

CCQM-K27 (a, b) Key Comparison – Determination of Ethanol in Aqueous Matrix

Final Report

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Introduction

Following a pilot study on the determination of ethanol in aqueous matrix (CCQM-P35), it was decided at the meeting of the CCQM held at Sèvres on 18 – 19 April 2002 to carry out a key comparison also based on the determination of ethanol in aqueous matrix. Ethanol is important forensically. For example, drink/drive regulations in most countries rely on not only accurate measurements but on ethanol standards in order to enforce the legislation. It is essential that countries have the ability to prepare and accurately measure such standards. Ethanol is also a commodity that is traded worldwide, e.g., wine. It is subject to excise duties, which can be large and vary from country to country. The accurate determination of ethanol content is not only essential but must be reproducible and equivalent across national boundaries.

This key comparison is designated as CCQM-K27a for forensic matrices and CCQM-K27b for commercial matrices. For the pilot study CCQM-P35 participants used gas chromatography with flame ionisation detection (GC-FID), titrimetry, isotope dilution gas-chromatography-mass spectrometry (GC-IDMS), gas chromatography-combustion-isotope ratio mass spectrometry (ID-GC-C-IRMS) and nuclear magnetic resonance spectroscopy (NMR). Results using NMR were somewhat scattered and the decision was made at the CCQM Organic Working Group meeting held at Sèvres on 14-15 April 2002 that the NMR method would be excluded from the key comparison in that participants could use NMR but those results would not be used in the calculation of the key comparison reference value (KCRV) or the uncertainty of the KCRV and would be excluded from the tables and graphs of equivalence. Results using NMR will be the subject of a separate report (analogous to a pilot study).

The participants were:

Australia, National Analytical Reference Laboratory (NARL)*
China, National Research Centre for Certified Reference Materials (NRCCRM)
France, Laboratoire National d'Essais (LNE)
Germany, Bundesanstalt für Materialforschung und -prüfung (BAM)
Japan, National Metrology Institute of Japan (NMIJ)
Korea, Korea Research Institute of Standards and Science (KRISS)

Russia, D. I. Mendeleev Institute for Metrology of Gosstandart of Russia (VNIIM)[†]
United Kingdom, Laboratory of the Government Chemist (LGC)
USA, National Institute of Standards and Technology (NIST)

* participant did not take part in the pilot study (CCQM-P35), consequently this participant's results will not be used in the determination of the key comparison reference value (KCRV) or the uncertainty of the KCRV.

[†] participant used a method (headspace-GC-FID) that had not been validated by the pilot study (CCQM-P35), consequently this participant's results will not be used in the determination of the key comparison reference value (KCRV) or the uncertainty of the KCRV.

Pilot Study

A pilot study (CCQM-P35) on the determination of ethanol in an aqueous matrix was held in 2001. The coordinating laboratories were BAM (responsible for NMR methods) and LGC (responsible for non-NMR methods and sample distribution). For this pilot study, participants were provided with two samples. One was an aqueous solution prepared by spiking gravimetrically with ethanol and represented forensic standards (Sample A). The reference value of this forensic sample (Sample A) was 1.072 ± 0.006 mg g⁻¹ (expanded uncertainty). The other was a commercial white wine, representing a traded commodity (Sample B) with a mean mass fraction of ethanol in white wine (non-NMR methods) of 101.56 ± 2.17 mg g⁻¹ (expanded uncertainty). Participants were free to use any analytical technique for this study. For those participants using NMR, additional information was provided by BAM. Non-NMR participants were required to carry out measurements using their own calibration standards. Participants were supplied with duplicate bottles of Samples A and B and were required to take two aliquots from each sample bottle and analyse each aliquot in each of two instrumental runs (8 determinations in all for each sample). Participants were requested to report results on an absolute basis (corrected for chemical purity of their calibration standard material) together with full uncertainty budgets.

Results were received from ten participants, some using more than one technique. There were five sets of results using GC-FID, one set using GC-IDMS, one set using ID-GC-C-IRMS, one result using titrimetry (Sample A only) and eight sets using NMR. The results using NMR were somewhat scattered, this was principally due to the participants using incorrect experimental conditions. The non-NMR results showed good accuracy for all methods used. For the non-NMR results, those of Sample B (RSD 2.3%) showed no better precision than those of Sample A (RSD also 2.3%) despite having a mass fraction of ethanol about 100 times that of Sample A. This was attributed to the fact that Sample A was a solution of ethanol in water whilst Sample B was a matrix solution which had the potential for interferences from the matrix affecting accuracy.

In terms of uncertainty of the non-NMR results, there were considerable differences between the reported uncertainties of the results for both Samples A and B. In part this

was a reflection of the different methods used, for example, ID-GC-C-IRMS is a very precise technique exhibiting very low uncertainties. The major contributions to the uncertainty budget for all participants were the precision of the measurements (both sample and calibration solutions) and the purity of the calibration material. For Sample B, for example, the uncertainty component for the precision of measurement varied from 0.13 mg g^{-1} to 0.98 mg g^{-1} between participants whilst the component due to calibration solution purity varied from 0.05 mg g^{-1} to 1.01 mg g^{-1} . It was these factors that accounted for the wide variation of uncertainties between participants, the calculation of the uncertainty budgets was reasonably consistent between participants. Following discussion of the results amongst participants at the 2002 meeting of the CCQM Organic Working Group the CCQM directed the Organic Working Group to proceed to a key comparison based on the use of the non-NMR methods used in the pilot study.

Key Comparison

The key comparison involved sending three samples to participants for measurement of the mass fraction of ethanol. Two samples (Samples A and B) were aqueous solutions that had been spiked gravimetrically with ethanol (at mass fractions of ethanol representing forensic standards, CCQM-K27a), the other (Sample C) was a commercial (red) wine (representing a traded commodity, CCQM-K27b). The commercial wine was stabilised by irradiation to prevent fermentation before opening.

A draft protocol was drawn up and circulated to prospective participants and to the Organic Working Group Chairman. The protocol was agreed and participation was finalised with samples being circulated to the participants in early August 2002. It was recommended in the protocol that for the commercial wine sample (Sample C) sterile containers should be used for all sample solutions and air-borne contamination should be avoided. This was to prevent fermentation after opening the sample, which could increase the ethanol mass fraction. It was also recommended that analysis of Sample C be carried out as soon as possible after opening to further minimise the risk of fermentation. It was specified that the samples and sample solutions should be stored in the dark at refrigerator temperature (not exceeding 4°C).

Participants were responsible for the methods they used (either GC-FID, GC-IDMS, ID-GC-C-IRMS or titrimetry) and for providing their own calibration and isotopic analogue materials (where appropriate). Participants were supplied with duplicate bottles of Samples A, B and C and were required to take two aliquots from each sample bottle and analyse each aliquot in each of two instrumental runs (8 determinations in all for each sample). Sample A and B vials each contained approximately 50 mL of sample, Sample C vials contained 250 mL of sample. Participants were requested to report results on an absolute basis (corrected for chemical purity of their calibration standard material) together with the associated overall uncertainty. It was also necessary for participants to submit a full uncertainty budget.

For measurement using GC-FID techniques the mass fraction of ethanol C_x in the samples, in mg g^{-1} , is given by the general equation:

$$C_X = \frac{C_Z \times A_S \times f_D}{A_C} \quad (1)$$

where:

C_Z is the mass fraction of ethanol in the calibration solution in mg g^{-1} ;
 A_S is the area of the ethanol peak in the chromatogram of the sample;
 A_C is the area of the ethanol peak in the chromatogram of the calibration standard solution;
 f_D is the sample dilution factor

For measurement using IDMS techniques the mass fraction of ethanol C_X in the samples, in mg g^{-1} , is given by the general equation:

$$C_X = C_Z \times \frac{M_Y}{M_X} \times \frac{M_{Zc}}{M_{Yc}} \times \frac{R_Z - R_{Bc}}{R_{Bc} - R_Y} \times \frac{R_Y - R_B}{R_B - R_Z}$$

where: C_Z = is the mass fraction of ethanol in the calibration solution in mg g^{-1}
 M_Y = Mass of spike Y added to the sample X to prepare the blend B
 M_{Zc} = Mass of calibration solution Z added to the spike Y to make calibration blend Bc
 M_X = Mass of sample X added to the spike Y to prepare the blend B
 M_{Yc} = Mass of spike Y added to the calibration solution Z to make calibration blend Bc
 R_Y = Ratio of unlabelled/labelled ion in spike solution
 R_Z = Ratio of unlabelled/labelled ion in sample/calibration solution
 R_B = Ratio of unlabelled/labelled ion in sample blend B
 R_{Bc} = Ratio of unlabelled/labelled ion in calibration blend Bc

Results

Dates of study: April 2002 to November 2002.

The following participants submitted full sets of results (date of measurement in brackets):

BAM (October 2002), LGC (August 2002), LNE (October 2002), NARL (September-October 2002), NIST (September-October 2002), NMIJ (September-October 2002), NRCCRM (October 2002), VNIIM (October-November 2002).

KRISS (October 2002) submitted results for Samples A and B only.

The results are shown in tabular form in Tables 1 to 3 and graphically in Figures 1 to 3. The uncertainty bars in Figures 1 to 3 represent expanded uncertainties. Figures 1 to 3 also show the key comparison reference value (KCRV) together with the upper and lower limits of the 95 % confidence interval (C. I.) of the KCRV as described in Appendix 1. The Tables and Graphs of Equivalence are shown in Appendix 2 as Tables 4 to 6 and Figures 4 to 6 respectively.

Uncertainty budgets for each of the participating NMIs are shown in Appendix 3 (Tables 7 to 15).

Discussion

For this key comparison participants used GC-FID, GC-IDMS or ID-GC-C-IRMS. These techniques were shown capable of producing accurate results in the corresponding pilot study (CCQM-P35). One participant used static headspace-GC-FID (technique not validated by pilot study CCQM-P35). The results of this key comparison show an improvement over those for the pilot study. The RSD for Sample A is 1.5% compared to 2.3% for a similar mass fraction for the pilot study. For the wine sample (Sample C) corresponding RSD's are 0.44% for this key comparison and 2.3% for the pilot study.

It should be noted that in this key comparison no participant withdrew or changed their results. No requests for follow up bilaterals were received.

With reference to uncertainties there were some differences between the reported uncertainties for all of the samples. As for the pilot study this was in part a reflection of the different methods used, for example, ID-GC-C-IRMS is a very precise technique exhibiting very low uncertainties. The principal components of the uncertainty budget for all participants, as set out in the protocol, were the precision of the measurements (both sample and calibration solutions) (Type A) and the purity of the calibration material (Type B). The precision and purity components varied substantially between participants and it is these factors that account for the variation of uncertainties between participants, the calculation of the uncertainty budgets was reasonably consistent between participants. Minor sources of uncertainty included balance linearity when carrying out weighing by difference. It was recognised that not all participants would carry out their measurements by the same method or use the same type of calibration procedure, consequently participants were asked to identify other uncertainty components applicable to their own procedure. As a consequence some participants included additional uncertainty components, relevant to their particular institute. These included an uncertainty contribution for evaporation (Tables 7a – 7c, 11b and 11c), a matrix effect for Sample C

(Table 7c), a recovery correction (Tables 7a – 7c) and the thermostating temperature used in conjunction with static headspace-GC-FID (Tables 15a – 15c).

Conclusions

This key comparison has demonstrated the ability of participating NMI's to measure ethanol in aqueous matrix both at a low mass fraction (0.8 mg g^{-1}) in forensic solutions and at the typical mass fraction of ethanol found in a wine matrix (80 mg g^{-1}). The measurements achieved here are an improvement over the corresponding pilot study (CCQM-P35), achieving better RSD values at both a low mass fraction of ethanol and at the mass fraction of ethanol found in wine. This demonstration of capability will enable forensic ethanol standards to be compared across national boundaries. Likewise the ability to measure the typical mass fraction of ethanol found in wine is important since such commodities are traded worldwide and are liable to varying levels of excise duty. Thus this successful key comparison has demonstrated a broad range of capability by NMI's for the measurement of ethanol both for forensic and excise purposes.

Acknowledgements

The participation of scientists from BAM (Germany), KRISS (Korea), LGC (United Kingdom), LNE (France), NARL (Australia), NIST (USA), NMIJ (Japan), NRCCRM (China) and VNIIM (Russia) is gratefully acknowledged.

Table 1 Results CCQM-K27a: Sample A

Laboratory	Technique	Mean Result mg g ⁻¹	Std. Uncertainty mg g ⁻¹	Exp. Uncertainty mg g ⁻¹
BAM	GC-FID	0.8029	0.0025	0.0049
KRISS	GC-FID	0.8013	0.0050	0.010
LGC	ID-GC-C-IRMS	0.8034	0.0004	0.0008
LNE	GC-IDMS	0.8227	0.0070	0.014
NARL	GC-IDMS	0.8045	0.0015	0.0034
NIST	GC-FID	0.8180	0.0027	0.0087
NMIJ	GC-FID	0.8029	0.0011	0.0030
NRCCRM	GC-FID	0.8048	0.0018	0.0036
VNIIM	Headspace- GC-FID	0.780	0.004	0.008

Gravimetric value = 0.8040 mg g⁻¹; Std. Deviation of the mean = 0.00325 mg g⁻¹
(excluding NARL and VNIIM); Degrees of freedom = 6 Coverage factor k = 2.447
Expanded uncertainty U = 0.0080 mg g⁻¹

Table 2 Results CCQM-K27a: Sample B

Laboratory	Technique	Mean Result mg g ⁻¹	Std. Uncertainty mg g ⁻¹	Exp. Uncertainty mg g ⁻¹
BAM	GC-FID	120.88	0.38	0.77
KRISS	GC-FID	120.55	0.69	1.38
LGC	ID-GC-C-IRMS	120.82	0.10	0.20
LNE	GC-IDMS	121.66	0.99	2.0
NARL	GC-IDMS	120.88	0.27	0.63
NIST	GC-FID	120.7	0.39	1.2
NMIJ	GC-FID	120.54	0.23	0.74
NRCCRM	GC-FID	120.73	0.30	0.60
VNIIM	Headspace- GC- FID	119.9	0.5	1.0

Gravimetric value = 120.90 mg g⁻¹; Std. Deviation of the mean = 0.145 mg g⁻¹
(excluding NARL and VNIIM); Degrees of freedom = 6 Coverage factor k = 2.447
Expanded uncertainty U = 0.35 mg g⁻¹

Table 3 Results CCQM-K27b: Sample C

Laboratory	Technique	Mean Result mg g ⁻¹	Std. Uncertainty mg g ⁻¹	Exp. Uncertainty mg g ⁻¹
BAM	GC-FID	81.11	0.26	0.51
KRISS	GC-FID	-	-	-
LGC	ID-GC-C-IRMS	81.35	0.08	0.15
LNE	GC-IDMS	81.07	0.73	1.5
NARL	GC-IDMS	81.33	0.33	0.66
NIST	GC-FID	81.28	0.31	0.79
NMIJ	GC-FID	81.60	0.11	0.31
NRCCRM	GC-FID	80.96	0.19	0.38
VNIIM	Headspace- GC-FID	80.4	0.6	1.2

Overall mean of mean results = 81.23 mg g⁻¹ (excluding NARL and VNIIM); Std. Deviation of the mean = 0.094 mg g⁻¹; Degrees of freedom = 5 Coverage factor k = 2.571 Expanded uncertainty U = 0.24 mg g⁻¹

Figure 1 Sample A Results showing KCRV and Upper and Lower Limits of the 95% C. I. of the KCRV (NARL and VNIIM excluded)

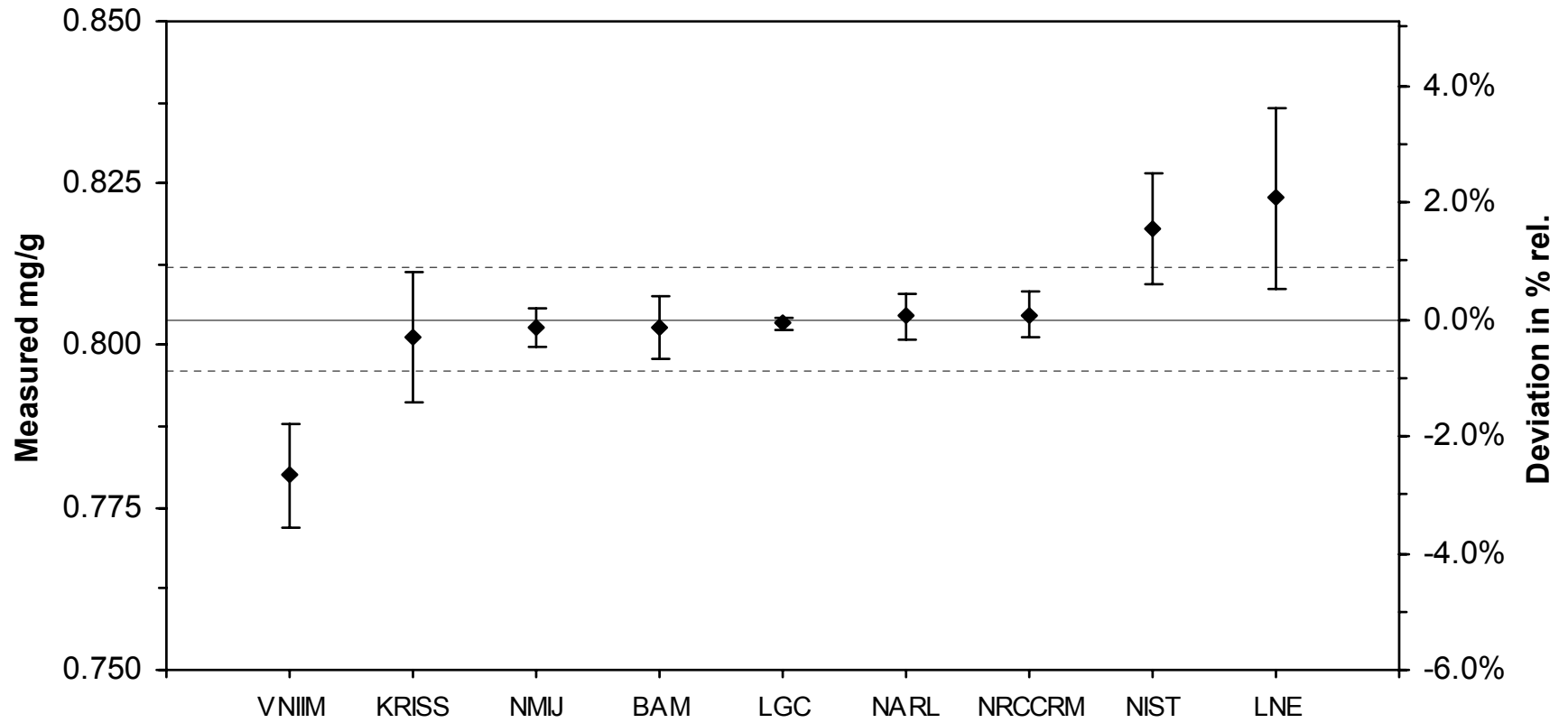


Figure 2 Sample B Results showing KCRV and Upper and Lower Limits of the 95% C. I. of the KCRV (NARL and VNIIM excluded)

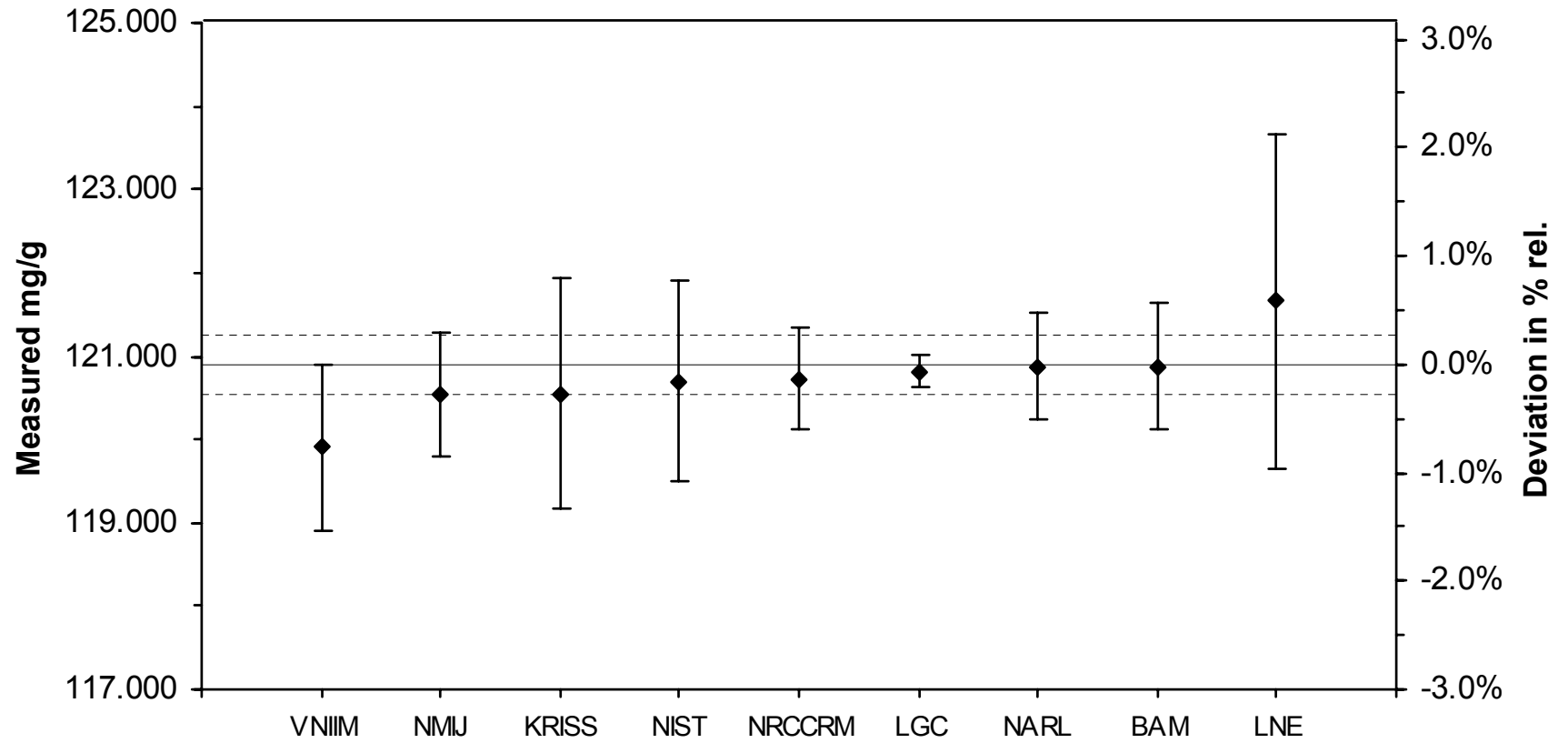
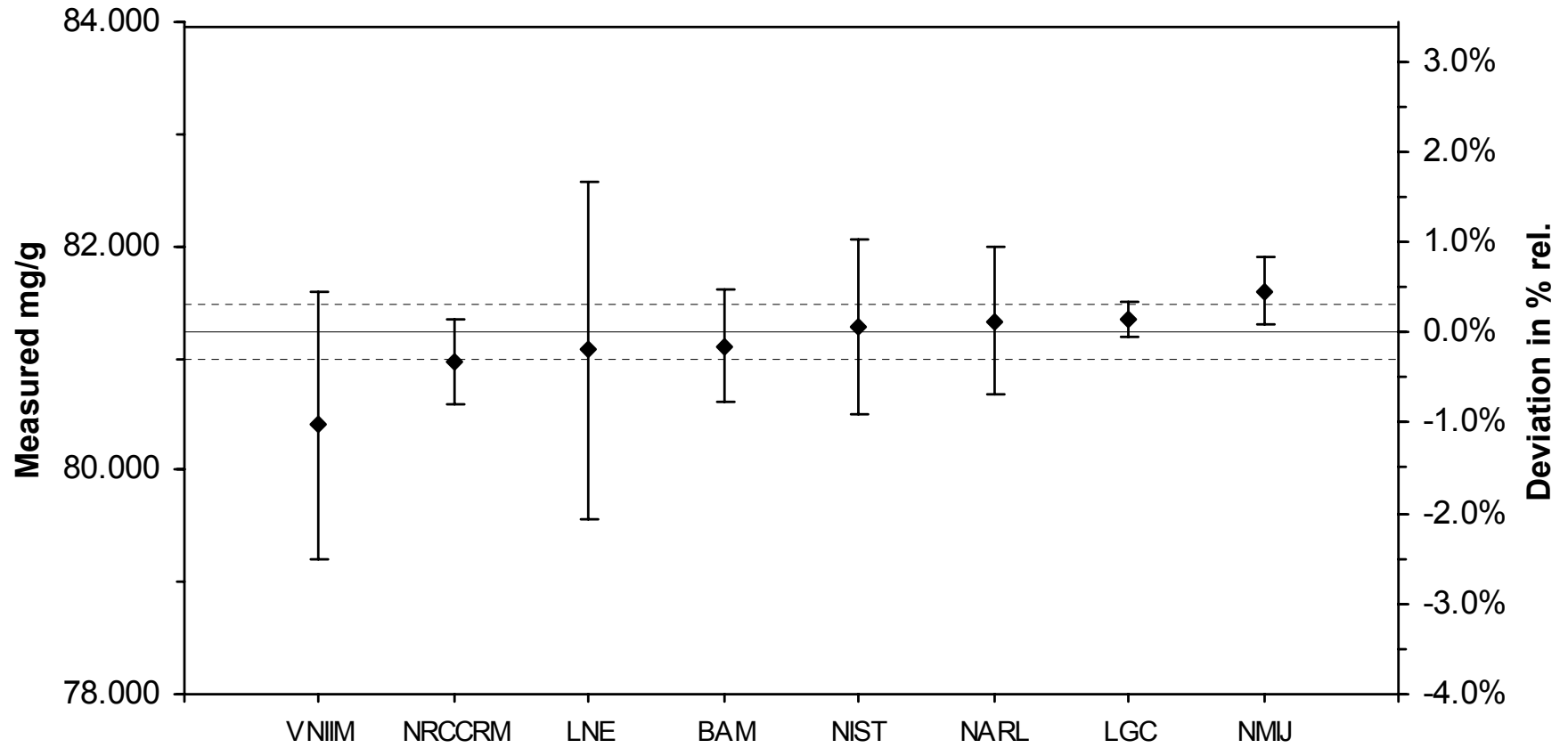


Figure 3 Sample C Results showing KCRV and Upper and Lower Limits of the 95% C. I. of the KCRV (NARL and VNIIM excluded)



Appendix 1

Key Comparison Reference Value (KCRV)

It was proposed that the KCRV for Samples A and B should be the gravimetrically prepared value with the standard deviation of the mean of the results taken as the standard uncertainty of the KCRV. For Sample C, it was proposed that the KCRV should be calculated as the mean of the results with the standard deviation of the mean taken as the standard uncertainty of the KCRV. This approach was agreed at a meeting of participants held at CSIR (Pretoria) in November 2002. The NARL results were not eligible to be included in the calculation of the KCRV (for Sample C) or the uncertainty of the KCRV (all samples) since NARL did not take part in the relevant pilot study (CCQM-P35). The VNIIM results were excluded from the calculation of the KCRV (Sample C) and the uncertainty of the KCRV (all samples) since VNIIM used a method (headspace-GC-FID) that had not been validated by the pilot study (CCQM-P35). The data contain a mix of degrees of freedom, consequently in order to calculate the coverage factor the Satterthwaite approximation is used. This results in a coverage factor for Sample A and B of 2.447 (6 degrees of freedom) and a coverage factor for Sample C of 2.571 (5 degrees of freedom). For Sample A, this calculation yields a KCRV of $0.8040 \pm 0.0080 \text{ mg g}^{-1}$ corresponding to a 95% confidence interval of 0.7960 mg g^{-1} to 0.8120 mg g^{-1} . For Sample B, the KCRV is $120.90 \pm 0.35 \text{ mg g}^{-1}$ corresponding to a 95% confidence interval of 120.55 mg g^{-1} to 121.25 mg g^{-1} . For Sample C the KCRV is $81.23 \pm 0.24 \text{ mg g}^{-1}$ corresponding to a 95% confidence interval of 80.99 mg g^{-1} to 81.47 mg g^{-1} . The Matrices and Graphs of Equivalence are shown in Appendix 2 as Tables 4 to 6 and Figures 4 to 6 respectively.

Appendix 2

Table 4 Matrix of Equivalence for Sample A (CCQM-K27a)

Measurand: mass fraction of ethanol in water

KCRV $0.8040 \pm 0.0080 \text{ mg g}^{-1}$

	KCRV																	
	D _i	U _i																
BAM	-0.0011	0.00879																
KRISS	-0.0027	0.01205																
LGC	-0.0006	0.00801																
LNE	0.0187	0.01544																
NARL	0.0005	0.00825																
NIST	0.0140	0.00956																
NMIJ	-0.0011	0.00811																
NRCCRM	0.0008	0.00828																
VNIIM	-0.0240	0.01053																
	BAM		KRISS		LGC		LNE		NARL		NIST		NMIJ		NRCCRM		VNIIM	
	D _{ij}	U _{ij}	D _{ij}	U _{ij}	D _{ij}	U _{ij}	D _{ij}	U _{ij}	D _{ij}	U _{ij}	D _{ij}	U _{ij}	D _{ij}	U _{ij}	D _{ij}	U _{ij}	D _{ij}	U _{ij}
BAM			0.002	0.011	-0.001	0.005	-0.020	0.015	-0.002	0.006	-0.015	0.008	0.000	0.005	-0.002	0.006	0.023	0.009
KRISS	-0.002	0.011			-0.002	0.010	-0.021	0.017	-0.003	0.010	-0.017	0.012	-0.002	0.010	-0.003	0.011	0.021	0.013
LGC	0.001	0.005	0.002	0.010			-0.019	0.014	-0.001	0.004	-0.015	0.009	0.001	0.003	-0.001	0.004	0.023	0.008
LNE	0.020	0.015	0.021	0.017	0.019	0.014			0.018	0.014	0.005	0.015	0.020	0.014	0.018	0.014	0.043	0.016
NARL	0.002	0.006	0.003	0.010	0.001	0.004	-0.018	0.014			-0.014	0.008	0.002	0.004	0.000	0.005	0.025	0.009
NIST	0.015	0.008	0.017	0.012	0.015	0.009	-0.005	0.015	0.014	0.008			0.015	0.008	0.013	0.008	0.038	0.010
NMIJ	0.000	0.005	0.002	0.010	-0.001	0.003	-0.020	0.014	-0.002	0.004	-0.015	0.008			-0.002	0.004	0.023	0.008
NRCCRM	0.002	0.006	0.003	0.011	0.001	0.004	-0.018	0.014	0.000	0.005	-0.013	0.008	0.002	0.004			0.025	0.009
VNIIM	-0.023	0.009	-0.021	0.013	-0.023	0.008	-0.043	0.016	-0.025	0.009	-0.038	0.010	-0.023	0.008	-0.025	0.009		

Table 5 Matrix of Equivalence for Sample B (CCQM-K27a)

Measurand: mass fraction of ethanol in water

KCRV $120.90 \pm 0.35 \text{ mg g}^{-1}$

	KCRV																	
	D_i	U_i																
BAM	-0.0200	0.81253																
KRISS	-0.3500	1.40942																
LGC	-0.0800	0.38377																
LNE	0.7600	2.00009																
NARL	-0.0200	0.67454																
NIST	-0.2000	1.15523																
NMIJ	-0.3600	0.66530																
NRCCRM	-0.1700	0.66674																
VNIIM	-1.0000	1.03971																
	BAM		KRISS		LGC		LNE		NARL		NIST		NMIJ		NRCCRM		VNIIM	
	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}
BAM			0.330	1.565	0.060	0.784	-0.780	2.112	0.000	0.938	0.180	1.198	0.340	0.901	0.150	0.959	0.980	1.244
KRISS	-0.330	1.565			-0.270	1.395	-1.110	2.392	-0.330	1.480	-0.150	1.609	0.010	1.455	-0.180	1.498	0.650	1.689
LGC	-0.060	0.784	0.270	1.395			-0.840	1.990	-0.060	0.642	0.120	1.281	0.280	0.645	0.090	0.630	0.920	1.019
LNE	0.780	2.112	1.110	2.392	0.840	1.990			0.780	2.049	0.960	2.133	1.120	2.031	0.930	2.063	1.760	2.204
NARL	0.000	0.938	0.330	1.480	0.060	0.642	-0.780	2.049			0.180	1.161	0.340	0.781	0.150	0.821	0.980	1.136
NIST	-0.180	1.198	0.150	1.609	-0.120	1.281	-0.960	2.133	-0.180	1.161			0.160	1.164	-0.030	1.163	0.800	1.327
NMIJ	-0.340	0.901	-0.010	1.455	-0.280	0.645	-1.120	2.031	-0.340	0.781	-0.160	1.164			-0.190	0.780	0.640	1.104
NRCCRM	-0.150	0.959	0.180	1.498	-0.090	0.630	-0.930	2.063	-0.150	0.821	0.030	1.163	0.190	0.780			0.830	1.157
VNIIM	-0.980	1.244	-0.650	1.689	-0.920	1.019	-1.760	2.204	-0.980	1.136	-0.800	1.327	-0.640	1.104	-0.830	1.157		

Table 6 Matrix of Equivalence for Sample C (CCQM-K27b)

Measurand: mass fraction of ethanol in wine

KCRV $81.23 \pm 0.24 \text{ mg g}^{-1}$

	KCRV															
	D_i	U_i														
BAM	-0.1200	0.55248														
LGC	0.1200	0.26474														
LNE	-0.1600	1.47178														
NARL	0.1000	0.67695														
NIST	0.0500	0.83271														
NMIJ	0.3700	0.32732														
NRCCRM	-0.2700	0.42500														
VNIIM	-0.8300	1.21401														
	BAM		LGC		LNE		NARL		NIST		NMIJ		NRCCRM		VNIIM	
	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}
BAM			-0.240	0.542	0.040	1.544	-0.220	0.828	-0.170	0.874	-0.490	0.565	0.150	0.638	0.710	1.301
LGC	0.240	0.542			0.280	1.468	0.020	0.669	0.070	0.823	-0.250	0.299	0.390	0.410	0.950	1.210
LNE	-0.040	1.544	-0.280	1.468			-0.260	1.593	-0.210	1.586	-0.530	1.476	0.110	1.505	0.670	1.872
NARL	0.220	0.828	-0.020	0.669	0.260	1.593			0.050	0.939	-0.270	0.687	0.370	0.750	0.930	1.359
NIST	0.170	0.874	-0.070	0.823	0.210	1.586	-0.050	0.939			-0.320	0.805	0.320	0.823	0.880	1.356
NMIJ	0.490	0.565	0.250	0.299	0.530	1.476	0.270	0.687	0.320	0.805			0.640	0.442	1.200	1.219
NRCCRM	-0.150	0.638	-0.390	0.410	-0.110	1.505	-0.370	0.750	-0.320	0.823	-0.640	0.442			0.560	1.255
VNIIM	-0.710	1.301	-0.950	1.210	-0.670	1.872	-0.930	1.359	-0.880	1.356	-1.200	1.219	-0.560	1.255		

Figure 4 CCQM-K27a
Degrees of Equivalence for Sample A

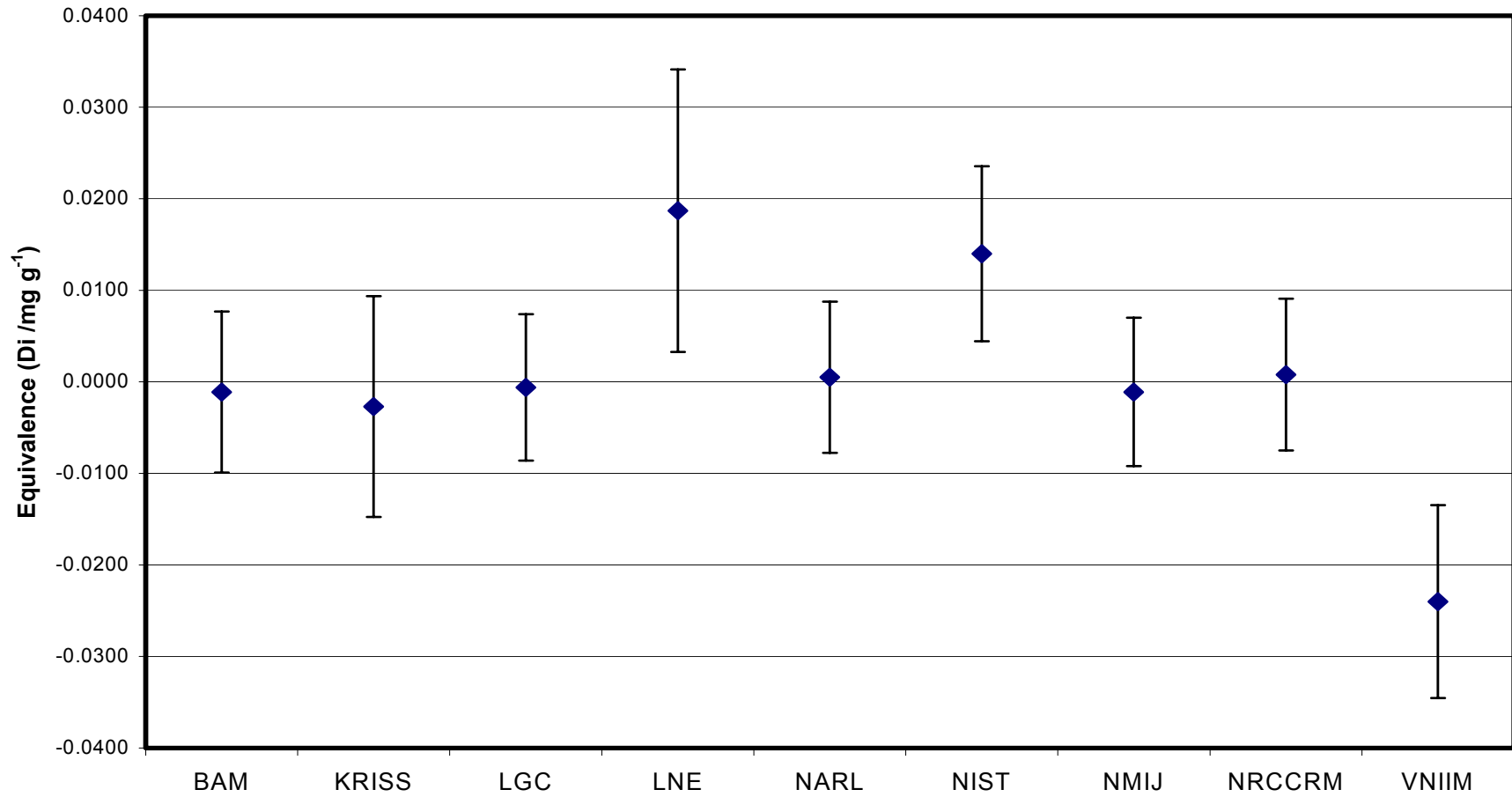


Figure 5 CCQM-K27a
Degrees of Equivalence for Sample B

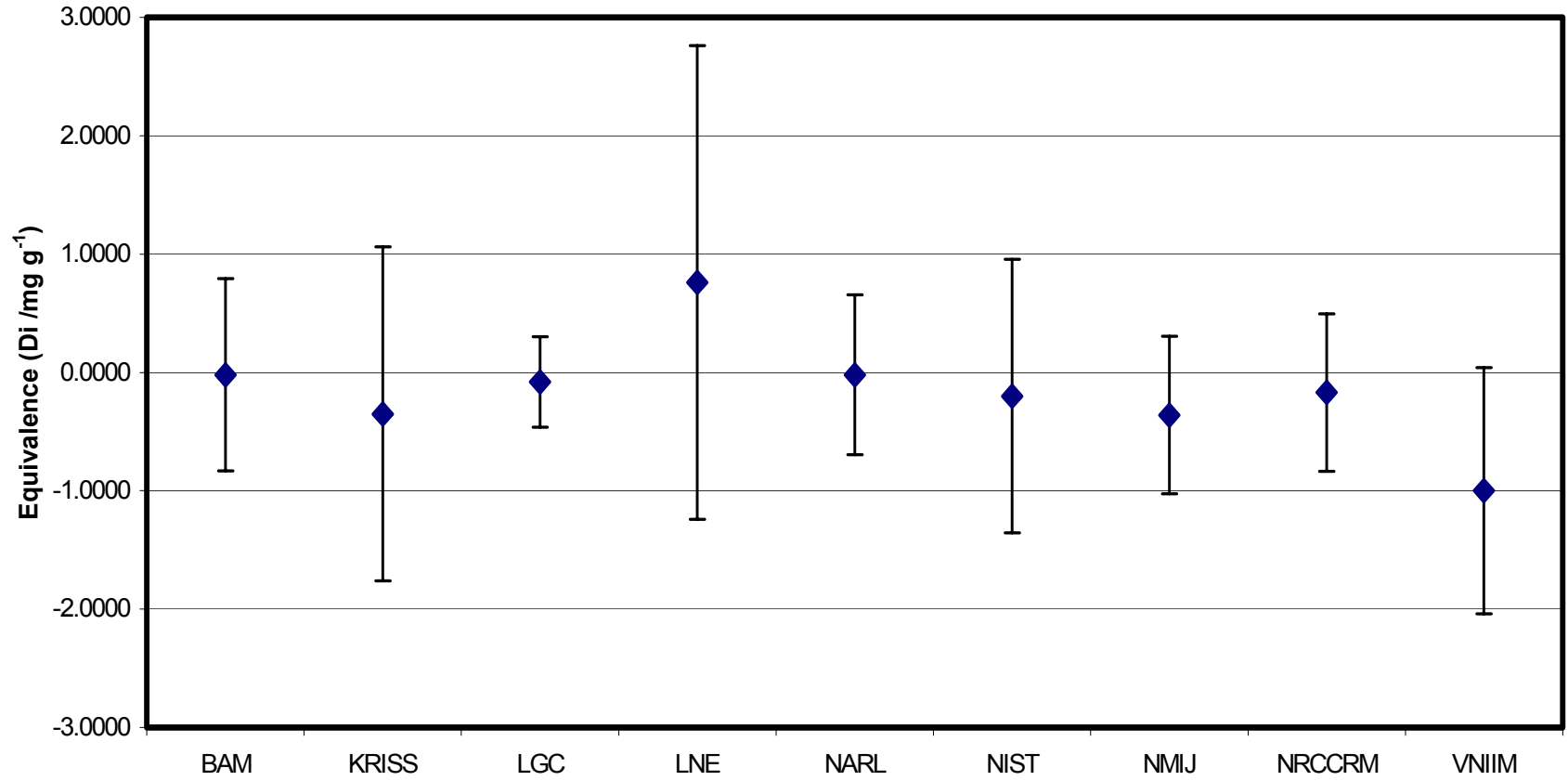
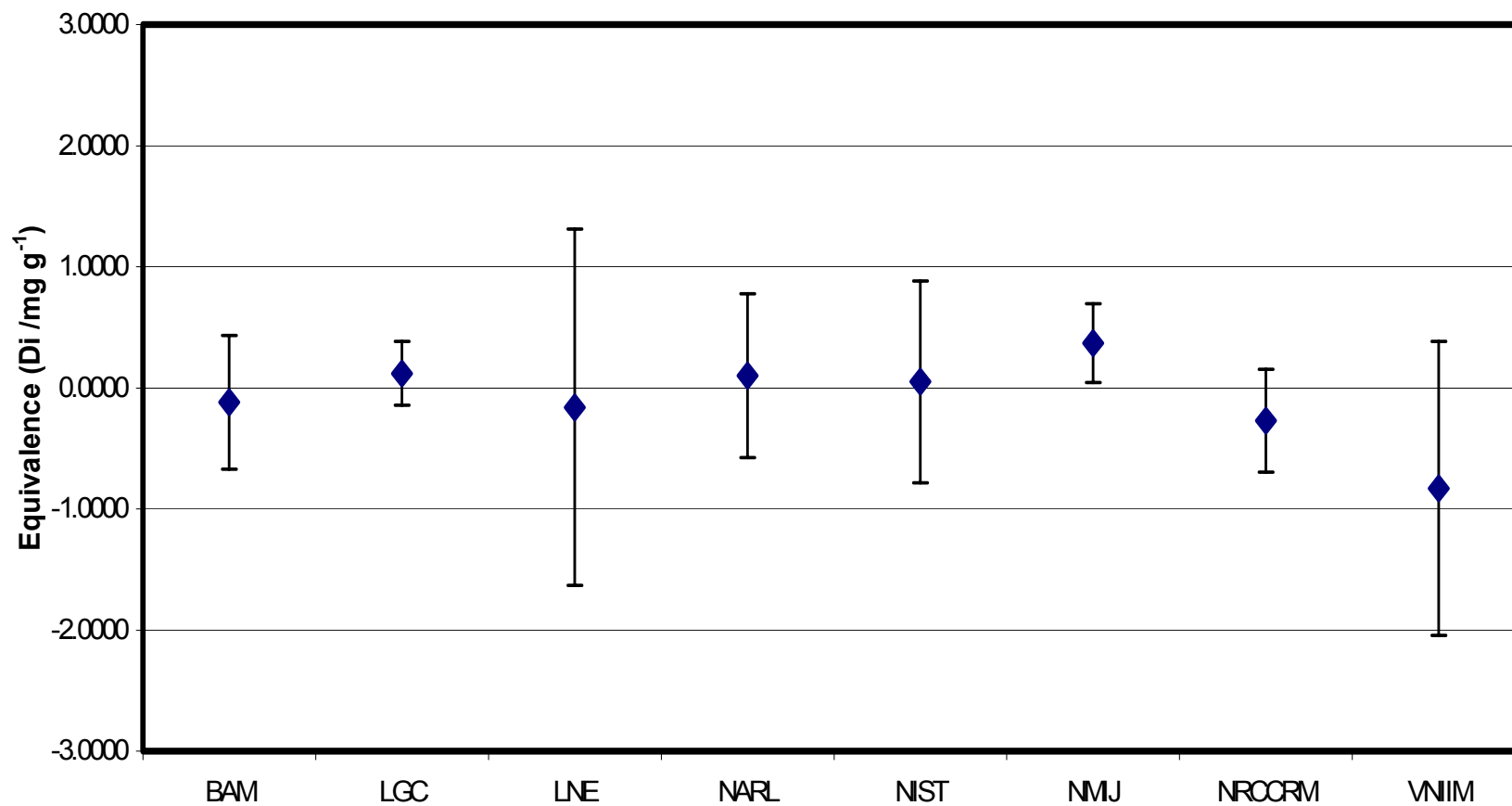


Figure 6 CCQM-K27b
Degrees of Equivalence for Sample C



Appendix 3

Uncertainty Budgets for Participating NMIs

Table 7a BAM – Sample A

Parameter	Uncertainty Type	Standard Uncertainty mg g⁻¹	Degrees of Freedom
Measurement	A	0.0003068	3
Sample mass	A	0.00002056	4
Internal standard mass	A	0.0002918	4
Purity of calibration material	B	0.0001894	100
Evaporation	B	0.000002809	100
Recovery correction	B	0.002407	100
Standard uncertainty		0.0025 mg g ⁻¹	
Coverage factor	2		
Combined expanded uncertainty		0.049 mg g ⁻¹	
Mean value of result		0.8029 mg g ⁻¹	

Table 7b BAM – Sample B

Parameter	Uncertainty Type	Standard Uncertainty mg g⁻¹	Degrees of Freedom
Measurement	A	0.1088	3
Sample mass	A	0.03153	4
Internal standard mass	A	0.05320	4
Purity of calibration material	B	0.02850	100
Evaporation	B	0.0004226	100
Recovery correction	B	0.3622	100
Standard uncertainty		0.38 mg g ⁻¹	
Coverage factor	2		
Combined expanded uncertainty		0.77 mg g ⁻¹	
Mean value of result		120.88 mg g ⁻¹	

Table 7c BAM – Sample C

Parameter	Uncertainty Type	Standard Uncertainty mg g⁻¹	Degrees of Freedom
Measurement	A	0.05978	3
Sample mass	A	0.02155	4
Internal standard mass	A	0.03596	4
Purity of calibration material	B	0.01916	100
Evaporation	B	0.0002842	100
Recovery correction	B	0.2436	100
Standard uncertainty		0.26 mg g ⁻¹	
Coverage factor	2		
Combined expanded uncertainty		0.51 mg g ⁻¹	
Mean value of result		81.11 mg g ⁻¹	

Table 8a KRISS – Sample A

Parameter	Uncertainty Type	Standard Uncertainty mg g⁻¹	Degrees of Freedom
Measurement precision of sample	A	0.0026	Low
Systematic contribution (includes purity of calibration material, measurement of calibration solution)	B	0.0043	52
Combined standard uncertainty		0.0050 mg g ⁻¹	
Coverage factor	2.01		
Combined expanded uncertainty		0.010 mg g ⁻¹	
Mean value of result		0.8013 mg g ⁻¹	

Table 8b KRISS – Sample B

Parameter	Uncertainty Type	Standard Uncertainty mg g ⁻¹	Degrees of Freedom
Measurement precision of sample	A	0.24	Low
Systematic contribution (includes purity of calibration material, measurement of calibration solution)	B	0.65	52
Combined standard uncertainty		0.69 mg g ⁻¹	
Coverage factor	2.00		
Combined expanded uncertainty		1.38 mg g ⁻¹	
Mean value of result		120.55 mg g ⁻¹	

Table 9a LGC – Sample A

Parameter	Uncertainty Type	Variance	Degrees of Freedom
Isotope ratio primary standard	B	5.05E-10	Large
Isotope ratio of spike	B	1.77E-10	Large
Isotope ratio calibration blend (gravimetric value)	A	1.65E-13	Large
Isotope ratio sample blend (measured value)	A	2.11E-08	9
Isotope ratio calibration blend (measured value)	A	6.35E-08	9
Mass of sample	B	6.09E-09	Large
Mass of spike added to sample	B	9.11E-09	Large
Mass of spike added to standard	B	3.98E-09	Large
Mass of standard	B	2.66E-09	Large
Mass fraction primary standard solution	B	4.18E-08	Large
Between blend variation	A	1.32E-08	7
Combined standard uncertainty (sq. rt. of sum of variances)		0.0004 mg g ⁻¹	
Coverage factor	2		
Combined expanded uncertainty		0.0008 mg g ⁻¹	
Mean value of result		0.8034 mg g ⁻¹	

Table 9b LGC – Sample B

Parameter	Uncertainty Type	Variance	Degrees of Freedom
Isotope ratio primary standard	B	1.05E-05	Large
Isotope ratio of spike	B	3.74E-06	Large
Isotope ratio calibration blend (gravimetric value)	A	3.17E-09	Large
Isotope ratio sample blend (measured value)	A	5.81E-04	9
Isotope ratio calibration blend (measured value)	A	8.94E-04	9
Mass of sample	B	1.66E-04	Large
Mass of spike added to sample	B	1.67E-04	Large
Mass of spike added to standard	B	1.70E-04	Large
Mass of standard	B	1.71E-04	Large
Mass fraction primary standard solution	B	9.57E-04	Large
Dilution factor	A	3.17E-04	Large
Between blend variation	A	6.08E-03	7
Combined standard uncertainty (sq. rt. of sum of variances)		0.10 mg g ⁻¹	
Coverage factor	2		
Combined expanded uncertainty		0.20 mg g ⁻¹	
Mean value of result		120.82 mg g ⁻¹	

Table 9c LGC – Sample C

Parameter	Uncertainty Type	Variance	Degrees of Freedom
Isotope ratio primary standard	B	7.33E-08	Large
Isotope ratio of spike	B	2.39E-08	Large
Isotope ratio calibration blend (gravimetric value)	A	3.96E-11	Large
Isotope ratio sample blend (measured value)	A	2.88E-04	9
Isotope ratio calibration blend (measured value)	A	3.46E-04	9
Mass of sample	B	7.40E-05	Large
Mass of spike added to sample	B	7.60E-05	Large
Mass of spike added to standard	B	7.71E-05	Large
Mass of standard	B	7.30E-05	Large
Mass fraction primary standard solution	B	4.34E-04	Large
Dilution factor	A	9.93E-05	Large
Between blend variation	A	4.26E-03	7
Combined standard uncertainty (sq. rt. of sum of variances)		0.08 mg g ⁻¹	
Coverage factor	2		
Combined expanded uncertainty		0.15 mg g ⁻¹	
Mean value of result		81.35 mg g ⁻¹	

Table 10a LNE – Sample A

Parameter	Uncertainty Type	Standard Uncertainty mg g⁻¹	Degrees of Freedom
Measured ratio in spiked sample	A	0.0042	3
Measured ratio in spiked standard solution	A	0.0041	3
Mass 45 in deuterated ethanol	A	0.00033	8
Mass 46 in deuterated ethanol	A	0.00018	8
Mass 49 in deuterated ethanol	A	0.000032	8
Mass 51 in deuterated ethanol	A	0.000028	8
Repeatability of EtOH purity det.	A	0.00321	7
Purity of ethanol standard	B	0.000236	Large
Mass of ethanol standard	B	0.00155	Large
Mass fraction water in standard solution	B	0.0000065	Large
Mass fraction standard solution in blend standard	B	0.000031	Large
Mass fraction spike in blend standard	B	0.000035	Large
Mass fraction spike in sample	B	0.000084	Large
Mass fraction of sample	B	0.000018	Large
Combined standard uncertainty		0.0070 mg g ⁻¹	
Coverage factor	2.0		
Combined expanded uncertainty		0.014 mg g ⁻¹	
Mean value of result		0.8277 mg g ⁻¹	

Table 10b LNE – Sample B

Parameter	Uncertainty Type	Standard Uncertainty mg g⁻¹	Degrees of Freedom
Measured ratio in spiked sample	A	0.492	3
Measured ratio in spiked standard solution	A	0.502	3
Mass 45 in deuterated ethanol	A	0.0024	8
Mass 46 in deuterated ethanol	A	0.00414	8
Mass 49 in deuterated ethanol	A	0.00071	8
Mass 51 in deuterated ethanol	A	0.000629	8
Repeatability of EtOH purity det.	A	0.340	7
Purity of ethanol standard	B	0.0356	Large
Mass of ethanol standard	B	0.243	Large
Mass fraction water in standard solution	B	0.000976	Large
Mass fraction standard solution in blend standard	B	0.00910	Large
Mass fraction spike in blend standard	B	0.0106	Large
Mass fraction spike in sample	B	0.0202	Large
Mass fraction of sample	B	0.554	Large
Combined standard uncertainty		0.99 mg g ⁻¹	
Coverage factor	2.0		
Combined expanded uncertainty		2.0 mg g ⁻¹	
Mean value of result		121.66 mg g ⁻¹	

Table 10c LNE – Sample C

Parameter	Uncertainty Type	Standard Uncertainty mg g⁻¹	Degrees of Freedom
Measured ratio in spiked sample	A	0.5668	3
Measured ratio in spiked standard solution	A	0.4020	3
Mass 45 in deuterated ethanol	A	0.001624	8
Mass 46 in deuterated ethanol	A	0.000924	8
Mass 49 in deuterated ethanol	A	0.00016	8
Mass 51 in deuterated ethanol	A	0.00014	8
Repeatability of EtOH purity det.	A	0.3346	7
Purity of ethanol standard	B	0.0233	Large
Mass of ethanol standard	B	0.153	Large
Mass fraction water in standard solution	B	0.00064	Large
Mass fraction standard solution in blend standard	B	0.003069	Large
Mass fraction spike in blend standard	B	0.00343	Large
Mass fraction spike in sample	B	0.00665	Large
Mass fraction of sample	B	0.1147	Large
Combined standard uncertainty		0.73 mg g ⁻¹	
Coverage factor	2.0		
Combined expanded uncertainty		1.5 mg g ⁻¹	
Mean value of result		81.07 mg g ⁻¹	

Table 11a NARL – Sample A

Parameter	Uncertainty Type	Standard Uncertainty	Degrees of Freedom
Method precision	A	0.0017	7
Mass fraction in calibration solution (mg g ⁻¹)	A	0.0005	27.5
Mass of sample in sample blend (g)	B	0.00004	Large
Mass of spike in sample blend (g)	B	0.00004	Large
Mass of standard in calibration blend (g)	B	0.00004	Large
Mass of spike in calibration blend (g)	B	0.00004	Large
Observed isotope amount ratio in spike	A	0.021	Large
Observed isotope amount ratio in sample and standard	A	22	Large
Combined standard uncertainty		0.0015 mg g ⁻¹	
Coverage factor	2.31		
Combined expanded uncertainty		0.0034 mg g ⁻¹	
Mean value of result		0.8045 mg g ⁻¹	

Table 11b NARL – Sample B

Parameter	Uncertainty Type	Standard Uncertainty	Degrees of Freedom
Method precision	A	0.0021	7
Mass fraction in calibration solution (mg g ⁻¹)	A	0.0005	27.5
Mass of sample in sample blend (g)	B	0.00004	Large
Mass of spike in sample blend (g)	B	0.00004	Large
Mass of standard in calibration blend (g)	B	0.00004	Large
Mass of spike in calibration blend (g)	B	0.00004	Large
Mass of sample solution after dilution (g)	B	0.00004	Large
Mass of sample taken for dilution (g)	A	0.00025	3.29
Observed isotope amount ratio in spike	A	0.0280	Large
Observed isotope amount ratio in sample and standard	A	24	Large
Combined standard uncertainty		0.27 mg g ⁻¹	
Coverage factor	2.31		
Combined expanded uncertainty		0.63 mg g ⁻¹	
Mean value of result		120.88 mg g ⁻¹	

Table 11c NARL – Sample C

Parameter	Uncertainty Type	Standard Uncertainty	Degrees of Freedom
Method precision	A	0.0005	7
Mass fraction in calibration solution (mg g ⁻¹)	A	0.0005	27.5
Mass of sample in sample blend (g)	B	0.00004	Large
Mass of spike in sample blend (g)	B	0.00004	Large
Mass of standard in calibration blend (g)	B	0.00004	Large
Mass of spike in calibration blend (g)	B	0.00004	Large
Mass of sample solution after dilution (g)	B	0.00004	Large
Mass of sample taken for dilution (g)	A	0.00050	3.29
Observed isotope amount ratio in spike	A	0.013	Large
Observed isotope amount ratio in sample and standard	A	1.4	Large
Matrix effect	A	0.0040	Large
Combined standard uncertainty		0.33 mg g ⁻¹	
Coverage factor	1.97		
Combined expanded uncertainty		0.66 mg g ⁻¹	
Mean value of result		81.33 mg g ⁻¹	

Table 12a NIST – Sample A

Parameter	Uncertainty Type	Standard Uncertainty mg g⁻¹	Degrees of Freedom
Measurement of samples	A	0.00082	3
Measurement of calibration standards	A	0.00000	4
Mass fraction calibration solution	B	0.00262	3
Combined standard uncertainty		0.00274 mg g ⁻¹	
Coverage factor	3.18		
Combined expanded uncertainty		0.0087 mg g ⁻¹	
Mean value of result		0.8180 mg g ⁻¹	

Table 12b NIST – Sample B

Parameter	Uncertainty Type	Standard Uncertainty mg g⁻¹	Degrees of Freedom
Measurement of samples	A	0.06240	3
Measurement of calibration standards	A	0.00030	7
Mass fraction calibration solution	B	0.38627	3
Combined standard uncertainty		0.39128 mg g ⁻¹	
Coverage factor	3.18		
Combined expanded uncertainty		1.2 mg g ⁻¹	
Mean value of result		120.7 mg g ⁻¹	

Table 12c NIST – Sample C

Parameter	Uncertainty Type	Standard Uncertainty mg g⁻¹	Degrees of Freedom
Measurement of samples	A	0.16150	3
Measurement of calibration standards	A	0.00020	7
Mass fraction calibration solution	B	0.26009	3
Combined standard uncertainty		0.30615 mg g ⁻¹	
Coverage factor	2.57		
Combined expanded uncertainty		0.79 mg g ⁻¹	
Mean value of result		81.28 mg g ⁻¹	

Table 13a NMIJ – Sample A

Parameter	Uncertainty Type	Standard Uncertainty mg g⁻¹	Degrees of Freedom
Method precision	A	0.00096	3
Purity of ethanol	B	0.00016	5
Balance linearity, mass fraction calibration solution	B	0.00046	Large
Density of calibration solution	A	0.0000007	4
Density of sample solution	A	0.0000019	4
Combined standard uncertainty		0.0011 mg g ⁻¹	
Coverage factor	2.78		
Combined expanded uncertainty		0.0030 mg g ⁻¹	
Mean value of result		0.8029 mg g ⁻¹	

Table 13b NMIJ – Sample B

Parameter	Uncertainty Type	Standard Uncertainty mg g⁻¹	Degrees of Freedom
Method precision	A	0.218	3
Purity of ethanol	B	0.0196	5
Balance linearity, mass fraction calibration solution	B	0.0691	Large
Density of calibration solution	A	0.0001	4
Density of sample solution	A	0.0004	4
Dilution ratio of sample	B	0.0370	Large
Combined standard uncertainty		0.232 mg g ⁻¹	
Coverage factor	3.18		
Combined expanded uncertainty		0.74 mg g ⁻¹	
Mean value of result		120.54 mg g ⁻¹	

Table 13c NMIJ – Sample C

Parameter	Uncertainty Type	Standard Uncertainty mg g⁻¹	Degrees of Freedom
Method precision	A	0.0990	3
Purity of ethanol	B	0.0160	5
Balance linearity, mass fraction calibration solution	B	0.0468	Large
Density of calibration solution	A	0.0001	4
Density of sample solution	A	0.0003	4
Dilution ratio of sample	B	0.0172	Large
Combined standard uncertainty		0.11 mg g ⁻¹	
Coverage factor	2.78		
Combined expanded uncertainty		0.31 mg g ⁻¹	
Mean value of result		81.60 mg g ⁻¹	

Table 14a NRCCRM – Sample A

Parameter	Uncertainty Type	Standard Uncertainty mg g⁻¹	Degrees of Freedom
Method precision	A	0.00041	3
Mass fraction calibration solution	B	0.0017	Large
Balance linearity, sample mass	B	0.00003	Large
Balance linearity, calibration compound mass	B	0.00013	Large
Balance linearity, internal standard mass, sample solution	B	0.00016	Large
Balance linearity, internal standard mass, calibration solution	B	0.00013	Large
Combined standard uncertainty		0.0018 mg g ⁻¹	
Coverage factor	2.0		
Combined expanded uncertainty		0.0036 mg g ⁻¹	
Mean value of result		0.8048 mg g ⁻¹	

Table 14b NRCCRM – Sample B

Parameter	Uncertainty Type	Standard Uncertainty mg g⁻¹	Degrees of Freedom
Method precision	A	0.15	3
Mass fraction calibration solution	B	0.253	Large
Balance linearity, sample mass	B	0.0046	Large
Balance linearity, calibration compound mass	B	0.020	Large
Balance linearity, internal standard mass, sample solution	B	0.023	Large
Balance linearity, internal standard mass, calibration solution	B	0.019	Large
Balance linearity, sample mass for dilution	B	0.038	Large
Balance linearity, diluted sample mass	B	0.00025	Large
Combined standard uncertainty		0.30 mg g ⁻¹	
Coverage factor	2.0		
Combined expanded uncertainty		0.60 mg g ⁻¹	
Mean value of result		120.73 mg g ⁻¹	

Table 14c NRCCRM – Sample C

Parameter	Uncertainty Type	Standard Uncertainty mg g⁻¹	Degrees of Freedom
Method precision	A	0.06	3
Mass fraction calibration solution	B	0.168	Large
Balance linearity, sample mass	B	0.0061	Large
Balance linearity, calibration compound mass	B	0.013	Large
Balance linearity, internal standard mass, sample solution	B	0.031	Large
Balance linearity, internal standard mass, calibration solution	B	0.013	Large
Balance linearity, sample mass for dilution	B	0.026	Large
Balance linearity, diluted sample mass	B	0.00025	Large
Combined standard uncertainty		0.19 mg g ⁻¹	
Coverage factor	2.0		
Combined expanded uncertainty		0.38 mg g ⁻¹	
Mean value of result		80.96 mg g ⁻¹	

Table 15a VNIIM – Sample A

Parameter	Uncertainty Type	Standard Uncertainty %	Degrees of Freedom
Method precision, chromatographic signal	A	0.5	9
Mass fraction calibration solution	B	0.17	Large
Thermostatting temperature	B	0.12	Large
Combined standard uncertainty %		0.54	
Combined standard uncertainty		0.004 mg g ⁻¹	
Coverage factor	2.0		
Combined expanded uncertainty		0.008 mg g ⁻¹	
Mean value of result		0.780 mg g ⁻¹	

Table 15b VNIIM – Sample B

Parameter	Uncertainty Type	Standard Uncertainty %	Degrees of Freedom
Method precision, chromatographic signal	A	0.4	9
Mass fraction calibration solution	B	0.12	Large
Thermostatting temperature	B	0.12	Large
Combined standard uncertainty %		0.42	
Combined standard uncertainty		0.5 mg g ⁻¹	
Coverage factor	2.0		
Combined expanded uncertainty		1.0 mg g ⁻¹	
Mean value of result		119.9 mg g ⁻¹	

Table 15c VNIIM – Sample C

Parameter	Uncertainty Type	Standard Uncertainty %	Degrees of Freedom
Method precision, chromatographic signal	A	0.7	9
Mass fraction calibration solution	B	0.17	Large
Thermostating temperature	B	0.12	Large
Combined standard uncertainty %		0.73	
Combined standard uncertainty		0.6 mg g ⁻¹	
Coverage factor	2.0		
Combined expanded uncertainty		1.2 mg g ⁻¹	
Mean value of result		80.4 mg g ⁻¹	