ASIA-PACIFIC METROLOGY PROGRAMME

Final Report

APMP Key Comparison of Volume of Liquids at 20 L and 100 mL

APMP.M.FF-K4

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Coordinated by:

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Final Report on APMP Key Comparion of Volume of Liquids at 20 L and 100 mL APMP.M.FF-K4

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Abstract

This report presents the results of a key comparison of liquid volume measurement conducted between ten participating institutes during the period July 2006 to August 2008 within the framework of the Asia Pacifica Metrology Program (APMP). The transfer standards comprised one 20 L volume measure and two 100 mL glass pycnometers. These transfer standards had been used in a similar CIPM key comparison CCM.FF-K4 in 2003 to 2005. The pilot institute was the National Measurement Institute, Australia (NMIA) which together with CENAM act as link laboratories to the CCM.FF-K4 comparison.

1. Introduction

At its meeting in December 2003, the Asia-Pacific Metrology Program (APMP) Technical Committee for Fluid Flow (TCFF) approved a key comparison for liquid volume to be piloted by the National Measurement Institute, Australia (NMIA). The objective of this comparison is to demonstrate the degree of equivalence of the volume measurement standards held at the participating institutes to the CCM.FF- K4 key comparison reference value (KCRV) and to provide supporting evidence for the calibration and measurement capabilities (CMCs) claimed by the participating members in the Asia-Pacific regions. The volume comparison was identified as APMP.M.FF-K4 by the Consultative Committee for Mass and Related Quantities (CCM) and the International Bureau Weights and Measures (BIPM) and APMP.

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2. Participating institutes

NMIA sent a questionnaire to members of the APMP TCM and APMP TCFF in July 2005 for preliminary planning of the volume comparisons. Ten members in the regions expressed interests in participating in this key comparison with NMIA the only institute that had taken part in a similar CIPM key comparison. In drawing up the provisional list of participating institutes, NMIA invited Centro Nacional de Metrologia (CENAM), Mexico, with the consensus of the participating institutes, to participate as a second link institute. This arrangement follows the APMP guidelines on conducting comparisons (APMP-G2) to ensure that APMP.M.FF-K4 is properly linked to the CCM.FF-K4. The pilot institute received a request to participate in the KC from MUSSD, Sri Lanka after the measurement had been started. The pilot institute considered the additional participation would not extend the comparison more than a month. The request of MUSSD for a late entry to this KC was accepted with the consent of all the participants.

Table 1: A list of participants along with contact persons

Participating Institute	**Contact Person**
National Measurement Institute, Australia (NMIA)	Dr John Man John.Man@measurement.gov.au
Centro Nacional de Metrologia (CENAM)	Mr Roberto Arias rarias@cenam.mx
National Metrology Institute of Japan, (NMIJ/AIST)	Dr Yoshiya Terao Terao.yoshia@aist.go.jp
Korea Research Institute of Standards and Science (KRISS)	Dr Yong Jae Lee yjlee@kriss.re.kr
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Vietnam Metrology Institute (VMI)	Mr Nguyen Hong Thai vmi@hn.vnn.vn
National Metrology Institute of South Africa (NMISA)	Mr BF van der Merwe bvdmerwe@nmisa.org
National Physical & Standards Laboratory (NPSL)	Mr Muhammad Arif Sheikh npslabc@isb.comsats.net.pk
Measurement Units Standards and Services Department (MUSSD)	Mr K.Premasiri Kumara metrolad@sltnet.lk

3. Schedule

The schedule was originally planned to start in July 2006 to June 2007. The transfer artefacts were accompanied with an ATA carnet for the temporary importation to a participating country/economy. The ATA carnet was valid for one year. Participants were requested to strictly adhere to the time schedule of 10 days for carrying out all the measurements. There had been a slight delay due to custom clearance of the artefacts in several participating economies. These delays together with the late entry of MUSSD deferred the completion date for the measurement schedule to August, 2007. The final calibration time schedule of the transfer artefacts and the date of reporting the measurement results were as given in Table 2.

Table 2: Circulation time schedule

Participants		Arrival / Departure	Report
CENAM	Mexico	Departure: 12 July 2006	21/8/2006
NMIA	Australia	23 July / 14 August 2006	28/8/2006
SCL	Hong Kong, China	17 August / 6 September 2006	17/10/2006
*KRISS	Korea	13 September / 29 September 2006	13/01/2007
NIM	China	11 October/ 25 October 2006	7/12/2006
NMISA	South Africa	10 November 2006/ 12 January 2007	22/02/2007
NIMT	Thailand	19 January/ 5 February 2007	22/12/2008
*NMIJ/AIST	Japan	12 February / 8 March 2007	30/3/2007
NPSL	Pakistan	16 April / 29 May 2007	No report
VMI	Vietnam	11 June / 28 June 2007	25/6/2007
MUSSD	Sri Lanka	4 July / 13 July 2007	25/7/2007
NMIA	Australia	30 July / 25 August 2007	29/10/2007

* Participated in the volume measurement of the 20 L artefact only.

4. Transfer package

4.1 20 L

The CENAM, Mexico had kindly agreed to supply one of the three 20 L pipettes (710-04 FYV) used in the CCM.FF-K4 as the transfer standard (TS) for the 20 L volume measurement. The volume of the artefact 710-04FYV had been changed by re-machining the flanges of the pipette before commencing this key comparison. The artefact was made of stainless steel with a built-in 4-wire Pt-100 temperature sensor. The temperature sensor had been sealed so as to prevent any change to the inner volume of the 20 L transfer standard. This sensor coupled with a hand held digital thermometer was used to measure the temperature of the water inside the 20 L pipette. Fittings for assembling and disassembling of the 20 L pipette were also supplied with the transfer package. A torque wrench was supplied by NMIA to provide reproducible torque values for assembling the transfer standard. The wrench had been set to 33.9 N.m for assembling purposes.

4.2 100 mL

The transfer standards for volume measurement at 100 mL were two commercially available glass pycnometers of Gay Lussac type supplied by CENAM. They were made out of boro-silicate glass and manufactured according to ISO 3507. The two pycnometers with serial numbers 03.01.17 and 03.04.03 had been used in the CCM.FF-K4. No temperature sensor was included in the transfer package.

5. Measurements

All participating institutes applied the gravimetric method to determine the volume of water. Participating institutes were asked to provide a source of pure (distilled or deionised) water for the evaluation of density of water using the recommended tables or formulas given in the literature. This information is presented in Table 3.

Table 3: Water characteristics and density formula used by participating institutes

Institutes	Water	De-aerated	Density Formula
CENAM	Filtered and Ion exchange	No	Tanaka et al [1]
NMIA	Single distilled	No	Tanaka et al [1]
SCL	Single distilled	No	NIST [2]
KRISS	Inverse osmosis and Ion Exchange	No	Tanaka et al [1]
NIM	De-ionised	No	Tanaka et al [1]
NMISA	Triple distilled and de-ionised	No	Tanaka et al [1]
NIMT	Double distilled	No	IUPAC Table
NMIJ/AIST	Tap water	No	Tanaka et al [1] Correction for impurity using Anton Paar densitometer
VMI	Single distilled	No	PTB-Mitteilungen [3]
MUSSD	Single distilled	No	Patterson and Morris [4]

Each participating institute used its own instruments to measure ambient conditions such as atmospheric pressure, ambient temperature and relative humidity during the volume measurements. Participating institutes were asked to perform 10 volume measurements for each artefact.

5.1 20 L Transfer standard

Participating institutes determined the volume of pure water that the transfer standard delivered at a reference temperature of 20 ºC after a "drip-off" time of 60 seconds. The "drip-off" time referred to the time allowed for draining out the remaining water inside the transfer standard after the cessation of the main flow. Each participating institute supplied an auxiliary tank for collecting the water delivered by the 20 L artefact and used its own method to determine the volume of water from the mass and density determination. The 20 L TS was cleaned and assembled according to the procedures described in the technical protocol. Measurements were performed after an acclimatisation time of the TS in the laboratory of at least one day. The 20 L TS was filled with pure water and remained in this condition for a period of at least 12 hours, allowing the water to fill out all tiny recesses between the flanges and allowing the transfer standard to reach thermal stability.

The cubic coefficient of expansion of the transfer standard material was stated as $(47.7 \pm 2.0) \times 10^{-6}$ ºC^{-1}. This value was recommended by the CENAM for the CCM.FF-K4 comparison. The uncertainty is expressed as standard uncertainty. The built-in temperature sensor coupled with the hand held digital thermometer supplied with the transfer package had been calibrated by the Temperature Laboratory at CENAM. An equation derived from the calibration results to convert resistance to temperature was presented in the technical protocol. The temperature calculation procedure required the use of the resistance at the Triple Point of Water. This value was given as 99.976 Ω in Appendix B of the technical protocol. NMIA measured the resistance of the sensor at the ice point by filling the upper part of the transfer standard with a mixture of distilled water and meshed ice. The resistance in Ohms (Ω) was read by the hand-held digital thermometer supplied with the transfer package. The measurements were carried out before and after the circulation schedule. The results were 99.975 Ω and 99.974 Ω respectively. The difference of these results was considered to have an insignificant contribution to the volume results of this KC.

5.2 100 mL Transfer standard

Participating institutes determined the volume of pure water that each of the two 100 mL glass pycnometers of the Gay-Lussac type was to contain, at a reference temperature of 20 ºC. Each participating institute used its own instruments and procedures to measure the water temperature contained in each pycnometer.

The pycnometers were not protected against evaporation by a supplementary cap. If the loss of water due to evaporation was found to be significant during weighing of the filled pycnometer, each participating institute might need to devise a procedure to measure the loss of water evaporation and take this into account in determining the volume. According to the manufacturer of the pycnometers, the cubic expansion coefficient was $(9.9 \pm 1) \times 10^{-6}$ °C $^{-1}$ (uncertainty is expressed as standard). This value was recommended to be used to determine the volume at the reference temperature.

6. Results

The technical protocol provided an appropriate format for reporting the following information to the pilot institute within six weeks after the measurements.

(i) Details of the participating institute's instruments and water source
(ii) Measurement results
(iii) Uncertainty budget determined in accordance to the ISO "Guide to the Expression of Uncertainty in Measurement ", 1993 (GUM) [5].

NPSL did not report its result to the pilot institute and did not response to numerous requests to do so. Measurement results of the 20 L artefact and of the two 100 mL artefacts from all other participating institutes are summarised in Table 4 and Table 5 respectively. Ten participants took part in the measurement of the volume of the 20 L artefact, whereas eight participants measured the volumes of the two 100 mL artefacts. The pilot institute measured each artefact twice. Each institute reported the measured volume value of the artefact with an expanded uncertainty and the coverage factor *k*.

Table 4: Measurement results of the 20 L artefact

Institute	20 L 710-04	Expanded uncertainty	Coverage factor, *k*
	mL	mL	
CENAM	19992.94	0.65	2.09
NMIA	19992.87	0.44	2
SCL	19992.50	0.50	2
KRISS	19992.87	0.44	2
NIM	19992.98	0.65	1.96
NMISA	19991.57	2.30	2.28
NIMT	19990.03	0.95	2
NMIJ/AIST	19993.10	2.20	2
VMI	19992.33	0.66	2
MUSSD	19993.39	0.72	2.19
NMIA	19992.85	0.44	2

Table 5: Measurement results of the two 100 mL artefacts

Institute	100 mL 03.04.03	Expanded uncertainty	Coverage factor, *k*	100 mL 03.01.17	Expanded uncertainty	Coverage factor, *k*
	mL	mL		mL	mL	
CENAM	99.4028	0.0027	2.02	100.9309	0.0033	2.02
NMIA	99.4040	0.0020	2	100.9332	0.0021	2
SCL	99.3992	0.0070	2	100.9283	0.0070	2
NIM	99.4029	0.0016	1.96	100.9336	0.0016	1.96
NMISA	99.3953	0.0104	2.37	100.9330	0.0045	2.37
NIMT	99.3894	0.0024	2	100.9177	0.0024	2
VMI	99.4078	0.0034	2	100.9361	0.0034	2
MUSSD	99.3360	0.0067	2	100.9227	0.0064	2
NMIA	99.4048	0.0020	2	100.9332	0.0021	2

6.1 Stability of artefacts

NMIA assessed the stability of the travelling artefacts by measuring the volume values of each artefact at the beginning and at the end of the circulation loop. The results are given in Table 6. The changes in volume values of all the artefacts were found to be small and well within their measurement uncertainties. No evidence of instability was found. This observation was consistent with those reported in the CCM.FF-K4. The measured volume difference of each artefact in Table 6 was used to estimate the uncertainty associated with each artefact due to drift, u_d, during the comparison. Assuming a rectangular distribution, u_d is calculated from the equation:

$$u_d = \sqrt{\frac{\Delta v^2}{12}} \tag{1}$$

Table 6: Volume change of the artefacts at the beginning and at the end of the circulation

Artefact	Initial (July, 2006)	Final (August, 2007)	Change in volume	u_d
	(mL)	(mL)	Δv (mL)	(mL)
20 L 710-04	19992.87	19992.85	0.02	0.0058
100 mL 03.04.03	99.4040	99.4048	-0.0008	0.0002
100 mL 03.01.17	100.9332	100.9332	0.0000	0.0000

7. Analysis and linking to CCM.FF-K4

A method based on generalised least-squares (GLS) estimation, which is sometimes known as Gauss-Markov estimation, was used to analyse the comparison results and to link these results to the CCM key comparison CCM.FF-K4. This analysis directly combined the APMP comparison results with the CCM.FF-K4 link institutes to estimate the degree of equivalence for each institute relative to the CCM.FF-K4 key comparison reference value (KCRV) and the degree of equivalence between pairs of participating institutes, as required by the Mutual Recognition Arrangement (MRA). No reference value of the APMP comparison results is calculated or required to link to the KCRV. This method had been used to link the 1 kg mass comparisons CCC.M.K-1 and APMP.M.M-K1 [6]. A brief description of the analysis is presented as follows.

The GLS estimation analysis can be expressed as

$$\boldsymbol{y} = \boldsymbol{X}\,\boldsymbol{\beta} + \boldsymbol{e} \tag{2}$$

where $\boldsymbol{y}$ is a column vector of the measurement results, $\boldsymbol{X}$ is a design matrix, $\boldsymbol{\beta}$ is a column vector of unknowns and $\boldsymbol{e}$ is a vector of random errors or disturbances. Each measurement is represented in a row of the design matrix $\boldsymbol{X}$, while the measurement result is in the corresponding row of vector $\boldsymbol{y}$.

The deviations of the two link institutes (NMIA and CENAM) from the KCRV are included in the analysis. From the final report on the CIPM key comparison of 20 L and 100 mL volume standards (CCM.FF-K4), the following values are obtained:

Table 7: Results of link institutes from CCM.FF-K4

v_o	NMIA - KCRV	CENAM - KCRV
20 L	(-0.10 ±0.42) mL	(-0.07 ±0.30) mL
100 mL	(0.0007 ±0.0017) mL	(-0.0008 ±0.0017) mL

The number following the symbol ± is the uncertainty determined with a coverage factor k = 2.

Eleven measurement results are reported for the 20 L artefact and nine measurement results for each of the 100 mL artefacts.

The equation describing each APMP comparison measurement for an artefact, x, can be written

$$v(\text{Int}_i)_p - v_o = \Delta_i - (v_o - v_x) + e_{i,p} \qquad (4)$$

where $v(\text{Int}_i)_p$ is the p^{th} value assigned to the artefact by institute i, v_o is the nominal volume of the artefact, v_x is the volume of the artefact, Δi is the bias of institute i, and $e_{i,p}$ is a random error associated with the measurement.

Similarly, the equation for the CCM.FF-K4 results of the two link institutes for the artefact x is

$$v_c(\text{LInt}_i) - K = \Delta_i - (K - v_c) + e_i \qquad (5)$$

where v_c is the average volume of the CCM.FF-K4 travelling standards, K is the key comparison reference value, and $v_c(\text{LInt}_i) - K$ is the measured deviation between the link institute i and the KCRV (see Table 7 above).

The known values are $v(\text{Int}_i)_p - v_o$ and $v_c(\text{LInt}_i) - K$. For the 20 L volume comparison measurement, the unknowns are Δ_1 to Δ_{10}, $v_o - v_x$, and $K - v_c$. Solving the 11 equations defined by (4) and the 2 equations defined by (5) directly requires an additional piece of information, such as the value for one of the parameters. The value of $K - v_c = 0$ was chosen to be the additional information or constraint. From equation (5), it is seen that the expected deviation of the ith link institute's result from the KCRV is Δ_i. In this case, the expected deviation of each participant's results from the KCRV is the values obtained for Δ_1 to Δ_{10} from the solution of the GLS estimation. The design matrix $\boldsymbol{X}$ has 14 rows and 12 columns. The constraint is in the 14th row of $\boldsymbol{X}$. The number of degrees of freedom, $\nu = 14 - 12$.

For each 100 mL artefact, the unknowns are Δ_1 to Δ_8, $v_o - v_x$, and $K - v_c$. The value of $K - v_c = 0$ was chosen as the constraint for solving the 9 equations defined by (4) and the 2 equations defined by (5). The design matrix $\boldsymbol{X}$ has 12 rows and 10 columns. The constraint is in the 12th row of $\boldsymbol{X}$. The number of degrees of freedom, $\nu = 12 - 10$.

The GLS solution to (2) is given by the results vector $\hat{\boldsymbol{\beta}}$ (the estimated value of $\boldsymbol{\beta}$):

$$\hat{\boldsymbol{\beta}} = \boldsymbol{C}\,\boldsymbol{X}^{\mathrm{T}}\,\boldsymbol{\Phi}^{-1}\,\boldsymbol{y} \qquad (6)$$

with uncertainty (variance-covariance) matrix $\boldsymbol{C}$

$$\boldsymbol{C} = (\boldsymbol{X}^{\mathrm{T}}\, \boldsymbol{\Phi}^{-1}\, \boldsymbol{X})^{-1}. \qquad (7)$$

Hence, $\hat{\beta}_1$ (the first element of $\hat{\boldsymbol{\beta}}$), is an estimate of the unknown Δ_1.

Matrix $\boldsymbol{\Phi}$ is an input uncertainty (variance-covariance) matrix. The diagonal terms of $\boldsymbol{\Phi}$ are the variances (standard uncertainty squared) associated with each measurement plus the $(u_d)^2$ variance associated with the instability of the artefact. Off-diagonal terms in $\boldsymbol{\Phi}$ allow known correlations between measurement results to be included in the analysis. Matrix $\boldsymbol{C}$ is the calculated variance-covariance matrix from which the uncertainties in the results of the analysis are obtained.

With the constraint $K - v_c = 0$, the elements of $\hat{\boldsymbol{\beta}}$ and the corresponding diagonal terms of $\boldsymbol{C}$ directly give the expected deviation of each participant's result from the KCRV and the variance associated with this deviation. For a pair of institutes *i* and *j*, $\hat{\beta}_i - \hat{\beta}_j$ is the difference of their deviations from the KCRV, and $C_{ii} + C_{jj} - 2C_{ij}$ is the variance associated with this difference.

Correlation in this comparison arises between the two measurement results of the pilot institute due to the uncertainty in the common reference standards and the uncertainty associated with the use of the common instruments for the measurements. A correlation coefficient of 0.8 is taken to correlate the uncertainty of the two measurement results. Correlated uncertainty also arises between the measurement results in the CCM and APMP comparisons for the link institutes. A correlation coefficient of 0.8 is used. In addition, all the measurement results for the 20 L artefact are correlated with each other due to the common source of traceability of the built-in temperature sensor to CENAM. Some measurement results are correlated through the uncertainty in the water density formula [1]. Off-diagonal terms are included in $\boldsymbol{\Phi}$ to account for all these correlations. In this analysis, the correlation of all measurement results through their common traceability to the BIPM working standard Pt-Ir kilogram (standard uncertainty 2.3 µg) and through the uncertainty in the air density formulae are considered insignificant.

The chi-squared test is applied to assess the consistency between the model and the measurement results. The observed chi-squared value χ^2_{obs} is given by [7]

$$\chi^2_{obs} = (\boldsymbol{y} - \boldsymbol{X}\hat{\boldsymbol{\beta}})^{\mathrm{T}}\, \hat{\boldsymbol{\Phi}}^{-1} (\boldsymbol{y} - \boldsymbol{X}\hat{\boldsymbol{\beta}}). \qquad (8)$$

The consistency check is regarded as a 'fail' if the probability of finding a chi-squared value $\chi^2(\nu)$ distributed with ν degrees of freedom larger than the observed value χ^2_{obs} is smaller than 5%:

$$P\{\chi^2(\nu) > \chi^2_{obs}\} < 0.05 \qquad (9)$$

7.1 Deviation from the CCM KCRV

Deviation and relative deviation from the CCM KCRV and the associated uncertainty for each participating institute for the 20 L and the two 100 mL artefacts are given in Tables 8 and 9 (Appendix 1). It is noted that the differences and uncertainties in Table 8 and Table 9 for the link institutes differ by no more than 0.04 mL and 0.0003 mL respectively from the CCM.FF-K4 values (see Table 7). Figures 1 to 3 show the relative difference of the volume value assigned by each participant from the KCRV, D_i, together with the expanded uncertainty associated with the volume value, $U(D_i)$. The zero value corresponds to the KCRV of CCM.FF-K4. From Figure 1, it is seen that for nine of the ten participating institutes, the relative deviations of their 20 L values from the KCRV are smaller than the expanded uncertainties associated with these values. The observed chi-squared value is calculated using equation (8) as 0.06 and the critical chi-squared value χ^2 (2, 0.05) for 2 degrees of freedom at 0.05 significant level is 5.99. The consistency between the model and the measurement results is confirmed because the value of χ^2 (2, 0.05) is larger than the value of χ^2_{obs}.

The comparison results of the two 100 mL artefacts are shown in Figures 2 and 3. It is observed that the results of six participants are consistent with each other and with the KCRV. Results assigned by two institutes appear to be much smaller than the KCRV. These anomalous results are possibly due to the significant loss of water as a result of evaporation of water from the pycnometer during the weighing process. The chi-squared test gives the following results:

03.04.03 artefact χ^2 (2, 0.05) = 5.99; χ^2_{obs} = 1.40
03.01.17 artefact χ^2 (2, 0.05) = 5.99; χ^2_{obs} = 0.34

It is seen that the value of χ^2 (2, 0.05) is larger than the χ^2_{obs} for both 100 mL artefacts measurement results. It is concluded that the equivalence of the measurement is established.

The effect of the correlation between the two measurements of the pilot institute, and between the measurements in the CCM and APMP for the two link institutes has been examined by using different correlation coefficient values (0, 0.5 and 0.8) in the data analysis. A maximum difference of 2×10^{-6} in D_i and 6×10^{-6} in $U(D_i)$ for all the institutes for the 20 L and 100 mL artefacts is observed, indicating that the effect of correlation on the degrees of equivalence is small.

An attempt was made to apply the GLS model to determine the overall degree of equivalence of the measurement results of the two 100 mL artefacts. In this analysis, the design matrix $\boldsymbol{X}$ has 21 rows and 11 columns. The constraint K - $v_c = 0$ is in the 21^{st} row. The inputs for this analysis are the same as those used for the analysis of the individual artefacts. An additional input is the correlated uncertainty between the two measurements of the 100 mL artefact for each institute. A solution is obtained for the overall degree of equivalence. However, the chi-squared test of these results indicates that the equivalence of measurements is rejected at a 5% level of significance. This inconsistency is probably due to the outlying values reported by two participating institutes (see Table 9).

The overall degree of equivalence for the 100 mL artefacts, $\overline{D}_i$, is determined as the arithmetic average of the degrees of equivalence, D_i, for each of the 100 mL artefact. A correlation coefficient of 1 is used to correlate the uncertainty between the two measurements of the 100 mL artefacts. The combined standard uncertainty of $\overline{D}_i$, $u(\overline{D}_i)$, is calculated as:

$$u(\overline{D}_i) = \frac{1}{n}\sum_i u(D_i).$$

This approach was also used to determine the overall degrees of equivalence for the three 20 L transfer standards and the six 100 mL transfer standards in the CCM.FF-K4. Values of $\overline{D}_i$ together with the associated uncertainty $U(\overline{D}_i)$ are presented in Table 10. A plot of the overall degree of equivalence for each participating institute for the 100 mL artefacts is presented in Figure 4.

7.2 Difference in assigned volume values between pair of institutes

The relative differences in the assigned volume values between institute *i* and institute *j*, $D_{i,j}$, the expanded uncertainties of the differences, $U(D_{i,j})$, and the ratio of these values are given in Tables 11 to 13. A measure of the degree of equivalence between a pair of institutes is provided by the magnitude of the ratio of $D_{i,j} / U(D_{i,j}) \leq 1$. For the 20 L volume values, the majority of the results of the participating institutes are consistent with each other. The 100 mL volume results show that six of the eight institutes are found to be equivalent to each other. The effect of water evaporation from the pycnometer during the weighing process coupled with an underestimate of the uncertainties associated with the assigned volume values may be the main reasons for these inconsistent results. The overall degree of equivalence between a pair of institutes for the two 100 mL artefacts, $\overline{D}_{ij}$, and the expanded uncertainty, $U(\overline{D}_{ij})$, and the ratio of these values are given in Table 14.

8. Conclusions

The majority of the 20 L results of the participating institutes are consistent with each other and with the KCRV of CCM.FF-K4. The result from one institute differs significantly from the KCRV and from the results of the other institutes.

The results of the two 100 mL artefacts reported by two institutes differ significantly from the KCRV and from the results of other participants. The assigned values are much smaller than the KCRV. One possible reason is due to the effect of water evaporation during the weighing process. It is advisable to use an artefact with a supplementary cap to minimise evaporation or to devise a procedure to measure the loss of water evaporation and take this into account in determining the volume.

One institute did not report its result to the pilot institute and did not respond to repeated requests to do so. A request of late entry from MUSSD, Sri Lanka to this key comparison was accepted with the consent of all participating institutes.

The pilot institute invited three participants to check their results while preparing the draft A report. NMIT made corrections to the assigned volume values and associated uncertainties for all the artefacts. SCL made a correction to the uncertainty value associated with the 100 mL measurement results. MUSSD reported that no numerical error was found in its results.

The pilot institute sent the draft A report to all participating institutes on 13 November 2009 with a code number in place of the institute name. All participants confirmed the receipt of the report. No objections were received to the proposal to use the draft A report as a basis for the preparation of the draft B report.

At the draft B stage, VMI made a correction to the uncertainty of its result for the two 100 mL artefacts. VMI reported that a mistake was made in the calculation of the uncertainty in which the resolution of its balance should be 0.01 mg instead of 0.01g. VMI changed the uncertainty from 0.0168 mL to 0.0035 mL. This change of uncertainty was presented to all participating institutes in February 2010. No objections to the proposed change were received. The revised uncertainty of VMI results is presented in this report.

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Appendix 1. Degrees of equivalence

Table 8: Deviation of the 20 L volume value assigned by each participating institute from the KCRV (key comparison reference value of CCM.FF-K4) and associated uncertainty, U (k=2), together with relative deviation, D_i, and associated expanded uncertainty, $U(D_i)$ (k=2).

	20 L 710-04			
	$v_i - KCRV$	U	D_i	$U(D_i)$
Institute	mL		$\times 10^{-6}$	
CENAM	-0.08	0.34	-4	17
NMIA	-0.11	0.46	-5	23
SCL	-0.47	0.58	-24	29
KRISS	-0.10	0.53	-5	26
NIM	0.01	0.71	1	36
NMISA	-1.40	2.32	-70	116
NMIT	-2.94	0.99	-147	50
NMIJ	0.13	2.22	6	111
VMI	-0.64	0.72	-32	36
MUSSD	0.42	0.78	21	39

Table 9: Deviation of the 100 mL volume value assigned by each participating institute from the KCRV (key comparison reference value of CCM.FF-K4) and associated uncertainty, U (k=2), together with relative deviation, D_i, and associated expanded uncertainty, $U(D_i)$ (k=2).

	03.04.03		03.01.17		03.04.03		03.01.17	
	$v_i - KCRV$	U	$v_i - KCRV$	U	D_i	$U(D_i)$	D_i	$U(D_i)$
Institute	mL				$\times 10^{-6}$			
CENAM	-0.0008	0.0020	-0.0007	0.0020	-8	20	-7	20
NMIA	0.0007	0.0020	0.0007	0.0020	7	20	7	20
SCL	-0.0043	0.0072	-0.0041	0.0072	-43	72	-41	72
NIM	-0.0006	0.0023	0.0012	0.0023	-6	23	12	23
NMISA	-0.0082	0.0105	0.0006	0.0048	-82	106	6	48
NMIT	-0.0141	0.0029	-0.0146	0.0029	-142	29	-147	29
VMI	0.0043	0.0038	0.0037	0.0038	44	38	37	38
MUSSD	-0.0675	0.0069	-0.0097	0.0066	-678	69	-97	66

Table 10: Overall degree of equivalence, $\overline{D_i}$, for artefacts 100 mL 03.04.03 and 03.01.17 and associated expanded uncertainty, $U(\overline{D_i})$ (k=2), for each participating institute.

	Overall DoE	
	$\overline{D_i}$	$U(\overline{D_i})$
Institute	$\times 10^{-6}$	
CENAM	-8	20
NMIA	7	20
SCL	-42	72
NIM	3	23
NMISA	-38	77
NMIT	-145	29
VMI	40	38
MUSSD	-388	68

Table 11: 20 L 710-04. Relative difference in assigned volume value $D_{i,j}$ between institutes *i* (left column) and *j* (top row), the expanded uncertainty $U(D_{i,j})$ and the ratio of $D_{i,j}$ to $U(D_{i,j})$

Relative difference in assigned volume values between institute *i* and institute *j*, $D_{i,j}\ \times 10^{-6}$

Inst.*i* \ inst *j*	**CENAM**	**NMIA**	**SCL**	**KRISS**	**NIM**	**NMISA**	**NMIT**	**NMIJ**	**VMI**	**MUSSD**
CENAM		1	19	1	-5	66	143	-11	28	-25
NMIA	1		18	0	-6	65	142	-12	27	-26
SCL	19	18		-18	-24	46	124	-30	9	-45
KRISS	1	0	-18		-6	65	142	-12	27	-26
NIM	-5	-6	-24	-6		71	148	-6	33	-20
NMISA	66	65	46	65	71		77	-76	-38	-91
NMIT	143	142	124	142	148	77		-154	-115	-168
NMIJ	-11	-12	-30	-12	-6	-76	-154		39	-15
VMI	28	27	9	27	33	-38	-115	39		-53
MUSSD	-25	-26	-45	-26	-20	-91	-168	-15	-53	

Relative expanded uncertainty of the difference in assigned volume values between institute *i* and institute *j*, $U(D_{i,j})\ \times 10^{-6}$ (k =2)

Inst.*i* \ inst *j*	**CENAM**	**NMIA**	**SCL**	**KRISS**	**NIM**	**NMISA**	**NMIT**	**NMIJ**	**VMI**	**MUSSD**
CENAM		24	29	27	36	116	50	111	36	39
NMIA	24		32	29	38	117	51	112	38	41
SCL	29	32		33	41	117	53	113	41	43
KRISS	27	29	33		39	117	52	112	39	42
NIM	36	38	41	39		119	57	115	46	48
NMISA	116	117	117	117	119		124	159	119	120
NMIT	50	51	53	52	57	124		120	57	59
NMIJ	111	112	113	112	115	159	120		115	48
VMI	36	38	41	39	46	119	57	115		48
MUSSD	39	41	43	42	48	120	59	48	48	

Ratio of $D_{i,j}$ to $U(D_{i,j})$

Inst.*i* \ inst *j*	**CENAM**	**NMIA**	**SCL**	**KRISS**	**NIM**	**NMISA**	**NMIT**	**NMIJ**	**VMI**	**MUSSD**
CENAM		0.05	0.66	0.04	-0.13	0.57	2.87	-0.10	0.77	-0.64
NMIA	0.05		0.57	0.00	-0.15	0.55	2.76	-0.11	0.70	-0.64
SCL	0.66	0.57		-0.56	-0.59	0.40	2.32	-0.27	0.21	-1.03
KRISS	0.04	0.00	-0.56		-0.15	0.55	2.73	-0.10	0.69	-0.63
NIM	-0.13	-0.15	-0.59	-0.15		0.59	2.58	-0.05	0.71	-0.42
NMISA	0.57	0.55	0.40	0.55	0.59		0.62	-0.48	-0.32	-0.76
NMIT	2.87	2.76	2.32	2.73	2.58	0.62		-1.28	-2.01	-2.84
NMIJ	-0.10	-0.11	-0.27	-0.10	-0.05	-0.48	-1.28		0.34	-0.30
VMI	0.77	0.70	0.21	0.69	0.71	-0.32	-2.01	0.34		-1.10
MUSSD	-0.64	-0.64	-1.03	-0.63	-0.42	-0.76	-2.84	-0.30	-1.10	

Table 12: 100 mL 03.04.03. Relative difference in assigned volume value $D_{i,j}$ between institutes i (left column) and j (top row), the expanded uncertainty $U(D_{i,j})$ and the ratio of $D_{i,j}$ to $U(D_{i,j})$

Relative difference in assigned volume values between institute i and institute j, $D_{i,j}$ $\times 10^{-6}$

Inst.*i* \ inst. *j*	**CENAM**	**NMIA**	**SCL**	**NIM**	**NMISA**	**NMIT**	**VMI**	**MUSSD**
CENAM		-15	35	-2	74	134	-52	670
NMIA	-15		50	13	89	149	-37	685
SCL	35	50		-37	39	99	-87	635
NIM	-2	13	-37		76	136	-50	672
NMISA	74	89	39	76		60	-126	596
NMIT	134	149	99	136	60		-186	536
VMI	-52	-37	-87	-50	-126	-186		722
MUSSD	670	685	635	672	596	536	722	

Relative expanded uncertainty of the difference in assigned volume values between institute i and institute j, $U(D_{i,j})$ $\times 10^{-6}$ (k =2)

Inst.*i* \ inst. *j*	**CENAM**	**NMIA**	**SCL**	**NIM**	**NMISA**	**NMIT**	**VMI**	**MUSSD**
CENAM		24	73	27	106	32	40	70
NMIA	24		73	26	106	31	39	70
SCL	73	73		72	126	74	78	97
NIM	27	26	72		105	30	38	69
NMISA	106	106	126	105		107	110	124
NMIT	32	31	74	30	107		42	72
VMI	40	39	78	38	110	42		75
MUSSD	70	70	97	69	124	72	75	

Ratio of $D_{i,j}$ to $U(D_{i,j})$

Inst.*i* \ inst. *j*	**CENAM**	**NMIA**	**SCL**	**NIM**	**NMISA**	**NMIT**	**VMI**	**MUSSD**
CENAM		-0.6	0.5	-0.1	0.7	4.1	-1.3	9.5
NMIA	-0.6		0.7	0.5	0.8	4.8	-0.9	9.8
SCL	0.5	0.7		-0.5	0.3	1.3	-1.1	6.5
NIM	-0.1	0.5	-0.5		0.7	4.5	-1.3	9.7
NMISA	0.7	0.8	0.3	0.7		0.6	-1.1	4.8
NMIT	4.1	4.8	1.3	4.5	0.6		-4.4	7.5
VMI	-1.3	-0.9	-1.1	-1.3	-1.1	-4.4		9.6
MUSSD	9.5	9.8	6.5	9.7	4.8	7.5	9.6	

Table 13: 100 mL 03.01.17. Relative difference in assigned volume value $D_{i,j}$ between institutes *i* (left column) and *j* (top row), the expanded uncertainty $U(D_{i,j})$ and the ratio of $D_{i,j}$ to $U(D_{i,j})$

Relative difference in assigned volume values between institute *i* and institute *j*, $D_{i,j}$ $\times 10^{-6}$

Inst.*i* \ inst. *j*	**CENAM**	**NMIA**	**SCL**	**NIM**	**NMISA**	**NMIT**	**VMI**	**MUSSD**
CENAM		-14	34	-20	-14	140	-44	90
NMIA	-14		48	-5	1	154	-30	104
SCL	34	48		-53	-47	106	-78	56
NIM	-20	-5	-53		6	160	-25	110
NMISA	-14	1	-47	6		153	-31	104
NMIT	140	154	106	160	153		-184	-50
VMI	-44	-30	-78	-25	-31	-184		134
MUSSD	90	104	56	110	104	-50	134	

Relative expanded uncertainty of the difference in assigned volume values between institute *i* and institute *j*, $U(D_{i,j})$ $\times 10^{-6}$ (k =2)

Inst.*i* \ inst. *j*	**CENAM**	**NMIA**	**SCL**	**NIM**	**NMISA**	**NMIT**	**VMI**	**MUSSD**
CENAM		24	73	26	50	32	40	67
NMIA	24		73	25	49	31	39	67
SCL	73	73		72	83	74	78	95
NIM	26	25	72		48	29	38	66
NMISA	50	49	83	48		51	57	78
NMIT	32	31	74	29	51		42	68
VMI	40	39	78	38	57	42		73
MUSSD	67	67	95	66	78	68	73	

Ratio of $D_{i,j}$ to $U(D_{i,j})$

Inst.*i* \ inst. *j*	**CENAM**	**NMIA**	**SCL**	**NIM**	**NMISA**	**NMIT**	**VMI**	**MUSSD**
CENAM		-0.6	0.5	-0.8	-0.3	4.4	-1.1	1.3
NMIA	-0.6		0.7	-0.2	0.0	5.0	-0.8	1.6
SCL	0.5	0.7		-0.7	-0.6	1.4	-1.0	0.6
NIM	-0.8	-0.2	-0.7		0.1	5.5	-0.7	1.7
NMISA	-0.3	0.0	-0.6	0.1		3.0	-0.5	1.3
NMIT	4.4	5.0	1.4	5.5	3.0		-4.4	-0.7
VMI	-1.1	-0.8	-1.0	-0.7	-0.5	-4.4		1.8
MUSSD	1.3	1.6	0.6	1.7	1.3	-0.7	1.8	

Table 14: 100 mL 03.04.03 and 03.01.17. Overall relative difference in assigned volume value $\overline{D}_{ij}$ between institutes *i* (left column) and *j* (top row), the expanded uncertainty $U(\overline{D}_{ij})$ and the ratio of $\overline{D}_{ij}$ to $U(\overline{D}_{ij})$.

Overall relative difference in assigned volume values between institute *i* and institute *j*, $\overline{D}_{ij}$ $\times 10^{-6}$

Inst.*i* \ inst. *j*	**CENAM**	**NMIA**	**SCL**	**NIM**	**NMISA**	**NMIT**	**VMI**	**MUSSD**
CENAM		-15	34	-11	30	137	-48	380
NMIA	-15		49	4	45	152	-33	395
SCL	34	49		-45	-4	103	-82	346
NIM	-11	4	-45		41	148	-37	391
NMISA	30	45	-4	41		107	-78	350
NMIT	137	152	103	148	107		-185	243
VMI	-48	-33	-82	-37	-78	-185		428
MUSSD	380	395	346	391	350	243	428	

Relative expanded uncertainty of the overall difference in assigned volume values between institute *i* and institute *j*, $U(\overline{D}_{ij})$ $\times 10^{-6}$ (k =2)

Inst.*i* \ inst. *j*	**CENAM**	**NMIA**	**SCL**	**NIM**	**NMISA**	**NMIT**	**VMI**	**MUSSD**
CENAM		29	75	31	79	35	43	71
NMIA	29		75	31	80	36	43	71
SCL	75	75		76	105	78	81	99
NIM	31	31	76		80	37	44	72
NMISA	79	80	105	80		82	86	102
NMIT	35	36	78	37	82		78	38
VMI	43	43	81	44	86	78		78
MUSSD	71	71	99	72	102	38	78	

Ratio of $\overline{D}_{ij}$ to $U(\overline{D}_{ij})$

Inst.*i* \ inst. *j*	**CENAM**	**NMIA**	**SCL**	**NIM**	**NMISA**	**NMIT**	**VMI**	**MUSSD**
CENAM		-0.5	0.5	-0.4	0.4	3.9	-1.1	5.4
NMIA	-0.5		0.7	0.1	0.6	4.3	-0.8	5.6
SCL	0.5	0.7		-0.6	0.0	1.3	-1.0	3.5
NIM	-0.4	0.1	-0.6		0.5	4.0	-0.8	5.5
NMISA	0.4	0.6	0.0	0.5		1.3	-0.9	3.4
NMIT	3.9	4.3	1.3	4.0	1.3		-2.4	6.4
VMI	-1.1	-0.8	-1.0	-0.8	-0.9	-2.4		5.5
MUSSD	5.4	5.6	3.5	5.5	3.4	6.4	5.5	

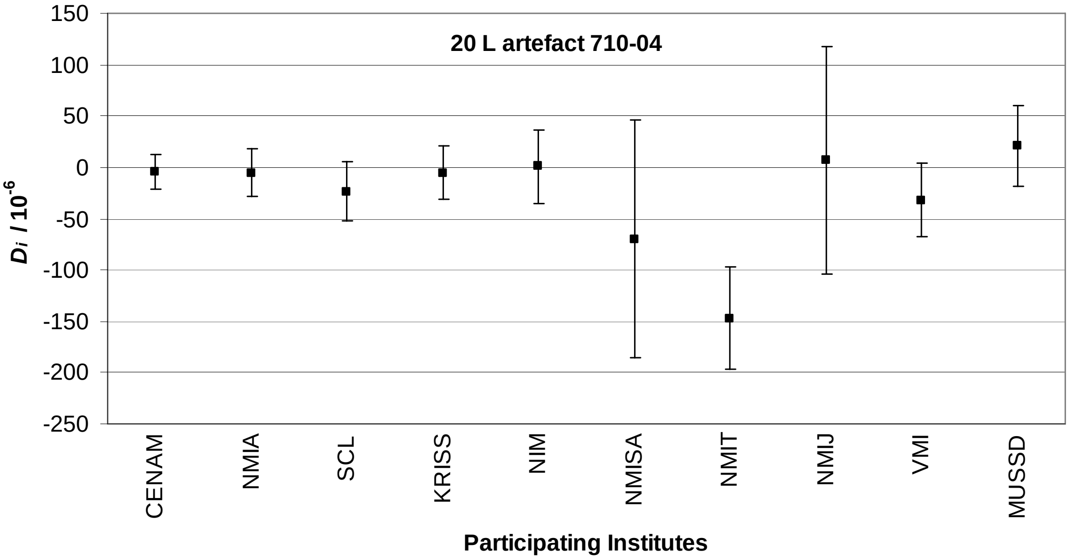

Figure 1: Relative difference between the volume value of the 20 L artefact 710-04 assigned by each participating institute from the KCRV (CCM.FF-K4) with bars representing expanded uncertainties U (k=2). Zero value corresponds to the KCRV of CCM.FF-K4.

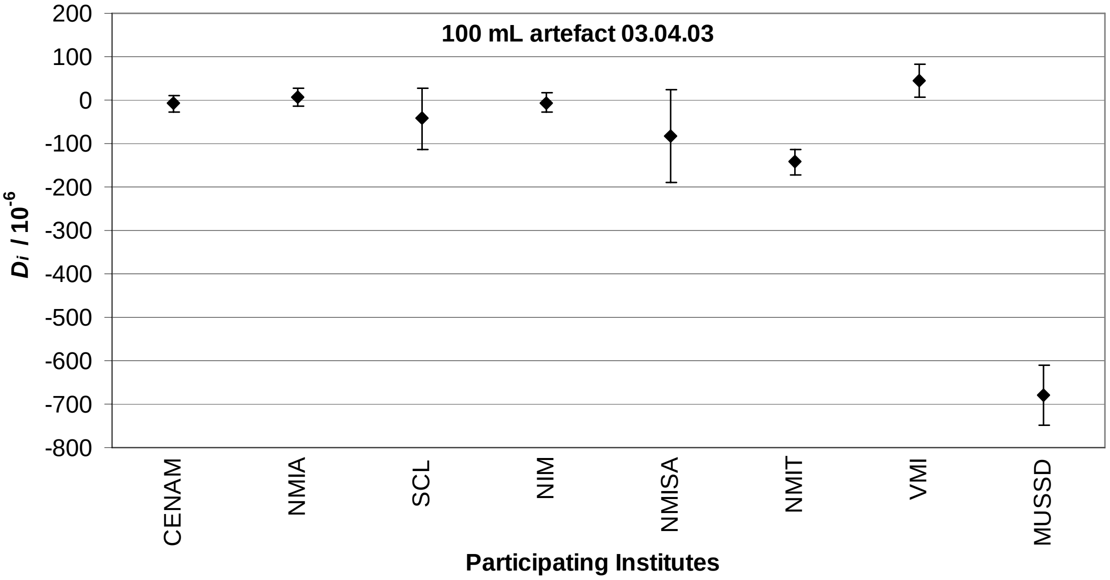

Figure 2: Relative difference between the volume value of the 100 mL artefact 03.04.03 assigned by each participating institute from the KCRV (CCM.FF-K4) with bars representing expanded uncertainties U (k=2). Zero value corresponds to the KCRV of CCM.FF-K4.

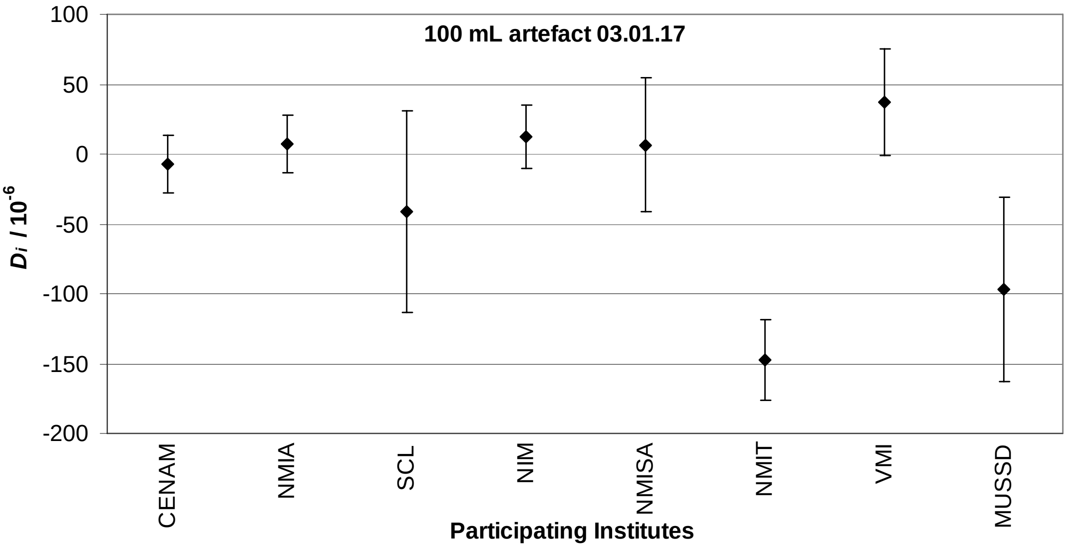

Figure 3: Relative difference between the volume value of the 100 mL artefact 03.01.17 assigned by each participating institute from the KCRV (CCM.FF-K4) with bars representing expanded uncertainties U (k=2). Zero value corresponds to the KCRV of CCM.FF-K4.

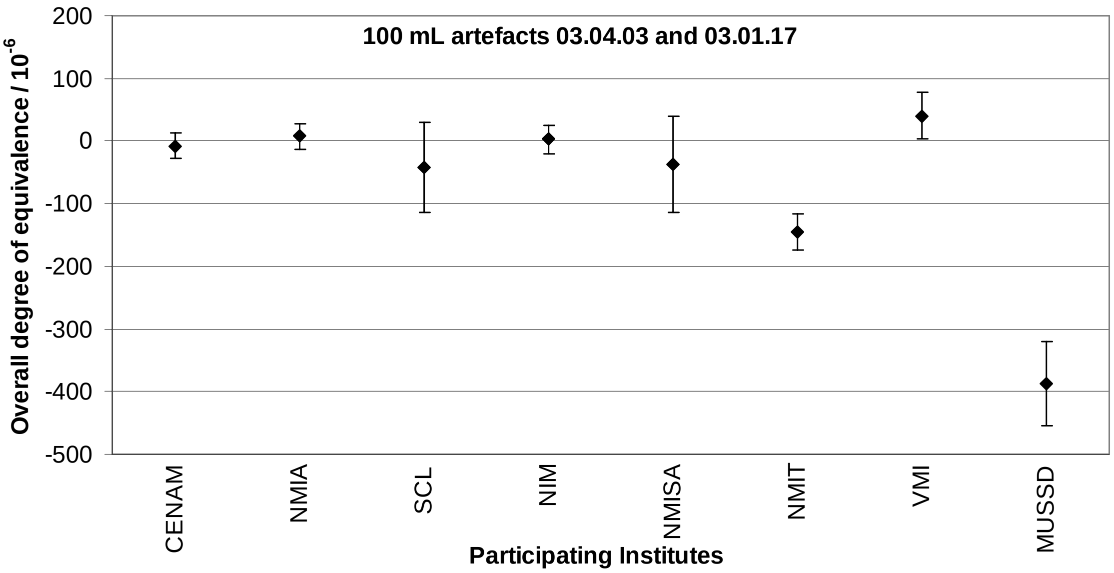

Figure 4: Overall relative difference between the volume value of the 100 mL artefacts 03.04.03 and 03.01.17 assigned by each participating institute from the KCRV (CCM.FF-K4) with bars representing expanded uncertainties U (k=2). Zero value corresponds to the KCRV of CCM.FF-K4.