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NPL REPORT
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OCTOBER 2007

NOT RESTRICTED

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ABSTRACT

Twenty-two standards of synthetic natural gas standards were submitted from ten different NMIs for a comparison using the harmonisation method developed by NPL. All standards had seven components. This method can remove the correlated variation in calibration data for multi-component mixtures and makes a significant improvement in fitting individual points to calibration curves. After removing the non-random variation from the data all the standards showed very good agreement with only a few outliers. The typical deviation from the calibration curves was around 0.05 % (relative) for the main components and less than 0.2 % for the butanes.

ISSN 1754-2928

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Approved on behalf of the Managing Director, NPL
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Abstract

Twenty-two standards of synthetic natural gas standards were submitted from ten different NMIs for a comparison using the harmonisation method developed by NPL. All standards had seven components. This method can remove the correlated variation in calibration data for multi-component mixtures and makes a significant improvement in fitting individual points to calibration curves. After removing the non-random variation from the data all the standards showed very good agreement with only a few outliers. The typical deviation from the calibration curves was around 0.05 % (relative) for the main components and less than 0.2 % for the butanes.

Introduction

There is a continuing requirement for improvements in the accuracy of multi-component standards of synthetic natural gas. The CCQM GAWG has carried out several key comparisons covering different compositions of synthetic natural gas. These comparisons have all used the "analytical" model for a key comparison in which the coordinating laboratory prepares a suite of standards at the same nominal concentrations; these standards are then distributed to each participant. This model for the organisation of a key comparison places a substantial burden on the coordinating laboratory since it must prepare a large suite of standards that must also be analysed before and after they have been distributed to participants.

This report describes the results of CQM-P87 which was organised according to the "preparative" model in which all participants prepare standards which are sent to the coordinating laboratory to perform the analysis. In addition, advantage was taken of the fact that all of the analysis was carried out by the coordinating laboratory to exploit the benefits of the harmonisation method developed by NPL. This enables multi-component standards having wider concentration ranges for the different components to be compared by fitting individual components on calibration curves for all standards optimise simultaneously for all components. Since the establishment of calibration curves for many standards and components may take an extended period of time, there can be significant drift in some measurement parameters. As long as these changes have a similar affect on all components, they can be separated from the random variations and thus compensated. The harmonisation method was developed by NPL to do this special calculation.

To gain further insight into the operation of the harmonisation method, this pilot study used standards that had been prepared by NMIs as part of their work on CCQM-K23 series of comparisons of synthetic natural gas. In this way, the results of a preparative comparison and an analytical comparison on the same standards could be compared.

Standards submitted

Twenty two standards were submitted to the coordinating laboratory for analysis. The gravimetric value and the associated standard uncertainty for each standard are listed in Table 1. These can be associated with the nominal amount fractions used for CCQM-K23 as follows:

> Seven standards had “high” methane corresponding to CCQM-K23a
> Seven standards had “medium” methane corresponding to CCQM-K23c, and
> Eight standards had “low” methane corresponding to CCQM-K23b.

The standard uncertainty of each of each of the 22 standards is plotted against its amount fraction in Figure 1. The points tend to group along vertical lines corresponding to the nominal amount fractions used in the three parts of CCQM-K23. For example, all of the methane amount fractions are clustered around the nominal values of 950, 820 and 750 mmol/mol. Also, many of the amount fractions of *i*-butane and *n*-butane in the “hi” and “med” standards are grouped close to 1 and 2 mmol/mol.

Analytical Method

The analysis method used a high-performance micro-packed column with a ten-port diaphragm sampling valve, placed in the main oven of a Varian 3800 GC. The column was packed with Porapak R (8.8 m long, 0.75 mm ID) and was connected to a thermal conductivity detector. It was made from 1/16” stainless steel tubing and packed with 100-120 mesh particles. The carrier gas was helium with a head pressure of 12 bar, the isothermal oven temperature was 160 Celsius.

This column has a very high separation power. Even when operating at this relatively high temperature there is baseline separation between nitrogen and methane. Although carbon dioxide and ethane naturally elute on the tail of the methane peak, there is no integration problem. Narrow peaks and good separation give a repeatable baseline allocation.

Harmonisation analysis

The harmonisation method has been published in full [Vargha 2005] and is summarised in Annex B of this report.

The Table lists the Concentration Correction factors (CCF) calculated for each cylinder. The CCFs are a consequence of any change in conditions over the time period of the analysis of the cylinders; hence larger values for the CCF indicate larger changes during the analysis. A value of unity represents the average condition. Consequently, the identities of the cylinders are omitted from the Table, since the CCF provides no information about the standard itself.

	CCF
	0.9925
	0.9965
	0.9970
	0.9972
	0.9973
	0.9975
	0.9979
	0.9982
	0.9987
	0.9990
	0.9998
	1.0004
	1.0012
	1.0012
	1.0012
	1.0025
	1.0026
	1.0032
	1.0033
	1.0037
	1.0041
	1.0051
Mean	**1.0000**
Std deviation	**0.0031**

Table 2: The concentration correction factor (CCF) for each of the 22 standards analysed for the study.

	Level	Nitrogen		Methane		Carbon dioxide		Ethane		Propane		n-Butane		iso-Butane	
		x	$u(x)$	x	$u(x)$	x	$u(x)$	x	$u(x)$	x	$u(x)$	x	$u(x)$	x	$u(x)$
BAM5039	**hi**	38.746	0.006	908.934	0.091	9.671	0.005	29.122	0.009	9.687	0.005	1.927	0.001	1.913	0.001
BAM6028	**lo**	66.583	0.017	765.880	0.096	28.466	0.007	88.876	0.040	32.294	0.016	9.857	0.006	8.043	0.005
CEM6338	**med**	55.896	0.006	822.227	0.017	20.012	0.002	70.811	0.005	20.140	0.013	5.116	0.009	5.776	0.001
CENAM31141	**med**	40.232	0.004	905.853	0.007	10.066	0.003	29.680	0.004	10.162	0.003	1.991	0.001	2.010	0.001
CENAM31080	**lo**	70.038	0.011	753.399	0.018	29.937	0.007	94.326	0.010	34.307	0.007	9.987	0.002	8.000	0.002
CENAM31145	**hi**	135.427	0.004	822.419	0.006	5.077	0.001	30.122	0.004	4.944	0.001	1.003	0.000	1.002	0.000
KRISS0748	**hi**	39.780	0.026	904.879	0.265	10.525	0.012	30.520	0.024	10.292	0.010	1.977	0.003	2.001	0.003
KRISS0400	**lo**	70.888	0.043	752.820	0.231	31.485	0.023	93.166	0.053	33.325	0.029	10.292	0.016	7.970	0.015
KRISS0773	**med**	136.864	0.038	820.496	0.195	5.157	0.011	30.565	0.023	4.940	0.005	0.951	0.002	1.004	0.002
LNE606316	**med**	131.728	0.258	821.812	1.603	5.508	0.010	34.135	0.036	4.764	0.010	0.951	0.002	1.102	0.002
LNE614734	**hi**	44.072	0.123	903.304	2.435	10.757	0.011	28.494	0.029	9.096	0.013	2.211	0.004	2.067	0.004
NMi226686	**hi**	40.557	0.009	905.599	0.090	9.993	0.006	29.874	0.008	9.982	0.006	1.991	0.002	2.000	0.002
NMI202677	**med**	135.184	0.012	822.840	0.044	5.003	0.003	29.976	0.008	4.997	0.003	0.997	0.001	0.999	0.001
NMi133436	**lo**	70.327	0.026	753.638	0.257	29.938	0.012	94.184	0.034	33.958	0.013	9.972	0.006	7.979	0.005
NMi133436*			*0.010*		*0.020*		*0.006*		*0.010*		*0.006*		*0.004*		*0.004*
NMIA8847	**hi**	42.512	0.005	900.803	0.011	10.645	0.003	31.237	0.005	10.549	0.003	2.115	0.002	2.127	0.002
NMIA8856	**lo**	65.528	0.007	769.403	0.016	28.462	0.005	88.422	0.006	31.354	0.005	8.810	0.001	8.001	0.004
NMIA8849	**med**	139.496	0.005	816.246	0.010	5.227	0.003	31.592	0.005	5.219	0.003	1.103	0.002	1.095	0.002
NMIJ31833	**lo**	66.472	0.003	772.374	0.024	29.946	0.002	85.033	0.004	30.428	0.002	7.560	0.002	8.186	0.002
NPL71	**hi**	40.187	0.013	905.920	0.030	9.967	0.004	29.915	0.023	2.038	0.004	9.995	0.002	1.967	0.002
NPL69	**med**	134.040	0.030	823.920	0.040	5.016	0.004	30.029	0.025	1.000	0.001	4.989	0.001	0.998	0.001
NPL95	**lo**	69.991	0.031	753.690	0.044	94.395	0.020	29.990	0.029	33.912	0.020	9.982	0.002	8.034	0.002
VNIIM	**lo**	68.940	0.080	751.100	0.180	30.210	0.035	95.070	0.145	37.250	0.060	9.884	0.015	7.512	0.015

Table 1 Gravimetric values and associated standard uncertainties (in mmol/mol) for each of the twenty two standards submitted. The column headed "level" indicates whether the methane amount fraction of the standard was high (K23a), medium (K23c) or low (K23b). NMi133436* refers to a corrected set of uncertainties submitted by NMi for standard 133426.

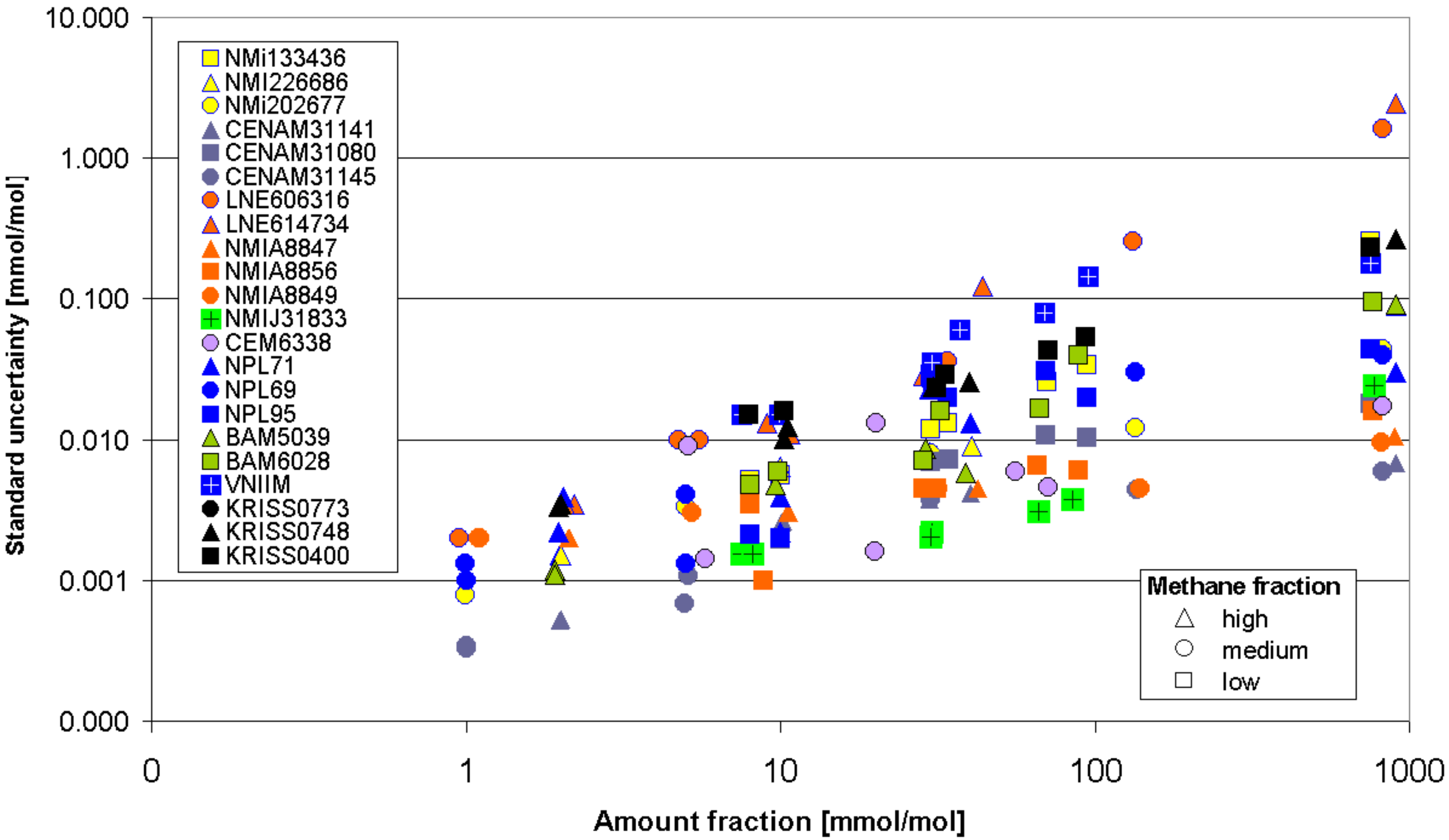
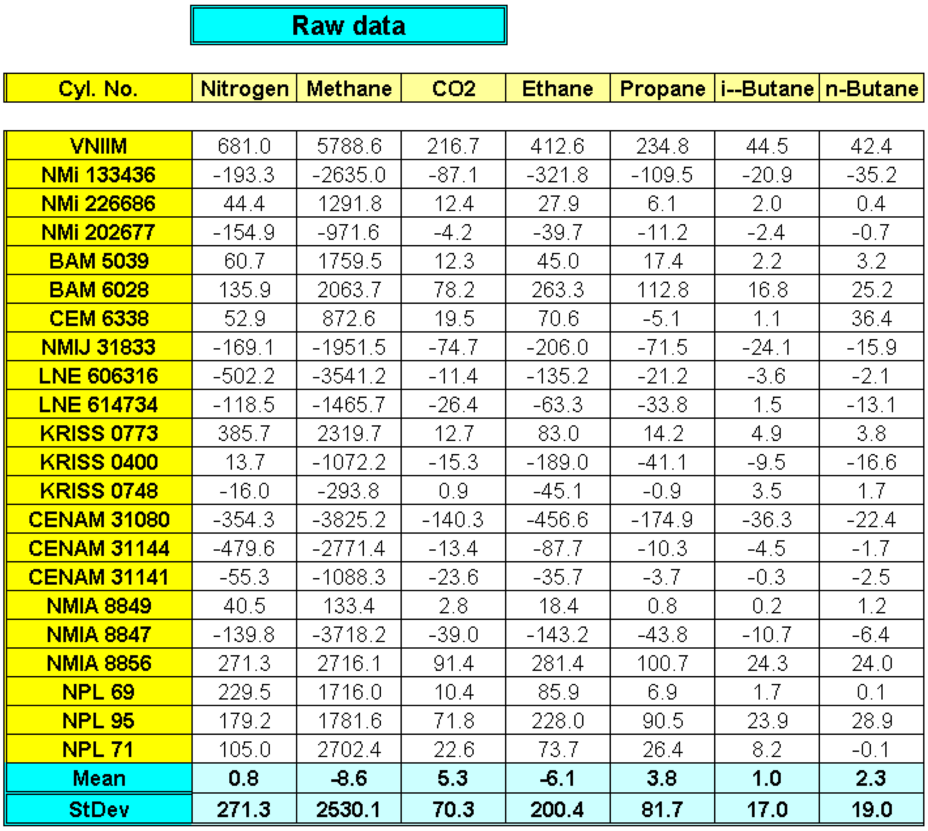
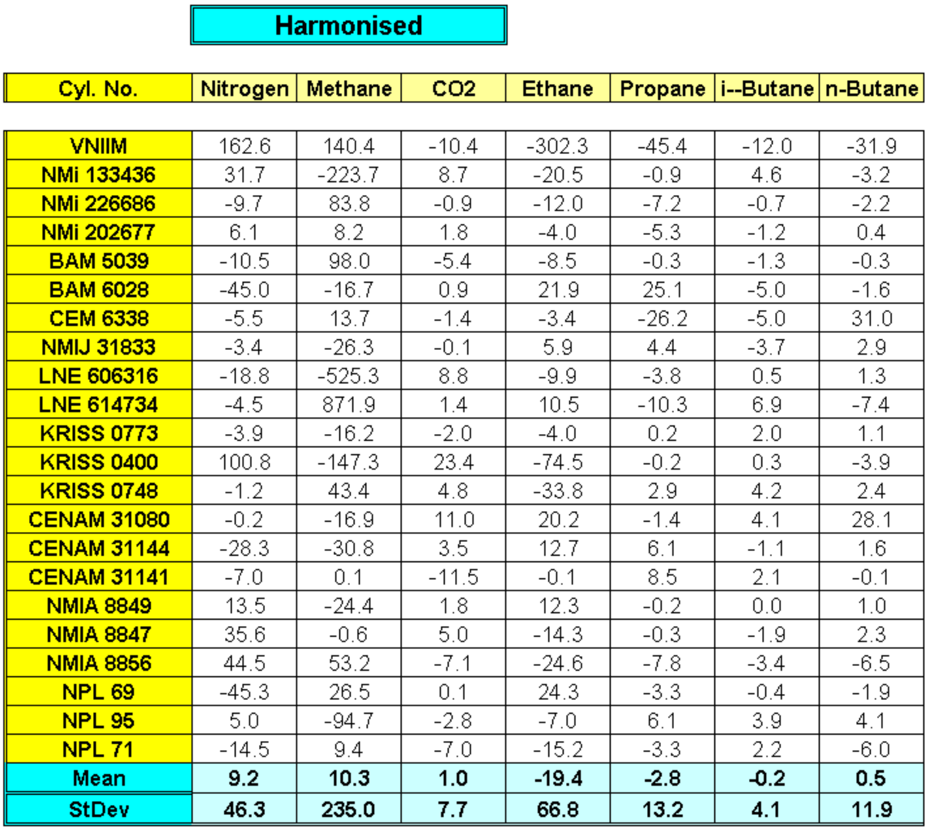


Figure 1 Gravimetric amount fraction and associated standard uncertainty for each of the 22 standards submitted for CCQM-P87.



Raw data

Cyl. No.	Nitrogen	Methane	CO2	Ethane	Propane	i--Butane	n-Butane
VNIIM	681.0	5788.6	216.7	412.6	234.8	44.5	42.4
NMi 133436	-193.3	-2635.0	-87.1	-321.8	-109.5	-20.9	-35.2
NMi 226686	44.4	1291.8	12.4	27.9	6.1	2.0	0.4
NMi 202677	-154.9	-971.6	-4.2	-39.7	-11.2	-2.4	-0.7
BAM 5039	60.7	1759.5	12.3	45.0	17.4	2.2	3.2
BAM 6028	135.9	2063.7	78.2	263.3	112.8	16.8	25.2
CEM 6338	52.9	872.6	19.5	70.6	-5.1	1.1	36.4
NMIJ 31833	-169.1	-1951.5	-74.7	-206.0	-71.5	-24.1	-15.9
LNE 606316	-502.2	-3541.2	-11.4	-135.2	-21.2	-3.6	-2.1
LNE 614734	-118.5	-1465.7	-26.4	-63.3	-33.8	1.5	-13.1
KRISS 0773	385.7	2319.7	12.7	83.0	14.2	4.9	3.8
KRISS 0400	13.7	-1072.2	-15.3	-189.0	-41.1	-9.5	-16.6
KRISS 0748	-16.0	-293.8	0.9	-45.1	-0.9	3.5	1.7
CENAM 31080	-354.3	-3825.2	-140.3	-456.6	-174.9	-36.3	-22.4
CENAM 31144	-479.6	-2771.4	-13.4	-87.7	-10.3	-4.5	-1.7
CENAM 31141	-55.3	-1088.3	-23.6	-35.7	-3.7	-0.3	-2.5
NMIA 8849	40.5	133.4	2.8	18.4	0.8	0.2	1.2
NMIA 8847	-139.8	-3718.2	-39.0	-143.2	-43.8	-10.7	-6.4
NMIA 8856	271.3	2716.1	91.4	281.4	100.7	24.3	24.0
NPL 69	229.5	1716.0	10.4	85.9	6.9	1.7	0.1
NPL 95	179.2	1781.6	71.8	228.0	90.5	23.9	28.9
NPL 71	105.0	2702.4	22.6	73.7	26.4	8.2	-0.1
Mean	**0.8**	**-8.6**	**5.3**	**-6.1**	**3.8**	**1.0**	**2.3**
StDev	**271.3**	**2530.1**	**70.3**	**200.4**	**81.7**	**17.0**	**19.0**



Harmonised

Cyl. No.	Nitrogen	Methane	CO2	Ethane	Propane	i--Butane	n-Butane
VNIIM	162.6	140.4	-10.4	-302.3	-45.4	-12.0	-31.9
NMi 133436	31.7	-223.7	8.7	-20.5	-0.9	4.6	-3.2
NMi 226686	-9.7	83.8	-0.9	-12.0	-7.2	-0.7	-2.2
NMi 202677	6.1	8.2	1.8	-4.0	-5.3	-1.2	0.4
BAM 5039	-10.5	98.0	-5.4	-8.5	-0.3	-1.3	-0.3
BAM 6028	-45.0	-16.7	0.9	21.9	25.1	-5.0	-1.6
CEM 6338	-5.5	13.7	-1.4	-3.4	-26.2	-5.0	31.0
NMIJ 31833	-3.4	-26.3	-0.1	5.9	4.4	-3.7	2.9
LNE 606316	-18.8	-525.3	8.8	-9.9	-3.8	0.5	1.3
LNE 614734	-4.5	871.9	1.4	10.5	-10.3	6.9	-7.4
KRISS 0773	-3.9	-16.2	-2.0	-4.0	0.2	2.0	1.1
KRISS 0400	100.8	-147.3	23.4	-74.5	-0.2	0.3	-3.9
KRISS 0748	-1.2	43.4	4.8	-33.8	2.9	4.2	2.4
CENAM 31080	-0.2	-16.9	11.0	20.2	-1.4	4.1	28.1
CENAM 31144	-28.3	-30.8	3.5	12.7	6.1	-1.1	1.6
CENAM 31141	-7.0	0.1	-11.5	-0.1	8.5	2.1	-0.1
NMIA 8849	13.5	-24.4	1.8	12.3	-0.2	0.0	1.0
NMIA 8847	35.6	-0.6	5.0	-14.3	-0.3	-1.9	2.3
NMIA 8856	44.5	53.2	-7.1	-24.6	-7.8	-3.4	-6.5
NPL 69	-45.3	26.5	0.1	24.3	-3.3	-0.4	-1.9
NPL 95	5.0	-94.7	-2.8	-7.0	6.1	3.9	4.1
NPL 71	-14.5	9.4	-7.0	-15.2	-3.3	2.2	-6.0
Mean	**9.2**	**10.3**	**1.0**	**-19.4**	**-2.8**	**-0.2**	**0.5**
StDev	**46.3**	**235.0**	**7.7**	**66.8**	**13.2**	**4.1**	**11.9**

Table 3 The absolute deviation ("absolute residual deviation") of each standard (in µmol/mol) from the best-fit regression curve for each component. The values are given for the data before and after the harmonisation process.

Results

The absolute deviations (in µmol/mol) for each standard for each component are given in Table 3 both before and after the harmonisation has been applied. The harmonised values are the results of the use of the set of CCFs in Table 2.

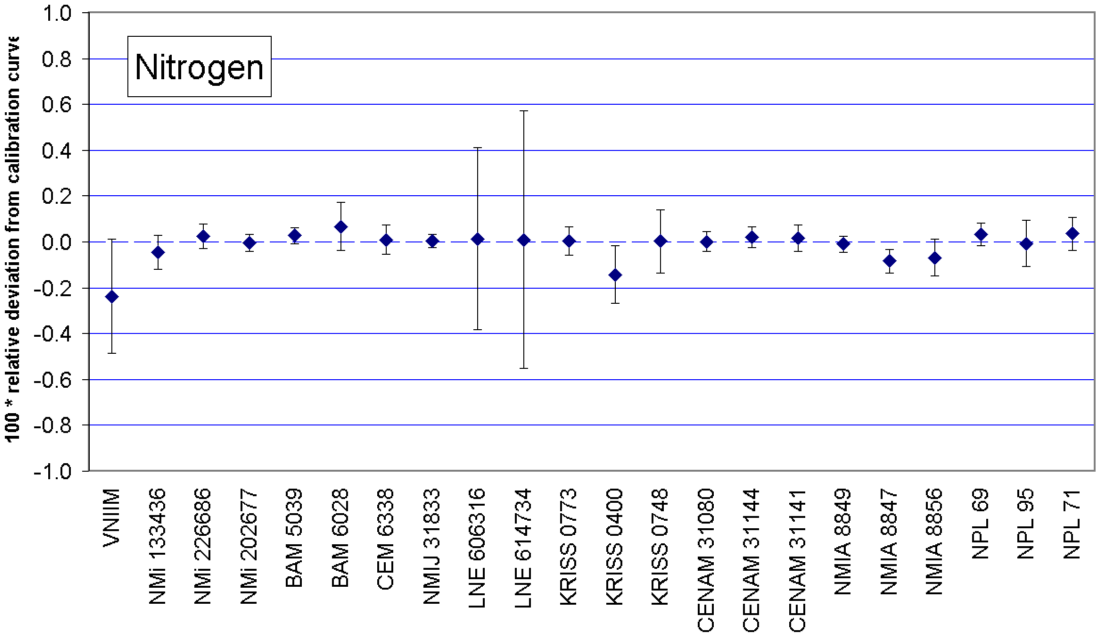
The relative deviations (in %) are plotted in the following seven Figures. In each case, the error bars represent the expanded uncertainty (**k**=2) in the residual deviation, which is a combination of the uncertainty in the gravimetric value of the standard and the uncertainty in the analysis of the standard.

The parameters for the best-fit calibration lines for each component are shown in Table 4, both for the raw and the harmonised data. As expected, the harmonisation process has very little influence on the best-fit lines themselves, it largely serves to reduce the deviations from the lines.

The mean, standard error of the mean (SEM) and standard deviation for the relative deviations (in %) for the 22 standards for each component are shown in Table 5. The standard deviation ranges from 0.027% for methane up to 0.2% for *n*-butane. The mean and standard deviation of the standard deviations of the 22 sets of analysis of each component are also shown in Table 5.

Comparison with CCQM-K23

Since the standards submitted for analysis in CCQM-P87 are at the nominal amount fractions used for the parts of CCQM-K23, it is possible to make a comparison of the results from the two exercises. Table 7, together with its three associated Figures, shows the standard deviation of all results in CCQM-P87 both before and after harmonisation. It can be seen that the harmonisation process has reduced the standard deviation of the results by a factor of three. Table 7 also shows the mean and standard deviation for a sub-set of results from CCQM-K23 (see Table 6) that corresponds to the standards submitted for this study.


Nitrogen
100 * relative deviation from calibration curve
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
VNIIM
NMi 133436
NMi 226686
NMi 202677
BAM 5039
BAM 6028
CEM 6338
NMIJ 31833
LNE 606316
LNE 614734
KRISS 0773
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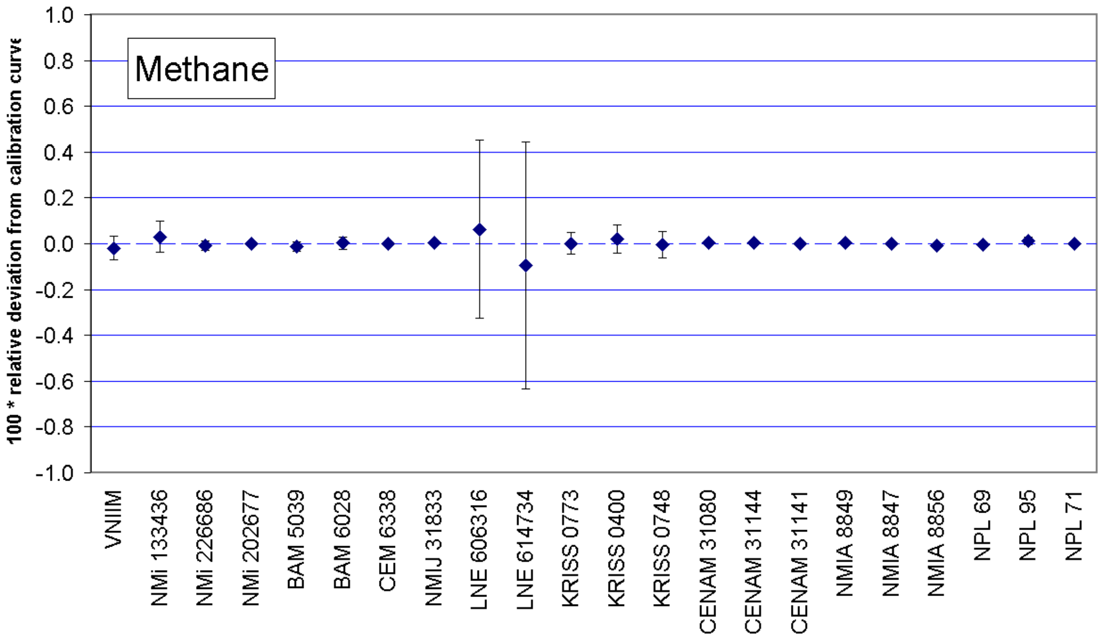
NPL 69
NPL 95
NPL 71


Methane
100 * relative deviation from calibration curve
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
VNIIM
NMi 133436
NMi 226686
NMi 202677
BAM 5039
BAM 6028
CEM 6338
NMIJ 31833
LNE 606316
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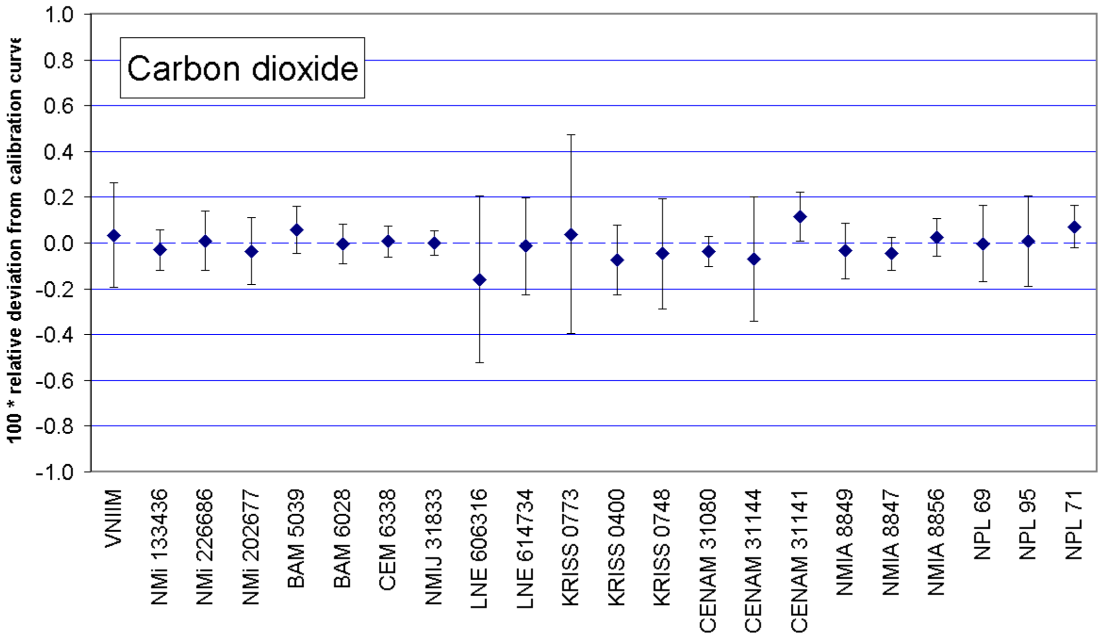
Carbon dioxide
100 * relative deviation from calibration curve
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
VNIIM
NMi 133436
NMi 226686
NMi 202677
BAM 5039
BAM 6028
CEM 6338
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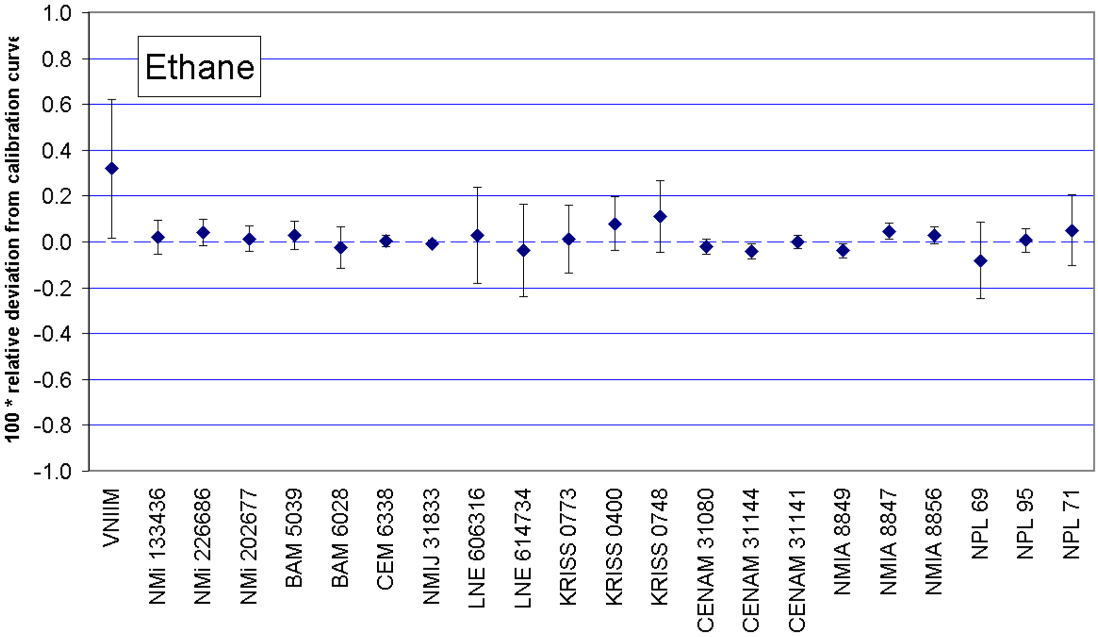
Ethane
100 * relative deviation from calibration curve
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
VNIIM
NMi 133436
NMi 226686
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BAM 5039
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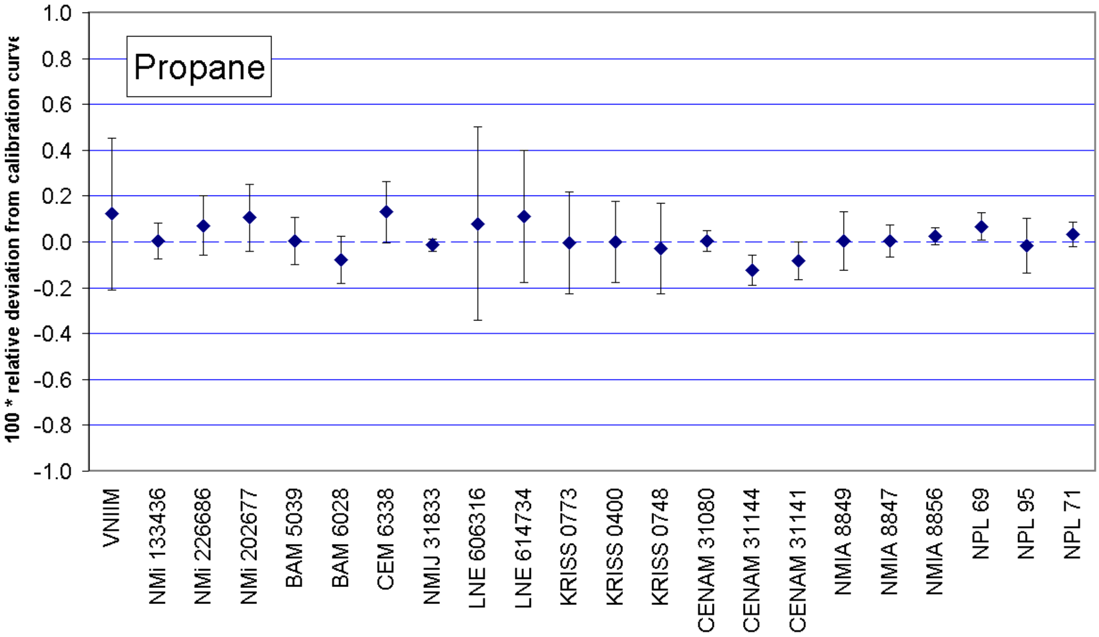
Propane
100 * relative deviation from calibration curve
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
VNIIM
NMi 133436
NMi 226686
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BAM 5039
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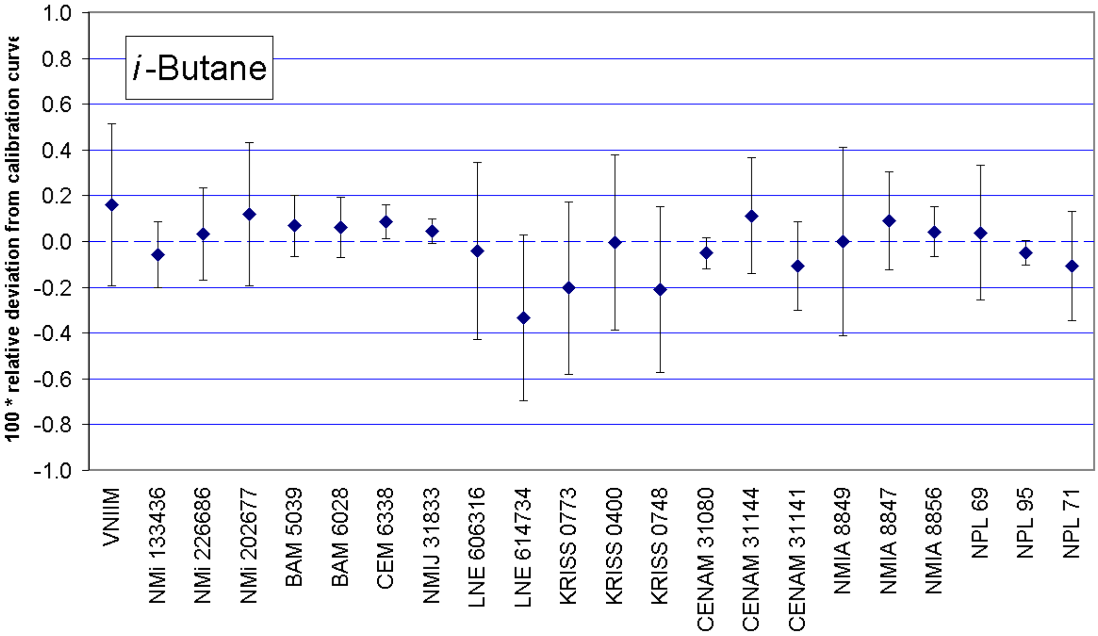
i-Butane
100 * relative deviation from calibration curve
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
VNIIM
NMi 133436
NMi 226686
NMi 202677
BAM 5039
BAM 6028
CEM 6338
NMIJ 31833
LNE 606316
LNE 614734
KRISS 0773
KRISS 0400
KRISS 0748
CENAM 31080
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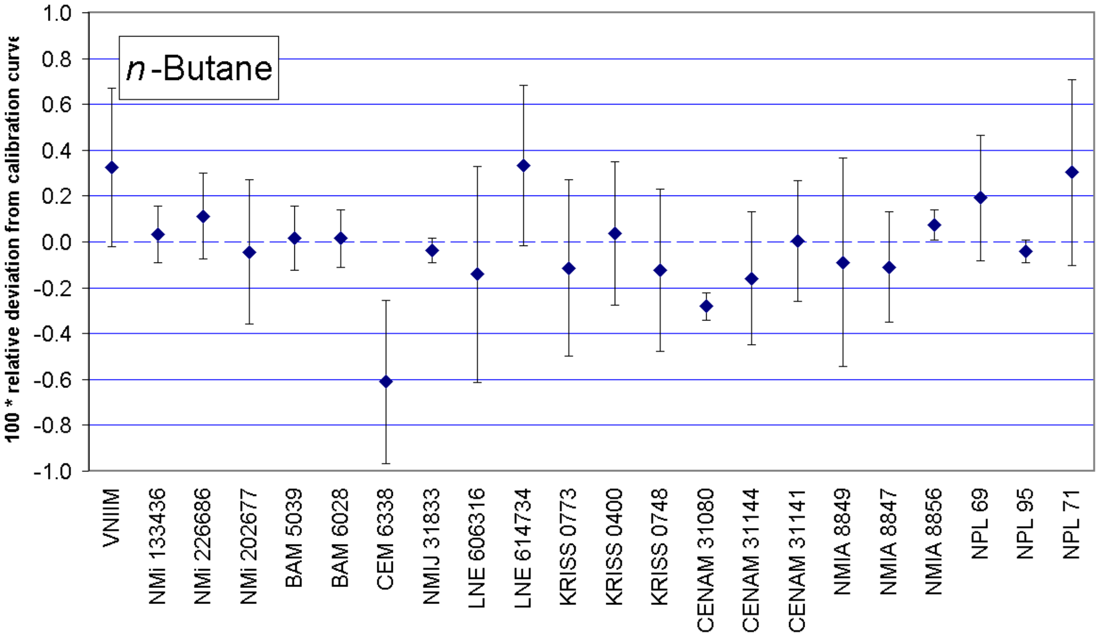
NPL 95
NPL 71


n-Butane
100 * relative deviation from calibration curve
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
VNIIM
NMi 133436
NMi 226686
NMi 202677
BAM 5039
BAM 6028
CEM 6338
NMIJ 31833
LNE 606316
LNE 614734
KRISS 0773
KRISS 0400
KRISS 0748
CENAM 31080
CENAM 31144
CENAM 31141
NMIA 8849
NMIA 8847
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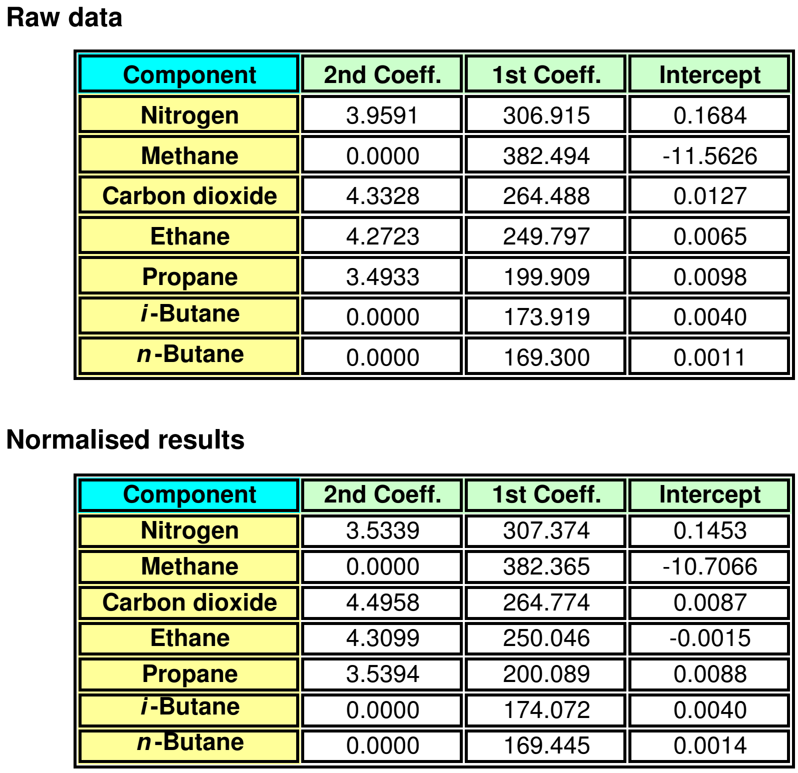
NPL 69
NPL 95
NPL 71



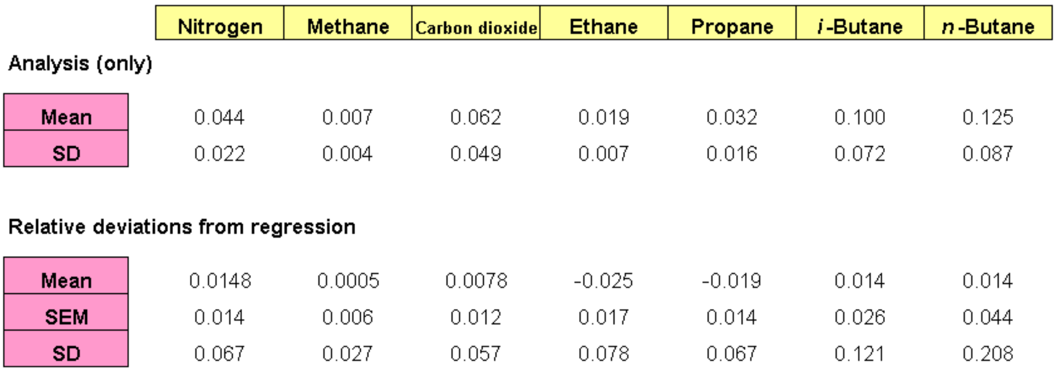
Raw data

Component	2nd Coeff.	1st Coeff.	Intercept
Nitrogen	3.9591	306.915	0.1684
Methane	0.0000	382.494	-11.5626
Carbon dioxide	4.3328	264.488	0.0127
Ethane	4.2723	249.797	0.0065
Propane	3.4933	199.909	0.0098
i-Butane	0.0000	173.919	0.0040
n-Butane	0.0000	169.300	0.0011

Normalised results

Component	2nd Coeff.	1st Coeff.	Intercept
Nitrogen	3.5339	307.374	0.1453
Methane	0.0000	382.365	-10.7066
Carbon dioxide	4.4958	264.774	0.0087
Ethane	4.3099	250.046	-0.0015
Propane	3.5394	200.089	0.0088
i-Butane	0.0000	174.072	0.0040
n-Butane	0.0000	169.445	0.0014

Table 4: Terms in equations of best regression fits for each component.

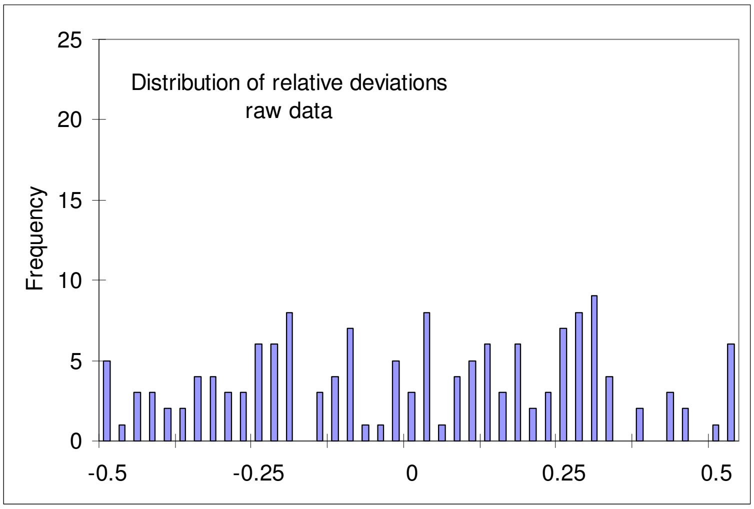


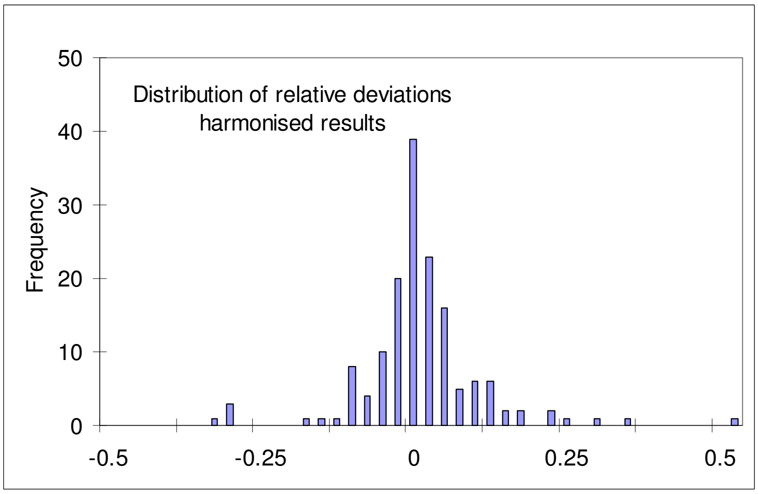
	Nitrogen	Methane	Carbon dioxide	Ethane	Propane	*i*-Butane	*n*-Butane
Analysis (only)							
Mean	0.044	0.007	0.062	0.019	0.032	0.100	0.125
SD	0.022	0.004	0.049	0.007	0.016	0.072	0.087
Relative deviations from regression							
Mean	0.0148	0.0005	0.0078	-0.025	-0.019	0.014	0.014
SEM	0.014	0.006	0.012	0.017	0.014	0.026	0.044
SD	0.067	0.027	0.057	0.078	0.067	0.121	0.208

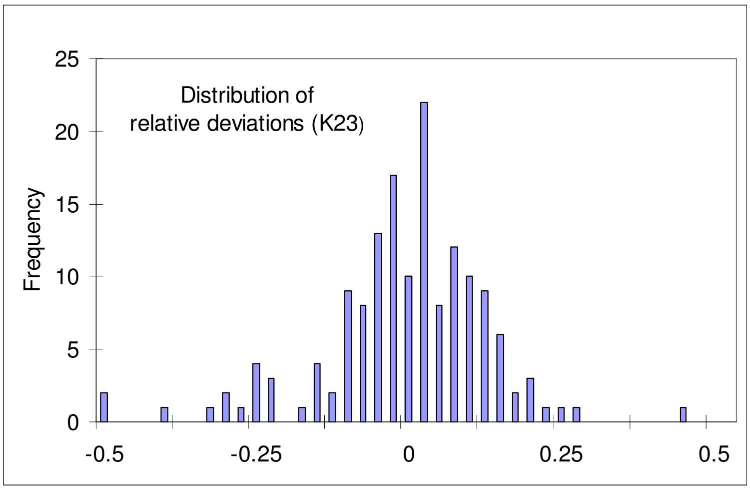
Table 5: Statistical measures for the analytical results and for the relative deviations from the regression lines. All expressed as relative measures (in %).

µmol/mol		Nitrogen		Methane		Carbon dioxide		Ethane		Propane		I-butane		n-butane	
		x	*U(X)*	*x*	*U(X)*	*x*	*U(X)*	*x*	*U(X)*	*x*	*U(X)*	*x*	*U(X)*	*x*	*U(X)*
VNIIM	**lo**	90.0	190.0	360.0	720.0	-78.0	98.0	-182.0	321.0	-87.0	109.0	-21.0	52.0	-30.0	52.0
NMi	**lo**	10.0	160.0	60.0	1000.0	2.0	80.0	-34.0	257.0	-18.0	100.0	-12.0	24.0	-12.0	37.0
NMi	**hi**	-27.2	72.2	-299.5	1114.5	5.7	29.9	-14.3	62.2	7.5	32.7	0.4	5.9	2.3	5.8
NMi	**med**	-121.2	171.7	-269.2	904.3	2.5	21.1	-15.5	91.4	0.8	16.4	1.1	4.3	1.3	3.4
BAM	**hi**	3.2	121.8	-47.8	906.3	14.3	50.1	21.7	91.0	8.2	50.0	4.9	16.1	-0.6	15.8
BAM	**lo**	-70.0	90.0	-20.0	610.0	-9.0	39.0	96.0	119.0	41.0	44.0	-12.0	14.0	5.0	16.0
BAM	**med**	-461.3	1100.3	-960.0	2451.6	-25.7	80.3	13.8	121.1	-15.4	54.4	-0.3	14.1	-1.2	14.1
NMIJ	**lo**	-60.0	130.0	-490.0	1740.0	25.0	90.0	-80.0	240.0	10.0	51.0	1.0	21.0	9.0	18.0
LNE	**med**	97.0	630.5	406.1	3901.0	6.5	21.1	2.6	75.7	3.8	24.0	1.1	4.5	2.6	4.9
LNE	**hi**	22.5	290.5	572.6	6000.0	-3.4	24.1	-0.9	66.9	-14.8	30.1	3.8	7.5	-5.3	7.4
KRISS	**med**	8.1	132.3	-37.5	745.2	-1.4	24.9	0.1	53.5	4.0	13.8	0.9	5.2	1.7	4.3
KRISS	**lo**	30.0	130.0	-50.0	780.0	19.0	59.0	-51.0	162.0	5.0	80.0	7.0	34.0	-8.0	35.0
KRISS	**hi**	48.7	94.6	-48.3	1000.3	-8.6	57.1	-31.2	62.1	4.0	24.1	2.7	7.1	1.0	7.1
CENAM	**lo**	-80.0	580.0	150.0	5930.0	-52.0	223.0	104.0	1206.0	-99.0	313.0	-2.0	101.0	43.0	141.0
CENAM	**med**	14.8	1300.2	0.0	0.0	2.9	36.6	56.8	340.4	4.3	65.3	-4.2	13.1	0.6	12.1
CENAM	**hi**	59.6	460.3	0.0	0.0	0.5	65.0	-46.9	240.5	-61.0	92.0	-5.0	17.1	3.7	17.1
NMIA	**med**	-61.9	276.3	-515.8	739.2	-0.9	13.7	-16.3	42.6	-4.6	14.5	-1.2	9.3	-0.4	10.2
NMIA	**hi**	-28.5	48.8	-414.1	459.3	-4.3	18.5	-14.1	31.6	-7.6	18.5	-2.0	9.3	-2.8	9.3
NMIA	**lo**	-40.0	110.0	400.0	1090.0	-24.0	55.0	76.0	128.0	52.0	48.0	9.0	21.0	21.0	17.0
NPL	**med**	0.8	123.8	2.9	582.8	0.3	10.5	3.7	53.2	-1.7	10.1	0.6	4.6	-2.3	3.9
NPL	**lo**	-70.0	140.0	80.0	620.0	-15.0	55.0	18.0	136.0	-7.0	65.0	-5.0	17.0	5.0	19.0
NPL	**hi**	-23.0	55.0	37.0	659.1	-3.2	19.8	5.4	67.9	-6.5	18.3	2.1	7.8	-5.0	6.7

Table 6 Degrees of equivalence and uncertainty for participating laboratories in corresponding phases of CCQM K23. The levels correspond with the parts of K23 as follows: hi=K23a, med=K23c, lo=23b.







Measure	Raw Data	Harmonised Results	Relative deviations from K23
Mean	0.0023	0.0011	-0.018
SEM	0.024	0.0084	0.011
SD	0.30	0.10	0.14

Table 7: Statistical measures applied to the relative deviations (in % relative to value) for the raw data and the normalised results.

Conclusions

This study has proved the word-wide comparability of the standards of synthetic natural gas prepared by the participants. The level of comparability is slightly better than the average uncertainties submitted by the laboratories. In general the estimates of uncertainty appear to be realistic, but in some cases there is evidence that the evaluation process could be improved.

The harmonisation process proved to be useful and effective in removing the non-random part of the variations in the raw measurement data. It is very interesting that whilst the absolute peak areas varied by approximately +/-0.3%, no changes were observed between the relative responses of the different components. Harmonisation plays a similar role in improving calibration data to that played by normalisation for measurement data. Providing the relative responses are stable, both methods can be used without any restriction in the case of harmonisation and with the simple restriction that all components must be measured when normalisation is used.

Reference

[1] G Vargha, M J T Milton, M G Cox, S Kamvissis 2005 “Harmonisation of coupled calibration curves to reduce correlated effects in the analysis of natural gas by gas chromatography”. *Journal of Chromatography A*, 1062, 239-245

[2] M J T Milton, F Guenther, W R Miller and A S Brown 2006 “Validation of the gravimetric values and uncertainties of independently prepared primary standard gas mixtures” *Metrologia* **43** L7-L10.

[3] Milton M J T, Harris P M, Smith I M, Brown A S, Goody B A 2006 Implementation of a generalized least-squares method for determining calibration curves from data with general uncertainty structures *Metrologia* **43** S291-S298.

Annex A – Mathematical description of the Harmonisation method

Suppose we carry out a calibration with *N* standard gas mixtures, each of which includes a total of *Q* components. During the analysis of standard mixture j, the amount (n_{ij}) of component i introduced into the GC from the sample loop can be calculated by use of the ideal gas law:

$$n_{ij} = \frac{p_j V}{T_j R} x_{ij} \tag{1}$$

where p_j is the pressure of the gas in the sample loop and T_j is its temperature at the time of the analysis, *V* is the volume of the sample loop and *R* is the ideal gas constant. The amount fraction of component i in standard j is denoted x_{ij} and is defined by

$$x_{ij} = \frac{n_{ij}}{n_j} \tag{2}$$

where the total amount of all components is

$$n_j = \sum_{i=1}^{Q} n_{ij} \tag{3}$$

Throughout this paper we present more general relationships that are valid for any value of q less than or equal to *Q*. The integrated area (y_{ij}) recorded by the detector in response to component i in standard j is

$$y_{ij} = r_i n_{ij} \tag{4}$$

where r_i is the relative response factor for the detector to component j. Expression (4) assumes that the detector has a proportional response. In some cases, there may be some non-linearity in the response of the detector in which case a quadratic term can be introduced. Substituting expression (4) into expression (1) leads to the measurement equation for this process:

$$y_{ij} = r_i \frac{p_j V}{T_j R} x_{ij} \tag{5}$$

3.2 Formulation of calibration curves using an ordinary least squares model

In line with the conventional approach to developing a calibration curve for each component i, we would fit the model equation

$$y_{ij} = \alpha_i + \beta_i x_{ij} + \eta_{ij} \tag{6}$$

to the measured data by linear regression, where represents an effect presumed to be random and aj allows for any offset in the detector output during analysis j. The use of this approach assumes that all uncertainties are associated with the y_{ij} and therefore those associated with the x_{ij} are negligible. Since the objective of this work is to develop a calibration curve that can be used to determine the value of an unknown, we fit an "inverse calibration" model of the form:

$$x_{ij} = a_i + b_i y_{ij} + e_{ij} \tag{7}$$

by minimising the sum of the squares of the residual deviations $\sum_{i,j}(x_{ij} - \hat{x}_{ij})^2$, where x is the measured value and $\hat{x}$ the corresponding model value. The use of this inverse calibration model is valid when any quadratic component in the response of the detector is small.

The principal objective of the harmonisation method described here is to remove the non-random effect from the measured data and hence to improve the fit of the calibration curves to the data. The method compensates for the systematic contribution to the residual deviations from the fitted lines and leads to a corrected set of measurement responses with the covariation reduced.

The harmonisation method is based on the use of a set of multiplicative correction factors ci that compensate for variations in ambient and instrumental conditions by correcting the ratio pj/Tj experienced during the analysis of standard j to "standard" conditions p0/T0 defined by

$$c_j \frac{p_j}{T_j} = \frac{p_0}{T_0} \tag{9}$$

Substitution of expression (9) into equation (5) leads to a modified measurement equation:

$$y_{ij} = \frac{r_i}{c_j} \frac{p_0 V}{T_0 R} x_{ij} \tag{10}$$

Although the c_j are shown in expression (9) as factors that are multiplied by the ratio of the pressure to the temperature, they also implicitly account for any other multiplicative effect including, for example, detector sensitivity changes. The modified measurement equation can be re-arranged into the form

$$x_{ij} = \frac{1}{r_i} \frac{T_0 R}{p_0 V} c_j y_{ij} \tag{11}$$

This form of the modified measurement equation mixes the errors in the ci with those in y_{ij} and r_i. Our studies show that this does not cause any significant difficulty in the examples considered here [8]. A modified regression model equation can now be fitted to the measured data

$$\hat{x}_{ij} = \hat{a}_i + \hat{b}_i c_j \hat{y}_{ij} + \hat{d}_i (c_j \hat{y}_{ij})^2 + e_{ij} \qquad (12)$$

where e_{ij} is a normally-distributed random variable with zero mean. This modified model equation differs from the model (7) by the introduction of the correction factors cj on the right-hand side and a quadratic term to model a quadratic deviation from linearity in the response of the detector.

For reasons given elsewhere [8], to obtain a physically feasible least squares solution to this model requires the introduction of a constraint. In the examples presented here, the constraint used is

$$\sum_{j=1}^{N} c_j = N \qquad (13)$$

The incorporation of this constraint is equivalent to imposing the requirement that the standard conditions (p_0/T_0) to which all measurements are corrected are the mean of all the measurement conditions:

$$\frac{p_0}{T_0} = \frac{1}{N} \sum_{j=1}^{N} \frac{p_j}{T_j} \qquad (14)$$

Annex B – Protocol for CCQM-P87

Objectives

The proposal for CCQM-P87 was approved at the meeting of the CCQM GAWG in October 2005. Its benefit will be that it brings added value to existing work carried out on synthetic natural gas for CCQM-K26. It will only require a small amount of additional work from participants. The data will be processed using NPL's published "harmonisation" method [1], which represents a development of the model established for "preparative comparisons" [2] by CCQM-P23 and CCQM-P41.

The results of the study will provide the best demonstration so far of the comparability of standards of synthetic natural gas prepared by NMIs. It will also provide insight into the results of CCQM-K23.

Participants

The study requires independent standards, which need not be from different laboratories. They should represent a spread across the three different mixtures used for CCQM-K23 (see Table). The following laboratories have agreed to send standards used for CCQM-K23 to NPL for use in CCQM-P87:

Multi-component preparative study			
			Coordinating lab = NPL
NPL (3)	NMi (3)	CENAM (?)	CEM(?)
BAM (3)	KRISS (3)	NRCCRM(?)	SMU(?)
NMIA (3)	NMIJ (1) (?)		LNE (?)
VNIIM (3)			
The numbers in brackets indicate the number of standards that will be supplied for the study.			
			Total = 12

Component [mmol/mol]	**Mixture 1**	**Mixture 2**	**Mixture 3**
nitrogen	40	70	135
carbon dioxide	10	30	5
ethane	30	94	30
propane	10	34	5
n-butane	2	10	1
iso-butane	2	8	1
methane	906	754	823

Table B1: Nominal values of standards used for CCQM-K23

Analytical method to be used by the coordinating laboratory

The analysis method uses two high-performance micro-packed columns in parallel with a ten-port diaphragm sampling valve, placed in the main oven of a Varian 3800 GC. A Porapak R column (8.8 m long, 0.75 mm ID) is connected to a thermal conductivity detector (TCD), and a Porapak P column (4.4 m long, 0.75 mm ID) is connected to a flame ionisation detector (FID). Both columns are made from 1/16" stainless steel tubing and packed with 100-120 mesh particles. The carrier gas is helium with a head pressure of 12 bar, the isothermal oven temperature is 160 Celsius.

These columns have very high separation power. Even when operating at this relatively high temperature there is baseline separation between nitrogen and methane. Although carbon dioxide and ethane naturally elute on the tail of the methane peak, there is no integration problem. Narrow peaks and good separation give a very repeatable baseline allocation.

Hydrocarbon components are separated on both columns and can be measured on both detectors. For lower concentration components, the FID improves the precision of the measurements.

For high quality gravimetric standards, harmonised calibration makes a very good fit. For example using the TCD we have achieved 0.05 % average relative deviation for 60 calibration points of the five main components of 12 newly prepared synthetic natural gas standards. This 0.05% covers all gravimetric, measurement and fitting uncertainty for the whole measurement range of these components. This makes it possible to compare standards with large concentration differences.

Timetable

- NPL prepares and distributes protocol and invites participation (Feb 06)
- Participants submit standards to NPL (by end April 06)
- Results available (June 06)
- Discussion of results at GAWG (Oct 06)
- Return of standards to participating laboratories (Nov 06)

Annex C - List of Participants

Laboratory	Country	Contact name	Address
BAM	Germany	Hans-Joachim Heine	Germany
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KRISS	South Korea	Jin Chun Woo	Korea Research Institute of Standards and Science, Division of Chemical Metrology & Materials Evaluation P. O. Box 102 Yusung, Taejon, 305-600, Korea
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