs in this report have been corrected for this error.

2 Introduction

For almost two decades, a number of national metrology institutes have developed and maintained Primary Standard gas Mixtures (PSM), which realize primary ratio’s of amount of substance for specific analytes. In analogy with primary measurement standards, in gas metrology these PSMs are used to create a measurement hierarchy. Small-scale comparison studies on PSMs between institutes are generally performed on a bilateral basis. This is the first time a key comparison on PSMs is organized on a world-wide scale under the auspices of CIPM, with the objective to provide a sound base from which international comparability can be extended.

It was decided that the initial choice of PSMs to be analysed should present a relatively straightforward analytical challenge and in advance the pre-set level of agreement was set to 1% relative. With the exception of three, the composition of the selected PSMs is relatively simple, containing one minor component in nitrogen, hence restricting the amount of possible uncertainty sources. More complex matrices should be assessed in later work. The selected PSMs for this comparison were individually prepared gravimetrically and thoroughly studied for their chemical composition and stability.

The 1% target had a direct impact on the choice of the analytical reference methods and it was decided that the preferred analytical methods would be:

- High accuracy mass spectroscopy,
- Isotope dilution mass spectroscopy,
- Gas chromatography,

- Chemiluminescence and Fluorescence,
- Non dispersive infrared.

In principle, laboratories not equipped or experienced in one of these techniques were allowed to participate by using other methods of analysis; their results are not included in this final report.

3 Participants

The invitation for participation in the comparison was sent in April 1993 to the potential participants. In the following table, the codes and acronyms for each participant are given.

Institute	Country	ID	code
National Physical Laboratory	England	NPL	51
National Institute for Standards and Technology	USA	NIST	52
Nederlands Meetinstituut	The Netherlands	NMi	53
Bundesanstalt für Materialforschung und -prüfung	Germany	BAM	54
Laboratoire National d'Essais	France	LNE	55
Korea Research Institute of Standards	Rep. of Korea	KRISS	56
National Research Laboratory of Metrology	Japan	NRLM	57
National Research Center for Certified Reference Materials	P.R. China	NRCCRM	58
D.I. Mendeleyev Institute for Metrology	Russia	VNIIM	59
National Office of Measures	Hungary	OMH	61

Table 3.1 - Participants key comparison

A small survey among participants concerning the main interest for participating, showed that the main interest is establishing comparability of existing PSMs and the testing of preparation and measurement capabilities.

4 Design of the comparison

For this first key comparison on PSMs, five major groups of gas mixtures and their nominal molar fractions were selected.

Group A: CO in Nitrogen $6\cdot10^{-2}$ mol/mol; $1000\cdot10^{-6}$ mol/mol; $100\cdot10^{-6}$ mol/mol.

Group B: CO_2 in Nitrogen $15\cdot10^{-2}$ mol/mol; $1000\cdot10^{-6}$ mol/mol; $100\cdot10^{-6}$ mol/mol.

Group C: NO in Nitrogen $1000 \cdot 10^{-6}$ mol/mol; $100 \cdot 10^{-6}$ mol/mol.

Group D: SO_2 in Nitrogen $1000 \cdot 10^{-6}$ mol/mol; $100 \cdot 10^{-6}$ mol/mol.

Group E1: natural gas type I

- Nitrogen	$4,0 \cdot 10^{-2}$	mol/mol
- Carbon dioxide	$1,0 \cdot 10^{-2}$	mol/mol
- Ethane	$3,0 \cdot 10^{-2}$	mol/mol
- Propane	$1,0 \cdot 10^{-2}$	mol/mol
- Butane	$0,2 \cdot 10^{-2}$	mol/mol
- Methane	$90,8 \cdot 10^{-2}$	mol/mol

Group E2: natural gas type II

- Nitrogen	$7,0 \cdot 10^{-2}$	mol/mol
- Carbon dioxide	$3,0 \cdot 10^{-2}$	mol/mol
- Ethane	$9,4 \cdot 10^{-2}$	mol/mol
- Propane	$3,4 \cdot 10^{-2}$	mol/mol
- Butane	$1,0 \cdot 10^{-2}$	mol/mol
- Methane	$76,2 \cdot 10^{-2}$	mol/mol

Group E3:natural gas type III

- Nitrogen	$14,4 \cdot 10^{-2}$	mol/mol
- Carbon dioxide	$0,5 \cdot 10^{-2}$	mol/mol
- Ethane	$3,0 \cdot 10^{-2}$	mol/mol
- Propane	$0,5 \cdot 10^{-2}$	mol/mol
- Butane	$0,1 \cdot 10^{-2}$	mol/mol
- Methane	$81,5 \cdot 10^{-2}$	mol/mol

NMi, being the pilot laboratory for this key comparison, prepared the gas mixtures and distributed the cylinders to the participating laboratories. In order to limit the time span of the comparison, multiple cylinders, containing gas mixtures of nominally the same composition were made available. All the mixtures were individually prepared and their compositions were verified before and after the comparison by combining these measurements with the maintenance scheme of the Dutch Primary Standard Gas Mixtures. No inconsistencies in the compositions were detected. In the group E mixtures, for economic reasons, a number of cylinders were transfilled from a parent cylinder.

Each group of gas mixtures was subsequently issued to participating laboratories, including the future measurement report (Enclosure 1) and protocol details (Enclosure 2). The pilot laboratory indicated nominal concentrations.

After analyses by participants, the cylinders had to be returned to NMi with sufficient pressure for re-analysis. Transport of cylinders to and from participating laboratories was organized on an agreed-shared cost basis. Some transport difficulties occurred. After receipt, the gravimetric composition was reported to the participant.

5 Measurement methods and calibration procedures

Each participant identified their measurement method for analysing the gas mixtures.

	group A CO	group B CO_2	group C NO	group D SO_2	group E multi component
NPL	NDIR	NDIR, GC-FID	Chemiluminescence	NDIR	-
NIST	GC-TCD/FID, NDIR	GC-TCD/FID	NDIR, Chemiluminescence	Fluorescence	GC -TCD/FID
NMi	NDIR	NDIR/ GC-TCD	Chemiluminescence	NDIR	GC-TCD
BAM	GC	GC-TCD/FID	-	-	GC
LNE	NDIR	NDIR	NDIR	NDIR	GC
KRISS	GC-TCD/FID	GC-TCD/FID	Chemiluminescence	NDIR, GC -DID	GC-USD/FID
NRLM	NDIR	NDIR	Chemiluminescence	NDIR	GC-TCD
NRCCRM	GC, NDIR	GC, NDIR	Chemiluminescence	NDIR, GC	GC
VNIIM	NDIR	NDIR	Chemiluminescence	NDIR	GC-TCD/FID
OMH	GC, NDIR	GC-TCD	Chemiluminescence	NDIR	GC-TCD/FID

Table 5.1 – Measurements methods

Participants identified their calibration procedure:

	group A CO	group B CO_2	group C NO	group D SO_2	group E multi component
NPL	Bracketing with PSM	bracketing with PSM	bracketing with PSM	bracketing with PSM	-
NIST	curve with PSM	curve with PSM	curve with PSM	curve with PSM	bracketing with 3 PSM
NMi	curve with PSM	curve with PSM	curve with PSM	curve with PSM	curve with PSM
BAM	1-point & independent validation	1-point & independent validation	-	-	bracketing with 2 PSM
LNE	bracketing with 3 PSM	bracketing with 3 PSM	bracketing with 3 PSM	bracketing with 3 PSM	bracketing with 3 PSM
KRISS	curve with PSM	curve with PSM	curve with PSM	curve with PSM	1 point with 1 PSM
NRLM	curve with PSM	curve with PSM	curve with PSM	curve with PSM	curve with PSM
NRCCRM	1 point with 2 PSM	1 point with 3 PSM	1 point with 2 PSM	1 point with 2 PSM	1 point with 3 PSM
VNIIM	curve with PSM	curve with PSM	curve with PSM	bracketing with 2 PSM	bracketing with 3 PSM
OHM	1-point with 1 PSM	1-point with 1 PSM	1-point with 1 PSM	curve with PSM	bracketing with PSM

Table 5.2 - Calibration procedure

Generally, the applied calibration procedure seems to depend on the availability of existing PSMs. Some institutes prepared new mixtures with compositions close to nominal compositions and where applicable, the newly prepared mixtures were checked against “older” suites. Where larger numbers of PSM are available, curve fitting over a wider concentration range is applied. Alternatively close bracketing or single -point calibrations are applied.

6 Method for evaluating degree of equivalence

In the guidelines and technical protocol of CIPM key comparison (May 1998) is stated that the degree of equivalence of measurement standards is taken to mean the degree to which these standards are consistent with reference values determined from the key comparison and hence are consistent with one another. The reference value is referred to as the *key comparison reference value* and, in most cases, it can be considered to be a close, but not necessarily the best, approximation to the SI value. The degree of equivalence of each national measurement standard is expressed quantitatively in terms of its deviation and the uncertainty of this deviation (with coverage factor k=2). The degree of equivalence between pairs of national measurement standards is expressed in terms of the difference of their deviations from the reference value and the uncertainty of this difference.

Usually all participants make analyses on the same artefact and the key comparison reference value is calculated from the mean of the individual results.
In the current comparison on gas mixtures, measurements were performed on individually prepared gas mixtures with different concentrations. Since the pilot laboratory prepared all the mixtures using the same methods and materials, the individual gravimetric reference values, although different, may be used for determining the consistency between the measurement standards of the participants.

Up till now, no detailed method has been provided, or is required by BIPM, to express the degree of equivalence E_A for the measurement standard of laboratory *A* with the key comparison reference value, just the functional relationship is given:

$E_A = f\,[(v_A - v_R),\ u\,(v_A),\ u\,(v_R)]$

The degree of equivalence $E_{(A,\,B)}$ between two national measurement standards is also given in terms of a functional relationship:

$E_{(A,\,B)} = f\,[d_A,\ d_B,\ u\,(d_A),\ u\,(d_B)]$,
where $d_A = v_A - v_R$, $d_B = V_B - v_R$, $u\,(d_A)$ is the standard uncertainty of d_A and depends on $u\,(v_A)$ and $u\,(v_R)$ and $u\,(d_B)$ is the standard uncertainty of d_B and depends on $u\,(v_B)$ and $u\,(v_R)$. Covariances should be taken into account.

For convenience, a method is given in this report that may be used to assess the quality of an individual measurement. This method was introduced by the European co-operation for Accreditation of Laboratories (Ref. EAL-P7).

$$E_n = \frac{x_{lab} - x_{grav}}{\sqrt{U_{lab}^2 + U_{grav}^2}} \qquad [1]$$

Where x_{lab} is the analysed concentration by the participant with the expanded uncertainty U_{lab}. U_{grav} is the expanded uncertainty of the gravimetric fraction x_{grav} .

Absolute values of E_n less than unity should be obtained for measurements to be equivalent to the key comparison reference values. In this key comparison the contribution of U_{grav} is relatively small.

A convenient method for assessing the equivalence between pairs of measurement standards is the calculation of the deviation Δx_n, normalised with respect to the stated uncertainties:

$$\Delta x_n = \frac{(x_{lab1} - x_{lab2}) - (x_{grav1} - x_{grav2})}{\sqrt{U_c^2}} \qquad [2]$$

$$U_c^2 = U^2(x_{lab1}) + U^2(x_{lab2}) + U^2(x_{grav1}) + U^2(x_{grav2}) - 2U(x_{grav1}, x_{grav2})$$

In the preparation procedure, the same parent gases were used to prepare the individual mixtures. This makes that the x_{grav} 's cannot be treated as being non-correlated, because they result (in part) from the same purity data. The uncertainties on x_{grav} 's are at least one order of magnitude smaller than the uncertainties in x_{lab} 's and the covariance term can be neglected.

Data on equivalence calculated by the methods above was presented in the draft final report, but it was decided to incorporate in this final report just the basic data needed for the functional relationships as input for the BIPM database for key comparisons.

In general, the reported uncertainties by participants were not consistent, as some laboratories prefer reporting of combined uncertainty over expanded uncertainty (k= 2 or 3). NPL, NIST, NMi, BAM, VNIIM, NRLM and KRISS reported uncertainties with k = 2; NRCCRM k=3; OMH and LNE k = 1; LNE for the natural gases k =2.
Uncertainty data in the tables and graphics are harmonised as expanded uncertainties with k=2.

7 Results

The data is presented in table 7.4 - 7.8e and include participants, lab codes, cylinder numbers, gravimetric and analysed fractions and the expanded uncertainties.
In the last column, the relative deviation from the gravimetric fraction is given as:

$$\Delta\,(\%) = \frac{reported\ value\ - assigned\ value}{assigned\ value} \times\ 100$$

In Annex I - 1 to 16, these deviations including the expanded uncertainties are presented graphically.

	Cylinder number	Gravimetric Fraction (mol/mol)	*U* (%) Gravimetry	Analysed Fraction (mol/mol)	*U* (%) Analysis	Δ (%)
NPL (51)	8495 A 8505 A 8520 A	$5{,}9963 \cdot 10^{-2}$ $9{,}9813 \cdot 10^{-4}$ $1{,}0106 \cdot 10^{-4}$	0,014 0,012 0,016	$5{,}996 \cdot 10^{-2}$ $9{,}989 \cdot 10^{-4}$ $1{,}011 \cdot 10^{-4}$	0,27 0,29 0,40	-0,01 0,08 0,04
NIST (52)	8498 A 8516 A 8526 A	$6{,}0036 \cdot 10^{-2}$ $9{,}9774 \cdot 10^{-4}$ $1{,}0112 \cdot 10^{-4}$	0,014 0,012 0,016	$6{,}010 \cdot 10^{-2}$ $9{,}984 \cdot 10^{-4}$ $1{,}012 \cdot 10^{-4}$	0,20 0,30 0,49	0,11 0,07 0,08
NMi (53)	8494 A 8504 A 8521 A	$6{,}0003 \cdot 10^{-2}$ $9{,}9834 \cdot 10^{-4}$ $1{,}0112 \cdot 10^{-4}$	0,014 0,012 0,016	$6{,}001 \cdot 10^{-2}$ $9{,}986 \cdot 10^{-4}$ $1{,}0114 \cdot 10^{-4}$	0,2 0,2 0,4	0,01 0,03 0,02
BAM (54)	8499 A 8501 A 8523 A	$6{,}0091 \cdot 10^{-2}$ $9{,}9737 \cdot 10^{-4}$ $1{,}0103 \cdot 10^{-4}$	0,014 0,012 0,016	$6{,}01 \cdot 10^{-2}$ $9{,}98 \cdot 10^{-4}$ $1{,}011 \cdot 10^{-4}$	0,5 0,5 0,5	0,01 0,06 0,07
LNE (55)	8493 A 8502 A 8527 A	$5{,}9994 \cdot 10^{-2}$ $9{,}9914 \cdot 10^{-4}$ $1{,}0097 \cdot 10^{-4}$	0,014 0,012 0,016	$6{,}0015 \cdot 10^{-2}$ $9{,}9959 \cdot 10^{-4}$ $1{,}0100 \cdot 10^{-4}$	0,04 0,18 0,10	0,04 0,05 0,03
KRISS (56)	8497 A 8509 A 8528 A	$6{,}0165 \cdot 10^{-2}$ $9{,}9822 \cdot 10^{-4}$ $1{,}0102 \cdot 10^{-4}$	0,014 0,012 0,016	$6{,}021 \cdot 10^{-2}$ $1{,}0081 \cdot 10^{-3}$ $1{,}0090 \cdot 10^{-4}$	0,07 0,18 0,31	0,07 0,99 -0,12
NRLM (57)	8490 A 8513 A 8522 A	$6{,}0017 \cdot 10^{-2}$ $9{,}9751 \cdot 10^{-4}$ $1{,}0101 \cdot 10^{-4}$	0,014 0,012 0,016	$6{,}002 \cdot 10^{-2}$ $9{,}975 \cdot 10^{-4}$ $1{,}0096 \cdot 10^{-4}$	0,5 0,5 0,5	0,00 0,00 -0,05
NRCCRM (58)	8491 A 8503 A 8525 A	$6{,}0024 \cdot 10^{-2}$ $9{,}9683 \cdot 10^{-4}$ $1{,}0099 \cdot 10^{-4}$	0,014 0,012 0,016	$6{,}01 \cdot 10^{-2}$ $9{,}97 \cdot 10^{-4}$ $1{,}013 \cdot 10^{-4}$	0,33 0,33 0,33	0,13 0,02 0,31
VNIIM (59)	8500 A 8507 A 8524 A	$5{,}9963 \cdot 10^{-2}$ $9{,}9756 \cdot 10^{-4}$ $1{,}0096 \cdot 10^{-4}$	0,014 0,012 0,016	$5{,}997 \cdot 10^{-2}$ $9{,}988 \cdot 10^{-4}$ $1{,}006 \cdot 10^{-4}$	0,13 0,30 0,50	0,01 0,12 -0,36
OMH (61)	8489 A 8514 A 8518 A	$6{,}0103 \cdot 10^{-2}$ $9{,}9802 \cdot 10^{-4}$ $1{,}0098 \cdot 10^{-4}$	0,014 0,012 0,016	$6{,}015 \cdot 10^{-2}$ $9{,}985 \cdot 10^{-4}$ $1{,}0073 \cdot 10^{-4}$	0,12 0,20 0,60	0,08 0,05 -0,25

Table 7.4 - Results CCQM-K1a: CO/N_2

	Cylinder number	Gravimetric Fraction (mol/mol)	*U* (%) Gravimetry	Analysed Fraction (mol/mol)	*U* (%) Analysis	Δ (%)
NPL (51)	8459 A	$1,5011 \cdot 10^{-1}$	0,006	$1,503 \cdot 10^{-1}$	0,20	0,13
	8473 A	$9,9438 \cdot 10^{-4}$	0,010	$9,985 \cdot 10^{-4}$	0,33	0,41
	8485 A	$9,9945 \cdot 10^{-5}$	0,008	$1,005 \cdot 10^{-4}$	0,50	0,56
NIST (52)	8452 A	$1,4995 \cdot 10^{-1}$	0,006	$1,4995 \cdot 10^{-1}$	0,25	0,00
	8468 A	$9,9510 \cdot 10^{-4}$	0,010	$9,966 \cdot 10^{-4}$	0,35	0,15
	8477 A	$9,9931 \cdot 10^{-5}$	0,008	$9,996 \cdot 10^{-5}$	0,50	0,03
NMi (53)	8454 A	$1,4953 \cdot 10^{-1}$	0,006	$1,497 \cdot 10^{-1}$	0,2	0,11
	8486 A	$9,9476 \cdot 10^{-4}$	0,010	$9,954 \cdot 10^{-4}$	0,2	0,06
	8480 A	$9,9917 \cdot 10^{-5}$	0,008	$1,001 \cdot 10^{-4}$	0,4	0,18
BAM (54)	8460 A	$1,4995 \cdot 10^{-1}$	0,006	$1,499 \cdot 10^{-1}$	0,3	-0,03
	8474 A	$9,9569 \cdot 10^{-4}$	0,010	$9,97 \cdot 10^{-4}$	0,4	0,13
	8484 A	$9,9945 \cdot 10^{-5}$	0,008	$9,94 \cdot 10^{-5}$	0,5	-0,55
LNE (55)	8458 A	$1,5017 \cdot 10^{-1}$	0,006	$1,503 \cdot 10^{-1}$	0,40	0,09
	8471 A	$9,9425 \cdot 10^{-4}$	0,010	$9,962 \cdot 10^{-4}$	0,36	0,20
	8479 A	$9,9935 \cdot 10^{-5}$	0,008	$9,962 \cdot 10^{-5}$	0,48	-0,32
KRISS (56)	8451 A	$1,4998 \cdot 10^{-1}$	0,006	$1,5003 \cdot 10^{-1}$	0,25	0,03
	8467 A	$9,9465 \cdot 10^{-4}$	0,010	$9,906 \cdot 10^{-4}$	1,03	-0,41
	8476 A	$9,9934 \cdot 10^{-5}$	0,008	$9,869 \cdot 10^{-5}$	0,92	-1,24
NRLM (57)	8453 A	$1,5003 \cdot 10^{-1}$	0,006	$1,500 \cdot 10^{-1}$	0,5	-0,02
	8469 A	$9,9460 \cdot 10^{-4}$	0,010	$9,919 \cdot 10^{-4}$	0,5	-0,27
	8478 A	$9,9979 \cdot 10^{-5}$	0,008	$9,975 \cdot 10^{-5}$	0,5	-0,23
NRCCRM (58)	8456 A	$1,5008 \cdot 10^{-1}$	0,006	$1,502 \cdot 10^{-1}$	0,33	0,08
	8466 A	$9,9585 \cdot 10^{-4}$	0,010	$9,944 \cdot 10^{-4}$	0,33	-0,15
	8475 A	$9,9810 \cdot 10^{-5}$	0,008	$9,948 \cdot 10^{-5}$	0,33	-0,33
VNIIM (59)	8455 A	$1,5013 \cdot 10^{-1}$	0,006	$1,496 \cdot 10^{-1}$	0,33	-0,35
	8463 A	$9,9487 \cdot 10^{-4}$	0,010	$9,81 \cdot 10^{-4}$	0,51	-1,39
	8487 A	$1,0003 \cdot 10^{-4}$	0,008	$1,04 \cdot 10^{-4}$	0,96	3,91
OMH (61)	8456 A	$1,5008 \cdot 10^{-1}$	0,006	$1,5015 \cdot 10^{-1}$	0,06	0,05
	8466 A	$9,9585 \cdot 10^{-4}$	0,010	$9,956 \cdot 10^{-4}$	0,20	-0,03
	8475 A	$9,9810 \cdot 10^{-5}$	0,008	$1,008 \cdot 10^{-4}$	1,42	0,99

Table 7.5 - Results CCQM-K1b: CO_2/N_2

	Cylinder number	Gravimetric Fraction (mol/mol)	*U* (%) Gravimetry	Analysed Fraction (mol/mol)	*U* (%) Analysis	Δ (%)
NPL (51)	9430 C 8647 A	$9{,}9977 \cdot 10^{-4}$ $1{,}0007 \cdot 10^{-4}$	0,012 0,014	$1{,}002 \cdot 10^{-3}$ $1{,}000 \cdot 10^{-4}$	0,3 0,4	0,22 -0,07
NIST (52)	8629 A 8641 A	$1{,}0000 \cdot 10^{-3}$ $1{,}0009 \cdot 10^{-4}$	0,012 0,014	$9{,}998 \cdot 10^{-4}$ $1{,}002 \cdot 10^{-4}$	0,47 0,53	-0,02 0,11
NMi (53)	9429 C 8638 A	$1{,}0006 \cdot 10^{-3}$ $1{,}0010 \cdot 10^{-4}$	0,012 0,014	$1{,}000 \cdot 10^{-3}$ $1{,}001 \cdot 10^{-4}$	0,3 0,4	-0,06 0,00
LNE (55)	9423 C 8646 A	$1{,}0001 \cdot 10^{-3}$ $1{,}0011 \cdot 10^{-4}$	0,012 0,014	$1{,}0002 \cdot 10^{-3}$ $1{,}0008 \cdot 10^{-4}$	0,14 0,08	0,01 -0,03
KRISS (56)	9428 C 8644 A	$1{,}0003 \cdot 10^{-3}$ $1{,}0013 \cdot 10^{-4}$	0,012 0,014	$1{,}0001 \cdot 10^{-3}$ $1{,}009 \cdot 10^{-4}$	0,22 0,69	-0,02 0,77
NRLM (57)	9425 C 8639 A	$1{,}0005 \cdot 10^{-3}$ $1{,}0015 \cdot 10^{-4}$	0,012 0,014	$1{,}0026 \cdot 10^{-3}$ $1{,}0039 \cdot 10^{-4}$	0,5 0,5	0,21 0,24
NRCCRM (58)	9422 C 8640 A	$1{,}0008 \cdot 10^{-3}$ $1{,}0016 \cdot 10^{-4}$	0,012 0,014	$1{,}047 \cdot 10^{-3}$ $1{,}058 \cdot 10^{-4}$	1,0 1,0	4,62 5,63
VNIIM (59)	9431 C 8637 A	$1{,}0009 \cdot 10^{-3}$ $1{,}0017 \cdot 10^{-4}$	0,012 0,014	$1{,}0068 \cdot 10^{-3}$ $1{,}018 \cdot 10^{-4}$	0,79 0,98	0,59 1,63
OMH (61)	9427 C 8645 A	$1{,}0012 \cdot 10^{-3}$ $1{,}0018 \cdot 10^{-4}$	0,012 0,014	$1{,}005 \cdot 10^{-3}$ $1{,}007 \cdot 10^{-4}$	0,4 1,0	0,38 0,52

Table 7.6 - Results CCQM-K1c: NO/N_2

	Cylinder number	Gravimetric Fraction (mol/mol)	U (%) Gravimetry	Analysed Fraction (mol/mol)	U (%) Analysis	Δ (%)
NPL (51)	8699 A 8687 A	$0,99944 \cdot 10^{-3}$ $1,1018 \cdot 10^{-4}$	0,026 0,010	$0,9991 \cdot 10^{-3}$ $1,1023 \cdot 10^{-4}$	0,32 0,37	- 0,03 0,05
NIST (52)	8700 A 8690 A	$1,0005 \cdot 10^{-3}$ $1,1006 \cdot 10^{-4}$	0,026 0,010	$1,0005 \cdot 10^{-3}$ $1,101 \cdot 10^{-4}$	0,37 0,6	0,00 0,04
NMi (53)	8708 A 8696 A	$9,9983 \cdot 10^{-4}$ $1,1016 \cdot 10^{-4}$	0,026 0,010	$1,0006 \cdot 10^{-3}$ $1,104 \cdot 10^{-4}$	0,3 0,5	0,08 0,22
LNE (55)	8703 A 8691 A	$9,9902 \cdot 10^{-4}$ $1,0999 \cdot 10^{-4}$	0,026 0,010	$9,999 \cdot 10^{-4}$ $1,1013 \cdot 10^{-4}$	0,18 0,68	0,09 0,13
KRISS (56)	8704 A 8692 A	$1,0003 \cdot 10^{-3}$ $1,0991 \cdot 10^{-4}$	0,026 0,010	$9,902 \cdot 10^{-4}$ $1,121 \cdot 10^{-4}$	0,22 0,54	-1,01 1,99
NRLM (57)	8705 A 8693 A	$9,9962 \cdot 10^{-4}$ $1,1001 \cdot 10^{-4}$	0,026 0,010	$9,9981 \cdot 10^{-4}$ $1,1034 \cdot 10^{-4}$	0,5 0,5	0,02 0,30
NRCCRM (58) - GC	8706 A 8694 A	$1,0001 \cdot 10^{-3}$ $1,1003 \cdot 10^{-4}$	0,026 0,010	$9,85 \cdot 10^{-4}$ $1,097 \cdot 10^{-4}$	0,27 0,27	-1,51 -0,30
NRCCRM - NDIR	8706 A 8694 A	$1,0001 \cdot 10^{-3}$ $1,1003 \cdot 10^{-4}$	0,026 0,010	$9,90 \cdot 10^{-4}$ $1,088 \cdot 10^{-4}$	0,27 0,27	-1,01 -1,12
VNIIM (59)	8707 A 8695 A	$1,0003 \cdot 10^{-3}$ $1,1004 \cdot 10^{-4}$	0,026 0,010	$1,0008 \cdot 10^{-3}$ $1,098 \cdot 10^{-4}$	0,5 0,91	0,05 -0,22
OMH (61)	8701 A 8689 A	$1,0000 \cdot 10^{-3}$ $1,1000 \cdot 10^{-4}$	0,026 0,010	$1,0011 \cdot 10^{-3}$ $1,0925 \cdot 10^{-4}$	0,2 0,2	0,11 -0,68

Table 7.7 - Results CCQM-K1d: SO_2/N_2

	Composition	Gravimetric Fraction (mol/mol)	*U* (%) Gravimetry	Analysed fraction (mol/mol)	*U* (%) Analysis	Δ (%)
NIST 8709A	Nitrogen	$3{,}9768 \cdot 10^{-2}$	0,016	$3{,}97 \cdot 10^{-2}$	0,50	-0,17
	Carbon dioxide	$1{,}0089 \cdot 10^{-2}$	0,014	$1{,}000 \cdot 10^{-2}$	1,30	-0,88
	Ethane	$3{,}0541 \cdot 10^{-2}$	0,018	$3{,}06 \cdot 10^{-2}$	0,65	0,19
type I	Propane	$0{,}9991 \cdot 10^{-2}$	0,022	$1{,}000 \cdot 10^{-2}$	0,60	0,09
gas	Butane	$0{,}2004 \cdot 10^{-2}$	0,028	$0{,}200 \cdot 10^{-2}$	0,50	-0,20
	Methane	$90{,}7601 \cdot 10^{-2}$	0,0012	$90{,}82 \cdot 10^{-2}$	0,50	0,07
NIST 8737A	Nitrogen	$7{,}0530 \cdot 10^{-2}$	0,01	$7{,}06 \cdot 10^{-2}$	0,28	0,10
	Carbon dioxide	$2{,}9813 \cdot 10^{-2}$	0,014	$2{,}96 \cdot 10^{-2}$	1,01	-0,71
	Ethane	$9{,}2925 \cdot 10^{-2}$	0,012	$9{,}31 \cdot 10^{-2}$	0,32	0,19
type II	Propane	$3{,}3022 \cdot 10^{-2}$	0,016	$3{,}30 \cdot 10^{-2}$	0,30	-0,07
gas	Butane	$1{,}0003 \cdot 10^{-2}$	0,024	$1{,}000 \cdot 10^{-2}$	0,30	-0,03
	Methane	$76{,}3700 \cdot 10^{-2}$	0,0032	$76{,}35 \cdot 10^{-2}$	0,30	-0,03
NIST 8645A	Nitrogen	$13{,}4714 \cdot 10^{-2}$	0,012	$13{,}48 \cdot 10^{-2}$	0,52	0,06
	Carbon dioxide	$0{,}5043 \cdot 10^{-2}$	0,016	$0{,}506 \cdot 10^{-2}$	1,98	0,34
	Ethane	$3{,}0940 \cdot 10^{-2}$	0,026	$3{,}09 \cdot 10^{-2}$	0,32	-0,13
type III	Propane	$0{,}5003 \cdot 10^{-2}$	0,026	$0{,}499 \cdot 10^{-2}$	0,80	-0,26
gas	Butane	$0{,}1001 \cdot 10^{-2}$	0,024	$0{,}1003 \cdot 10^{-2}$	0,40	0,20
	Methane	$82{,}3293 \cdot 10^{-2}$	0,0024	$82{,}30 \cdot 10^{-2}$	0,30	-0,04
NMi 8666A	Nitrogen	$3{,}9768 \cdot 10^{-2}$	0,016	$3{,}980 \cdot 10^{-2}$	0,3	0,08
	Carbon dioxide	$1{,}0089 \cdot 10^{-2}$	0,014	$1{,}007 \cdot 10^{-2}$	0,5	-0,19
	Ethane	$3{,}0541 \cdot 10^{-2}$	0,018	$3{,}052 \cdot 10^{-2}$	0,3	-0,07
type I	Propane	$0{,}9991 \cdot 10^{-2}$	0,022	$0{,}9970 \cdot 10^{-2}$	0,4	-0,21
gas	Butane	$0{,}2004 \cdot 10^{-2}$	0,028	$0{,}1995 \cdot 10^{-2}$	0,7	-0,45
	Methane	$90{,}7601 \cdot 10^{-2}$	0,0012	$90{,}80 \cdot 10^{-2}$	0,2	0,04
NMi 8737A	Nitrogen	$7{,}0530 \cdot 10^{-2}$	0,01	$7{,}054 \cdot 10^{-2}$	0,3	0,01
	Carbon dioxide	$2{,}9813 \cdot 10^{-2}$	0,014	$2{,}984 \cdot 10^{-2}$	0,4	0,09
	Ethane	$9{,}2925 \cdot 10^{-2}$	0,012	$9{,}294 \cdot 10^{-2}$	0,3	0,02
type II	Propane	$3{,}3022 \cdot 10^{-2}$	0,016	$3{,}302 \cdot 10^{-2}$	0,3	-0,01
gas	Butane	$1{,}0003 \cdot 10^{-2}$	0,024	$1{,}000 \cdot 10^{-2}$	0,4	-0,03
	Methane	$76{,}3700 \cdot 10^{-2}$	0,0032	$76{,}42 \cdot 10^{-2}$	0,2	0,07
NMi 8639A	Nitrogen	$13{,}4962 \cdot 10^{-2}$	0,012	$13{,}47 \cdot 10^{-2}$	0,5	-0,19
	Carbon dioxide	$0{,}5041 \cdot 10^{-2}$	0,016	$0{,}5039 \cdot 10^{-2}$	0,5	-0,04
	Ethane	$3{,}1326 \cdot 10^{-2}$	0,026	$3{,}137 \cdot 10^{-2}$	0,3	0,14
type III	Propane	$0{,}4999 \cdot 10^{-2}$	0,026	$0{,}5003 \cdot 10^{-2}$	0,5	0,08
gas	Butane	$0{,}0996 \cdot 10^{-2}$	0,024	$0{,}09955 \cdot 10^{-2}$	0,7	-0,05
	Methane	$82{,}2671 \cdot 10^{-2}$	0,0024	$82{,}24 \cdot 10^{-2}$	0,2	-0,03

Table 7.8a - Results CCQM-K1e, -K1f, -K1g: Natural gases

	Composition	Gravimetric fraction (mol/mol)	*U* (%) Gravimetry	Analysed Fraction (mol/mol)	*U* (%) Analysis	Δ (%)
BAM 8663A type I gas	Nitrogen	$3,9768 \cdot 10^{-2}$	0,016	$3,93 \cdot 10^{-2}$	1,02	-1,18
	Carbon dioxide	$1,0089 \cdot 10^{-2}$	0,014	$1,01 \cdot 10^{-2}$	0,99	0,11
	Ethane	$3,0541 \cdot 10^{-2}$	0,018	$3,05 \cdot 10^{-2}$	0,98	-0,13
	Propane	$0,9991 \cdot 10^{-2}$	0,022	$1,00 \cdot 10^{-2}$	1,00	0,09
	Butane	$0,2004 \cdot 10^{-2}$	0,028	$0,200 \cdot 10^{-2}$	2,00	-0,20
	Methane	$90,7601 \cdot 10^{-2}$	0,0012	not reported		
BAM 8731A type II gas	Nitrogen	$7,0009 \cdot 10^{-2}$	0,01	$7,00 \cdot 10^{-2}$	1,00	-0,01
	Carbon dioxide	$2,9757 \cdot 10^{-2}$	0,014	$2,97 \cdot 10^{-2}$	1,01	-0,19
	Ethane	$9,2584 \cdot 10^{-2}$	0,012	$9,24 \cdot 10^{-2}$	0,97	-0,20
	Propane	$3,3024 \cdot 10^{-2}$	0,016	$3,30 \cdot 10^{-2}$	0,91	-0,07
	Butane	$1,0025 \cdot 10^{-2}$	0,024	$1,00 \cdot 10^{-2}$	1,00	-0,25
	Methane	$76,4594 \cdot 10^{-2}$	0,0032	not reported		
BAM 8644A type III gas	Nitrogen	$13,5591 \cdot 10^{-2}$	0,012	$13,5 \cdot 10^{-2}$	0,74	-0,44
	Carbon dioxide	$0,5043 \cdot 10^{-2}$	0,016	$0,505 \cdot 10^{-2}$	0,99	0,14
	Ethane	$3,0879 \cdot 10^{-2}$	0,026	$3,07 \cdot 10^{-2}$	0,98	-0,58
	Propane	$0,5003 \cdot 10^{-2}$	0,026	$0,500 \cdot 10^{-2}$	1,00	-0,06
	Butane	$0,1001 \cdot 10^{-2}$	0,024	$0,100 \cdot 10^{-2}$	2,00	-0,10
	Methane	$82,2479 \cdot 10^{-2}$	0,0024	not reported		
LNE 8722A type I gas	Nitrogen	$3,9790 \cdot 10^{-2}$	0,016	$3,961 \cdot 10^{-2}$	1,00	-0,45
	Carbon dioxide	$1,0105 \cdot 10^{-2}$	0,014	$0,997 \cdot 10^{-2}$	1,00	-1,34
	Ethane	$3,0528 \cdot 10^{-2}$	0,018	$3,033 \cdot 10^{-2}$	0,66	-0,65
	Propane	$1,0006 \cdot 10^{-2}$	0,022	$0,997 \cdot 10^{-2}$	1,00	-0,36
	Butane	$0,2003 \cdot 10^{-2}$	0,028	$0,2033 \cdot 10^{-2}$	2,46	1,50
	Methane	$90,7563 \cdot 10^{-2}$	0,0012	$90,76 \cdot 10^{-2}$	0,44	0,00
LNE 8730A type II gas	Nitrogen	$7,0009 \cdot 10^{-2}$	0,01	$7,013 \cdot 10^{-2}$	0,57	0,17
	Carbon dioxide	$2,9757 \cdot 10^{-2}$	0,014	$2,989 \cdot 10^{-2}$	0,33	0,45
	Ethane	$9,2584 \cdot 10^{-2}$	0,012	$9,243 \cdot 10^{-2}$	0,32	-0,17
	Propane	$3,3024 \cdot 10^{-2}$	0,016	$3,305 \cdot 10^{-2}$	0,61	0,08
	Butane	$1,0025 \cdot 10^{-2}$	0,024	$0,998 \cdot 10^{-2}$	1,00	-0,45
	Methane	$76,4594 \cdot 10^{-2}$	0,0032	$76,45 \cdot 10^{-2}$	0,39	-0,01
LNE 8633A type III gas	Nitrogen	$13,4875 \cdot 10^{-2}$	0,012	$13,460 \cdot 10^{-2}$	0,45	-0,20
	Carbon dioxide	$0,50447 \cdot 10^{-2}$	0,016	$0,4908 \cdot 10^{-2}$	1,20	-2,71
	Ethane	$3,0954 \cdot 10^{-2}$	0,026	$3,095 \cdot 10^{-2}$	0,65	-0,01
	Propane	$0,5003 \cdot 10^{-2}$	0,026	$0,5033 \cdot 10^{-2}$	0,60	0,60
	Butane	$0,09962 \cdot 10^{-2}$	0,024	$0,0986 \cdot 10^{-2}$	1,01	-1,02
	Methane	$82,3121 \cdot 10^{-2}$	0,0024	$82,32 \cdot 10^{-2}$	0,36	0,01

Table 7.8b - Results CCQM-K1e, -K1f, -K1g: Natural gases

	Composition	Gravimetric Fraction (mol/mol)	*U* (%) Gravimetry	Analysed fraction (mol/mol)	*U* (%) Analysis	Δ (%)
KRISS	Nitrogen	3,9925 · 10^{-2}	0,016	3,969 · 10^{-2}	0,25	-0,59
8717A	Carbon dioxide	1,0089 · 10^{-2}	0,014	1,016 · 10^{-2}	0,25	0,70
	Ethane	3,0487 · 10^{-2}	0,018	3,048 · 10^{-2}	0,25	-0,02
type I	Propane	0,9991 · 10^{-2}	0,022	0,988 · 10^{-2}	0,30	-1,11
gas	Butane	0,2004 · 10^{-2}	0,028	0,2007 · 10^{-2}	0,35	0,15
	Methane	90,7498 · 10^{-2}	0,0012	90,591 · 10^{-2}	0,15	-0,17
KRISS	Nitrogen	7,0009 · 10^{-2}	0,01	7,008 · 10^{-2}	0,26	0,10
8734A	Carbon dioxide	2,9757 · 10^{-2}	0,014	2,983 · 10^{-2}	0,37	0,25
	Ethane	9,2584 · 10^{-2}	0,012	9,236 · 10^{-2}	0,22	-0,24
type II	Propane	3,3024 · 10^{-2}	0,016	3,290 · 10^{-2}	0,25	-0,38
gas	Butane	1,0025 · 10^{-2}	0,024	1,002 · 10^{-2}	0,25	-0,05
	Methane	76,4594 · 10^{-2}	0,0032	76,472 · 10^{-2}	0,15	0,02
KRISS	Nitrogen	13,4741 · 10^{-2}	0,012	13,392 · 10^{-2}	0,27	-0,61
8643A	Carbon dioxide	0,5048 · 10^{-2}	0,016		0,3	0,04
	Ethane	3,0968 · 10^{-2}	0,026	0,505 · 10^{-2}	0,25	-0,90
type III	Propane	0,5006 · 10^{-2}	0,026	3,069 · 10^{-2}	0,3	-0,32
gas	Butane	0,0997 · 10^{-2}	0,024	0,499 · 10^{-2}	0,4	0,90
	Methane	82,3235 · 10^{-2}	0,0024	0,1006 · 10^{-2}	0,15	0,05
				82,361 · 10^{-2}		
NRLM	Nitrogen	3,9790 · 10^{-2}	0,016	3,9748 · 10^{-2}	0,11	-0,11
8720A	Carbon dioxide	1,0105 · 10^{-2}	0,014	1,0118 · 10^{-2}	0,11	0,13
	Ethane	3,0528 · 10^{-2}	0,018	3,0535 · 10^{-2}	0,14	0,02
type I	Propane	1,0006 · 10^{-2}	0,022	1,0015 · 10^{-2}	0,11	0,09
gas	Butane	0,2003 · 10^{-2}	0,028	0,2010 · 10^{-2}	0,37	0,35
	Methane	90,7563 · 10^{-2}	0,0012	90,7663 · 10^{-2}	0,08	0,01
NRLM	Nitrogen	7,0129 · 10^{-2}	0,01	7,0158 · 10^{-2}	0,17	0,04
8729A	Carbon dioxide	2,9853 · 10^{-2}	0,014	2,9848 · 10^{-2}	0,09	-0,02
	Ethane	9,2411 · 10^{-2}	0,012	9,2386 · 10^{-2}	0,14	-0,03
type II	Propane	3,3022 · 10^{-2}	0,016	3,2966 · 10^{-2}	0,14	-0,17
gas	Butane	1,0012 · 10^{-2}	0,024	1,0014 · 10^{-2}	0,22	0,02
	Methane	76,4565 · 10^{-2}	0,0032	76,4425· 10^{-2}	0,09	-0,02
NRLM	Nitrogen	13,5527 · 10^{-2}	0,012	13,5421 · 10^{-2}	0,08	-0,08
8640A	Carbon dioxide	0,5048 · 10^{-2}	0,016	0,5055 · 10^{-2}	0,16	0,14
	Ethane	3,0823 · 10^{-2}	0,026	3,0803 · 10^{-2}	0,14	-0,06
type III	Propane	0,5007 · 10^{-2}	0,026	0,5006 · 10^{-2}	0,23	-0,02
gas	Butane	0,1002 · 10^{-2}	0,024	0,1003 · 10^{-2}	0,55	0,10
	Methane	82,2587 · 10^{-2}	0,0024	82,2426 · 10^{-2}	0,08	-0,02

Table 7.8c - Results CCQM-K1e, -K1f, -K1g: Natural gases

	Composition	Gravimetric Fraction (mol/mol)	*U* (%) Gravimetry	Analysed Fraction (mol/mol)	*U* (%) Analysis	Δ (%)
NRCCRM 8719A type I gas	Nitrogen	$3,9925 \cdot 10^{-2}$	0,016	$3,984 \cdot 10^{-2}$	0,19	-0,21
	Carbon dioxide	$1,0089 \cdot 10^{-2}$	0,014	$1,007 \cdot 10^{-2}$	0,24	0,19
	Ethane	$3,0487 \cdot 10^{-2}$	0,018	$3,043 \cdot 10^{-2}$	0,17	-0,19
	Propane	$0,9991 \cdot 10^{-2}$	0,022	$0,999 \cdot 10^{-2}$	0,35	-0,01
	Butane	$0,2004 \cdot 10^{-2}$	0,028	$0,2007 \cdot 10^{-2}$	0,33	0,15
	Methane	$90,7498 \cdot 10^{-2}$	0,0012	$90,77 \cdot 10^{-2}$	NR	0,02
NRCCRM 8727A type II gas	Nitrogen	$7,0129 \cdot 10^{-2}$	0,01	$6,992 \cdot 10^{-2}$	0,11	-0,30
	Carbon dioxide	$2,9853 \cdot 10^{-2}$	0,014	$2,982 \cdot 10^{-2}$	0,19	-0,11
	Ethane	$9,2411 \cdot 10^{-2}$	0,012	$9,236 \cdot 10^{-2}$	0,13	-0,06
	Propane	$3,3022 \cdot 10^{-2}$	0,016	$3,299 \cdot 10^{-2}$	0,23	-0,10
	Butane	$1,0012 \cdot 10^{-2}$	0,024	$1,000 \cdot 10^{-2}$	0,24	-0,12
	Methane	$76,4565 \cdot 10^{-2}$	0,0032	$76,49 \cdot 10^{-2}$	NR	0,04
NRCCRM 8619A type III gas	Nitrogen	$13,4648 \cdot 10^{-2}$	0,012	$13,44 \cdot 10^{-2}$	0,18	-0,18
	Carbon dioxide	$0,5048 \cdot 10^{-2}$	0,016	$0,504 \cdot 10^{-2}$	0,28	-0,16
	Ethane	$3,1020 \cdot 10^{-2}$	0,026	$3,099 \cdot 10^{-2}$	0,15	-0,10
	Propane	$0,5006 \cdot 10^{-2}$	0,026	$0,499 \cdot 10^{-2}$	0,28	-0,32
	Butane	$0,0997 \cdot 10^{-2}$	0,024	$0,1028 \cdot 10^{-2}$	0,32	3,11
	Methane	$82,3276 \cdot 10^{-2}$	0,0024	$82,36 \cdot 10^{-2}$	NR	0,04
VNIIM 8724A type I gas	Nitrogen	$3,9790 \cdot 10^{-2}$	0,016	$3,98 \cdot 10^{-2}$	1,0	0,03
	Carbon dioxide	$1,0105 \cdot 10^{-2}$	0,014	$1,02 \cdot 10^{-2}$	1,0	0,94
	Ethane	$3,0528 \cdot 10^{-2}$	0,018	$3,03 \cdot 10^{-2}$	1,0	-0,75
	Propane	$1,0006 \cdot 10^{-2}$	0,022	$0,99 \cdot 10^{-2}$	1,0	-1,06
	Butane	$0,2003 \cdot 10^{-2}$	0,028	$0,200 \cdot 10^{-2}$	1,0	-0,15
	Methane	$90,7563 \cdot 10^{-2}$	0,0012	$90,8 \cdot 10^{-2}$	NR	0,05
VNIIM 8736A type II gas	Nitrogen	$7,0530 \cdot 10^{-2}$	0,01	$7,00 \cdot 10^{-2}$	1,0	-0,75
	Carbon dioxide	$2,9813 \cdot 10^{-2}$	0,014	$3,00 \cdot 10^{-2}$	1,0	0,63
	Ethane	$9,2925 \cdot 10^{-2}$	0,012	$9,31 \cdot 10^{-2}$	1,0	0,19
	Propane	$3,3022 \cdot 10^{-2}$	0,016	$3,26 \cdot 10^{-2}$	1,0	-1,28
	Butane	$1,0003 \cdot 10^{-2}$	0,024	$1,00 \cdot 10^{-2}$	0,7	-0.03
	Methane	$76,3700 \cdot 10^{-2}$	0,0032	$76,4 \cdot 10^{-2}$	NR	0,04
VNIIM 8629A type III gas	Nitrogen	$13,4631 \cdot 10^{-2}$	0,012	$13,5 \cdot 10^{-2}$	1,0	0,27
	Carbon dioxide	$0,5044 \cdot 10^{-2}$	0,016	$0,503 \cdot 10^{-2}$	1,0	-0,28
	Ethane	$3,1022 \cdot 10^{-2}$	0,026	$3,09 \cdot 10^{-2}$	1,0	-0,39
	Propane	$0,5003 \cdot 10^{-2}$	0,026	$0,498 \cdot 10^{-2}$	1,0	-0,46
	Butane	$0,0996 \cdot 10^{-2}$	0,024	$0,100 \cdot 10^{-2}$	0,7	0,40
	Methane	$82,3299 \cdot 10^{-2}$	0,0024	$82,3 \cdot 10^{-2}$	NR	-0,04

Table 7.8d - Results CCQM-K1e, -K1f, -K1g: Natural gases

	Composition	Gravimetric Fraction (mol/mol)	U (%) Gravimetry	Analysed Fraction (mol/mol)	U (%) Analysis	Δ (%)
OMH 8718A	Nitrogen	$3{,}9925 \cdot 10^{-2}$	0,016	$3{,}9886 \cdot 10^{-2}$	0,2	-0,10
	Carbon dioxide	$1{,}0089 \cdot 10^{-2}$	0,014	$1{,}0088 \cdot 10^{-2}$	0,2	-0,01
	Ethane	$3{,}0487 \cdot 10^{-2}$	0,018	$3{,}0467 \cdot 10^{-2}$	0,2	-0,07
type I gas	Propane	$0{,}9991 \cdot 10^{-2}$	0,022	$0{,}9982 \cdot 10^{-2}$	0,2	-0,09
	Butane	$0{,}2004 \cdot 10^{-2}$	0,028	$0{,}2005 \cdot 10^{-2}$	0,2	0,05
	Methane	$90{,}7498 \cdot 10^{-2}$	0,0012	$90{,}756 \cdot 10^{-2}$	0,06	0,01
OMH 8728A	Nitrogen	$7{,}0129 \cdot 10^{-2}$	0,01	$7{,}0134 \cdot 10^{-2}$	0,1	0,01
	Carbon dioxide	$2{,}9853 \cdot 10^{-2}$	0,014	$2{,}9869 \cdot 10^{-2}$	0,2	0,05
	Ethane	$9{,}2411 \cdot 10^{-2}$	0,012	$9{,}2387 \cdot 10^{-2}$	0,1	-0,03
type II gas	Propane	$3{,}3022 \cdot 10^{-2}$	0,016	$3{,}3036 \cdot 10^{-2}$	0,2	0,04
	Butane	$1{,}0012 \cdot 10^{-2}$	0,024	$1{,}0013 \cdot 10^{-2}$	0,2	0,01
	Methane	$76{,}4565 \cdot 10^{-2}$	0,0032	$76{,}456 \cdot 10^{-2}$	0,06	0,00
OMH 8641A	Nitrogen	$13{,}5125 \cdot 10^{-2}$	0,012	$13{,}509 \cdot 10^{-2}$	0,1	-0,03
	Carbon dioxide	$0{,}5054 \cdot 10^{-2}$	0,016	$0{,}5054 \cdot 10^{-2}$	0,3	0,00
	Ethane	$3{,}0948 \cdot 10^{-2}$	0,026	$3{,}0964 \cdot 10^{-2}$	0,2	0,05
type III gas	Propane	$0{,}5014 \cdot 10^{-2}$	0,026	$0{,}5018 \cdot 10^{-2}$	0,2	0,08
	Butane	$0{,}1004 \cdot 10^{-2}$	0,024	$0{,}1006 \cdot 10^{-2}$	0,2	0,20
	Methane	$82{,}2850 \cdot 10^{-2}$	0,0024	$82{,}286 \cdot 10^{-2}$	0,06	0,00

Table 7.8e - Results CCQM-K1e, -K1f, -K1g: Natural gases

8 Conclusions

8.1 General conclusions

From the results of CCQM-K1, one can conclude that co-ordinated activities in the field of Primary Standard gas Mixtures do indeed lead to an international comparability within 1 %, with the exception of an occasional outlier.

National measurement standards for gas mixture composition vary in number, concentration range and frequency of maintenance. In a number of cases, gravimetric mixtures were prepared prior to analysing the key comparison cylinders.

Uncertainty sources are generally well identified (e.g. preparation, parent gases, stability, repeatability of measurements, calibration function). Quantification and propagation is not always given in detail. Reporting uncertainty was not consistent; but reporting in terms of the expanded uncertainty (k=2) became more popular during the comparison.

Calibration procedures vary from single-point calibration to curve fitting with suites of PSMs.

The applied analytical reference methods for the various groups of gases are in most cases compatible.

8.2 CO in Nitrogen

There is an agreement better than 0,5% for the PSMs except for KRISS at $1000 \cdot 10^{-6}$ mol/mol. The uncertainties from BAM and NRLM are somewhat pessimistic.

8.3 CO_2 in Nitrogen

For the three concentrations VNIIM deviates. For $15 \cdot 10^{-2}$ mol/mol there is agreement better than 0,5%. As concentrations get lower the challenge becomes bigger. NPL and KRISS drift away at $1000 \cdot 10^{-6}$ and $100 \cdot 10^{-6}$.

8.4 SO_2 in Nitrogen

NRCCRM applies two reference methods which lead to different results. KRISS and NRCCRM both deviate at $1000 \cdot 10^{-6}$ and $100 \cdot 10^{-6}$ mol/mol level, joint by OMH at 100 □10^{-6}. OMH seems optimistic in their uncertainty statements.

8.5 NO in Nitrogen

LNE reports a small uncertainty budget for both concentrations but is consistent with the reference values. NRCCRM deviates for both concentrations. NRLM and VNIIM both report lager uncertainties at $1000 \cdot 10^{-6}$ mol/mol and are therefore consistent with the reference value. KRISS and VNIIM deviate at $100 \cdot 10^{-6}$ mol/mol level.

8.6 Natural gas

For nitrogen there is scatter within the 1% band. Due to lager reported uncertainties by BAM, LNE and VNIIM the measurement are in most cases consistent with the reference values. NRCCRM deviates due to their relative small uncertainty. The same applies to KRISS for two gases.

For carbon dioxide there is scatter within the 1 % band, taking into consideration that LNE reported to have little experience in the analysis of natural gas and that their major objective for participation is getting a first impression. NIST, BAM and VNIIM reported relatively large uncertainties, however it keeps them consistent. BAM is pessimistic in its uncertainty for carbon dioxide.

For ethane there is some scatter within the 1 % band. LNE, although having little experience, is consistent. BAM again a little pessimistic. KRISS has an uncertainty, which is relatively small, for that reason, two out of three values are not consistent. NRCCRM and NRLM are consistent.

For propane there is more scatter within the 1 % band, with three outliers, 21 out of 27 measurements are consistent with the reference values. NRLM and KRISS are a bit optimistic about their uncertainties.

For butane there is some scatter within the 1 % band. One strong outlier from NRCCRM and a smaller one from KRISS. Again some pessimism from BAM.

For methane there is little scatter within the 0,25 % band. BAM did not report their values and NRCCRM and VNIIM did not report their uncertainties. NIST, NMI and LNE are pessimistic about their uncertainties.

For natural gas, OMH reported small uncertainties but is consistent!