Final Report

CCM.V-K1 intercomparison

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Abstract

This report describes the first CCM key comparison in capillary viscometry at eleven National Metrology Institutes (NMIs) which was carried out between May and July 2002. Furthermore, seven NMIs which do not maintain an independent viscosity scale took part in this comparison. Five Newtonian liquids with nominal kinematic viscosities of 10 mm^2/s at 20 °C, 1300 mm^2/s at 20 °C, 400 mm^2/s at 40 °C, 40 mm^2/s at 100 °C and 40000 mm^2/s at 20 °C were used to determine the degrees of equivalence between the individual NMIs and the key comparison reference value (KCRV). The relative standard uncertainty of the KCRV extends from 0,05% at 400 mm^2/s to 0,15% at 40 mm^2/s and 100 °C. From the total number of 74 measurements carried out by all the participating NMIs, 18 showed a deviation from the KCRV greater than was covered by the measurement uncertainty.

CONTENTS

1. Introduction

The Ad–Hoc Working Group on Viscosity at BIPM decided on October 26, 2001, to organize a first key comparison on viscosity with PTB acting as the pilot laboratory. All laboratories eligible under the rules of the Mutual Recognition Arrangement (MRA) were invited to participate in this key comparison. The key comparison reference value should, however, be based only on the results of laboratories maintaining an independent viscosity scale. Eleven participants tracing back their viscosity scale directly to the viscosity of water [1], and seven additional participants took part in this key comparison.

The aim of the present intercomparison was

- to check the viscosity scale at low viscosities (close to the viscosity of water), in particular with respect to kinetic energy correction and surface tension correction (standard liquid A)
- to check the step–up procedure from water to 40000 mm^2/s (standard liquid C)
- to check the viscosity measurements at temperatures up to 100 °C (standard liquid B).

2. Participants

List of laboratories maintaining an independent viscosity scale, and names of the persons responsible:

Bureau National de Métrologie – Laboratoire National d'Essais (BNM-LNE) ***France***:
Mohamed Megharfi, Emmanuel Mahé

Cannon Instrument Company (Cannon) ***USA***:
Richard Hoover

Central Office of Measures (GUM) ***Poland***:
Mrs. Jadwiga Nawra

Consiglio Nazionale delle Ricerche–Istituto di Metrologia “G. Colonnetti” (CNR-IMGC) ***Italy***:
Salvatore Lorefice

National Metrology Institute of Japan,
National Institute of Advanced Industrial Science and Technology (NMIJ/AIST) ***Japan***:
Kenichi Fujii, Yasumitsu Kurano

Nederlands Meetinstituut, Van Swinden Laboratorium (NMi VSL) ***The Netherlands***:
Rob H. Bergmans, Mrs. Inge van Andel

National Research Center for Certified Reference Materials (NRCCRM) ***P.R.China***:
Xu Xuelin

Physikalisch–Technische Bundesanstalt Braunschweig (PTB) ***Germany***:
Harro Bauer, Günther Klingenberg

Slovak Institute of Metrology / Slovenský Metrologický Ústav (SMU) ***Slovakia***:
Dusan Trochta

Marmara Arastirma Merkezi / Ulusal Metroloji Enstitüsü TUBITAK (UME) ***Turkey***:
Vahit Ciftci, Orhan Sakarya

D.I. Mendeleyev Institute for Metrology (VNIIM) ***Russian Federation***:
Mrs. Natalia Domostroyeva

List of laboratories with a scale based on other NMIs and names of the persons responsible:

Bundesamt für Eich- und Vermessungswesen (BEV) ***Austria***:
Norbert Kuhn

Centro Nacional de Metrologia (CENAM) ***México***:
Mrs. Sonia Trujillo

Institutul National de Metrologie (INM) ***Romania***:
Mrs. Ana Popescu

Portuguese Institute for Quality (IPQ) ***Portugal***:
Carlos Nieto de Castro, Mrs. Maria do Ceu Ferreira

National Institute for Standards (NIS) ***Egypt***:
Mostafa Mekawy, Nabil El-Sayed

National Physical Laboratory (NPL India) ***India***:
Tripurari Lal

National Metrology Laboratory (SIRIM Berhad) ***Malaysia***:
Mohd Fazrul Hisyam bin Mohd Nor

3. Viscosity scales of the participants

Most of the participants used Ubbelohde viscometers for the basic calibration with water (GUM, IMGC-CNR, PTB, SMU, UME, VNIIM); three used U-tube viscometers (BNM-LNE, NMIJ/AIST, NRCCRM); one participant applied Ostwald viscometers (NMi VSL); and one employed Cannon-Ubbelohde master viscometers, Cannon-Ubbelohde standard viscometers and Cannon-master viscometers (Cannon).
In order to obtain the surface tension correction, dimensional measurements of the viscometers were carried out by BNM-LNE, GUM, NRCCRM, SMU; liquids of well-known surface tensions and viscosities were used by IMGC-CNR, PTB, UME; ASTM D 2162 was applied by Cannon; special methods were used by NMIJ/AIST, VNIIM; and in the case of the Ostwald viscometer (NMi VSL), this correction was not necessary.
For the calculation of the kinetic energy correction term, most participants used the Cannon-Manning-Bell formula [2] (BNM-LNE, GUM, NMIJ/AIST, SMU, UME); two applied the temperature dependence of the viscosity of water (IMGC-CNR, NMi

VSL); one relied on a method starting from the assumption of similarity of viscometers of different size (PTB); one used ASTM D 446 (Cannon); and one applied an empirical approach (VNIIM).

For the step-up procedure as well as for the comparison measurements, Ubbelohde viscometers were used except by NMi VSL (Ostwald viscometers); Cannon (Cannon-Ubbelohde master viscometers, Cannon-Ubbelohde standard viscometers, Cannon-master viscometers); and NMIJ/AIST (U-tube viscometers).

All additional participants used Ubbelohde viscometers with the exception of INM which employed Cannon-master viscometers.

Additional information about the viscosity scales of several participants can be found in [3]. A booklet on its viscosity measurement uncertainties is available from Cannon [4].

4. Liquid samples

The measurements were to be carried out on samples of three standard liquids provided by PTB as the pilot laboratory. The standard liquids A and B were poly-α-olefines and the liquid C was a polyisobutylene. For each liquid and each temperature, samples of 250 ml were supplied. Samples B1, B2 and B3 were the same liquid but taken from different batches. For this reason, a distinction was made between the standard liquids B1 for 20 °C, B2 for 40 °C and B3 for 100 °C. The following data, including standard uncertainties were disseminated by the pilot laboratory:

Standard liquid A at 20 °C: approximate kinematic viscosity: 10 mm²/s; density: (0,79520 ± 0,00008) g/cm³, surface tension: (27,93 ± 0,25) mN/m

Standard liquid B1 at 20 °C: approximate kinematic viscosity: 1300 mm²/s, density: (0,84568 ± 0,00010) g/cm³, surface tension: (30,49 ± 0,25) mN/m

Standard liquid B2 at 40 °C: approximate kinematic viscosity: 400 mm²/s, density: (0,83368 ± 0,00010) g/cm³, surface tension: (30,10 ± 0,25) mN/m

Standard liquid B3 at 100 °C: approximate kinematic viscosity: 40 mm²/s, density: (0,79792 ± 0,00021) g/cm³, surface tension: (26,34 ± 0,58) mN/m

Standard liquid C at 20 °C: approximate kinematic viscosity: 40000 mm²/s, density: (0,88858 ± 0,00010) g/cm³, surface tension: (28,85 ± 0,32) mN/m

For all standard liquids, the long-term stability of the kinematic viscosity was better than 0,1% over six months. Exposure to bright light and high temperatures had to be avoided. It was not permitted to open the sealed glass bottles before the measurements were started. The oils could be heated to 70℃ to facilitate filling of the viscometers. The bottles had to be closed between samplings.

5. Organization of the intercomparison:

Chronology of the measurements:

April 26th, 2002 (pilot laboratory): Mailing of the standard liquids, the report forms, the timetable, and the technical protocol to the participants

May 20th, 2002 (all participants): Start of the comparison measurements

June 28th, 2002 (all participants): Termination of the comparison measurements

July 26th, 2002 (all participants): Submission of the results to the pilot laboratory

October 1st, 2002* (pilot laboratory): Submission of draft report A to the participants

November 15th, 2002 (BIPM): 3rd meeting of the Ad-Hoc Working Group on Viscosity

December 20th, 2002 (pilot laboratory): Submission of draft B

* As there was some delay in obtaining the measurement results from all participants, the Executive Secretary of the Ad-Hoc Working Group on Viscosity agreed to extend the period until October 15th, 2002.

6. Comments on the intercomparison

The participants received the samples before May 20, 2002, with the exception of CENAM (June 03) and VNIIM (July 09). The comparison measurements were carried out between May 20 and July 22. Some participants did not measure all samples. The pilot laboratory corrected the following results to target temperature:

BNM-LNE: A, B1, B2, B3, C
Cannon: A, B1, B2, B3, C
IMGC-CNR: B3
NMIJ/AIST: A, B1, B2, C
UME: B2, B3

CENAM: B2
INM: B2
IPQ: A, B1
NIS Egypt: A, B1, B2, C
NPL India: A, B1, B2, B3
SIRIM: A, B3.

The uncertainty of the viscosity measurement of the participants had to be calculated in accordance with the Guide to the Expression of Uncertainty in Measurement [5]. The pilot laboratory provided an example of the uncertainty calculation in case the viscosity was determined with two viscometers of same size (approximately the same viscometer constant).

7. Results of the CCM.V – K1 intercomparison

During the discussion on the results of the intercomparison at the meeting of the Ad-Hoc Working Group on Viscosity on November 15, 2002, it was decided

- to use the results of all participants with independent scales to calculate the reference value. The use of the weighted mean in connection with a chi-squared test to carry out an overall consistency check of the results obtained, allows discrepant measurements to be identified at the 5% level of significance for liquids A, B3 and C. It was not possible to identify the reason for the discrepancy of these measurements. The calculation of the reference value without using the data from these discrepant measurements would show a perfect situation that differs from reality. This reflects the experience of many experts in this field that unexpected deviations may occasionally occur in measurements with capillary viscometers which are not covered by the uncertainty budget. Such deviations might be caused by undetected cleaning problems.
- to use the arithmetic mean value as reference value since it provides the most realistic picture of the calibration work in viscometry. In addition, the results were calculated for the weighted mean value, the median and the weighted median as reference value. For all five liquids used in this intercomparison the arithmetic mean value was used since the relative differences from the weighted mean and the median did not exceed 0,04% and 0,1%, respectively.

CCM.V-K1 INTERCOMPARISON

Participants	Liquid A				Liquid B1				Liquid B2				Liquid B3				Liquid C			
	ν_i /(mm²/s)	u_i' / 10^{-3}	D_i /10^{-2} (mm²/s)	$U(D_i)$ /10^{-2} (mm²/s)	ν_i /(mm²/s)	u_i' / 10^{-3}	D_i /(mm²/s)	$U(D_i)$ /(mm²/s)	ν_i /(mm²/s)	u_i' / 10^{-3}	D_i /(mm²/s)	$U(D_i)$ /(mm²/s)	ν_i /(mm²/s)	u_i' / 10^{-3}	D_i / 10^{-1} (mm²/s)	$U(D_i)$ / 10^{-1} (mm²/s)	ν_i /(mm²/s)	u_i' / 10^{-3}	D_i / 10^{2} (mm²/s)	$U(D_i)$ / 10^{2} (mm²/s)
BNM-LNE	9,6355	1,00	-1,6	1,8	1281,50	2,00	-4,1	4,7	393,230	2,00	-0,8	1,5	39,890	1,00	0,1	0,8	36499,0	2,00	-0,9	1,4
Cannon	9,6659	0,64	1,4	1,2	1286,10	1,77	0,5	4,2	394,208	1,40	0,1	1,0	39,850	1,07	-0,3	0,8	36677,8	2,15	0,9	1,5
GUM	9,6633	0,38	1,1	0,8	1285,98	0,92	0,4	2,3	394,209	0,73	0,1	0,6					36571,0	1,45	-0,2	1,0
IMGC-CNR	9,5970	0,65	-5,5	1,2	1284,24	0,84	-1,3	2,2	393,690	0,60	-0,4	0,5	39,607	0,83	-2,7	0,7	36556,0	0,96	-0,3	0,7
NMIJ / AIST	9,6590	0,28	0,7	0,6	1286,49	0,42	0,9	1,4	394,389	0,39	0,3	0,4					36554,3	0,61	-0,3	0,5
NMI VSL	9,6530	0,80	0,1	1,5	1285,00	2,00	-0,6	4,8	394,400	1,75	0,3	1,3					36440,0	2,50	-1,5	1,7
NRCCRM	9,6598	0,41	0,8	0,8	1285,80	0,68	0,2	1,9									36501,0	1,82	-0,9	1,3
PTB	9,6557	0,47	0,4	0,9	1285,99	0,78	0,4	2,1	394,160	0,74	0,1	0,6	39,948	0,63	0,7	0,5	36532,3	0,93	-0,6	0,7
SMU	9,6537	0,85	0,2	1,5	1284,10	1,22	-1,5	3,0	393,320	1,21	-0,8	0,9					36604,0	1,80	0,2	1,2
UME	9,6726	0,96	2,1	1,7	1289,16	1,40	3,6	3,4	395,137	1,32	1,1	1,0	39,984	1,15	1,0	0,9	36801,4	1,65	2,1	1,2
VNIIM	9,6558	0,46	0,4	0,9	1286,90	0,63	1,3	1,8	394,010	0,80	-0,1	0,6	39,996	0,81	1,2	0,7	36726,0	0,96	1,4	0,7
Additional participants																				
BEV	9,6640	1,30	1,2	2,5	1288,20	1,77	2,6	4,7	394,510	1,51	0,4	1,2								
CENAM	9,6566	1,03	0,5	2,0	1288,28	1,26	2,7	3,4	394,331	1,26	0,3	1,0	39,950	1,27	0,7	1,1	36888,6	2,53	3,0	1,9
INM	9,6452	0,69	-0,7	1,4	1283,68	0,70	-1,9	2,0	396,929	2,40	2,9	1,9					36635,1	1,20	0,5	1,0
IPQ	9,6497	2,50	-0,2	4,8	1283,75	2,50	-1,8	6,5	394,050	2,40	0,0	1,9								
NIS Egypt	9,6824	1,58	3,0	3,1	1294,27	32,60	8,7	84,4	394,768	20,90	0,7	16,5					37303,4	6,13	7,2	4,6
NPL India	9,6718	1,26	2,0	2,5	1287,37	1,52	1,8	4,0	394,950	1,26	0,9	1,0	39,997	1,32	1,2	1,1				
SIRIM	9,6046	3,20	-4,7	6,2									39,768	0,80	-1,1	0,7				
Reference value	ν_R / (mm²/s)	U' / 10^{-3}	U / 10^{-2} (mm²/s)		ν_R / (mm²/s)	U' / 10^{-3}	U /(mm²/s)		ν_R / (mm²/s)	U' / 10^{-3}	U /(mm²/s)		ν_R / (mm²/s)	U' / 10^{-3}	U / 10^{-1} (mm²/s)		ν_R / (mm²/s)	U' / 10^{-3}	U / 10^{2} (mm²/s)	
	9,6519	1,28	1,23		1285,57	0,90	1,16		394,075	0,90	0,353		39,879	2,96	1,179		36587,5	1,77	0,649	

Table 1: Results of the CCM.V-K1 intercomparsion. Symbols as defined in the text.

The measurement results are compiled in Table 1. A cross indicates that the participant did not take part in the intercomparison of this liquid. ν_i is the kinematic viscosity, $u_i^{'}$ the relative standard measurement uncertainty stated by each participant, and *n* the number of participants. The reference value (arithmetic mean value)

$$\nu_R = \frac{1}{n}\sum_{i=1}^{n}\nu_i \tag{1}$$

as well as the uncertainty (*k* = 2) of this mean value

$$U = 2 \cdot \sqrt{\frac{1}{n(n-1)}} \cdot \sqrt{\sum_{i=1}^{n}(\nu_i - \nu_R)^2} \tag{2}$$

and the relative uncertainty of the mean value $U^{'} = U / \nu_R$ are calculated. The quantity $U^{'}$ can be found in the line “Reference value” of Table 1, followed by U.
The degrees of equivalence are calculated with the aid of the following two formulas privately communicated by R. Davis, BIPM. The offset

$$D_i = \nu_i - \frac{1}{n}\sum_{j=1}^{n}\nu_j \tag{3}$$

is the difference of the viscosity obtained by institute i from the reference value. Equation (3) is regarded as the working equation within the meaning of the “Guide to the Expression of Uncertainty in Measurement” [5] with the influence quantities $\nu_1 ... \nu_n$. For a laboratory, i, whose result is used to compute ν_R, the variance of the offset is

$$u^2(D_i) = \frac{1}{n^2}\sum_{j=1}^{n}u_j^2 + \left(1 - \frac{2}{n}\right)u_i^2 \tag{4}$$

with $u_i = \nu_R \cdot u_i^{'}$, and the expanded uncertainty of the offset (*k* = 2):

$$U(D_i) = 2 \cdot u(D_i)\,. \tag{5}$$

For a laboratory, i, whose result is not used to compute ν_R, the variance of the offset is simply

$$u^2(D_i) = \frac{1}{n^2}\sum_{j=1}^{n}u_j^2 + u_i^2\,. \tag{6}$$

The degrees of equivalence D_i and $U(D_i)$ between institute i and the reference value can be seen from Table 1.

The degrees of equivalence between institute i and institute j are

$$D_{i,j} = \nu_i - \nu_j \qquad (7)$$

$$U(D_{i,j}) = \sqrt{4u_i^2 + 4u_j^2} \qquad (8)$$

and can be calculated from the information available in Table 1.

In the middle part of Table 1 the results for the additional participants are listed.

The relative uncertainty of the reference value for liquids A, B1 and B2 is about 0,1%, whereas for liquid B3 0,3% and for liquid C 0,2% are obtained. This is a good result which is comparable with the most recent EUROMET intercomparisons [3]. There is an increase in measurement uncertainty at higher viscosity (liquid C) as well as at higher temperatures (liquid B3). In the case of the liquid B3, it is to be noted that only six participants contributed to the reference value.

The data from Table 1 are additionally plotted in Fig. 1 to Fig. 5.

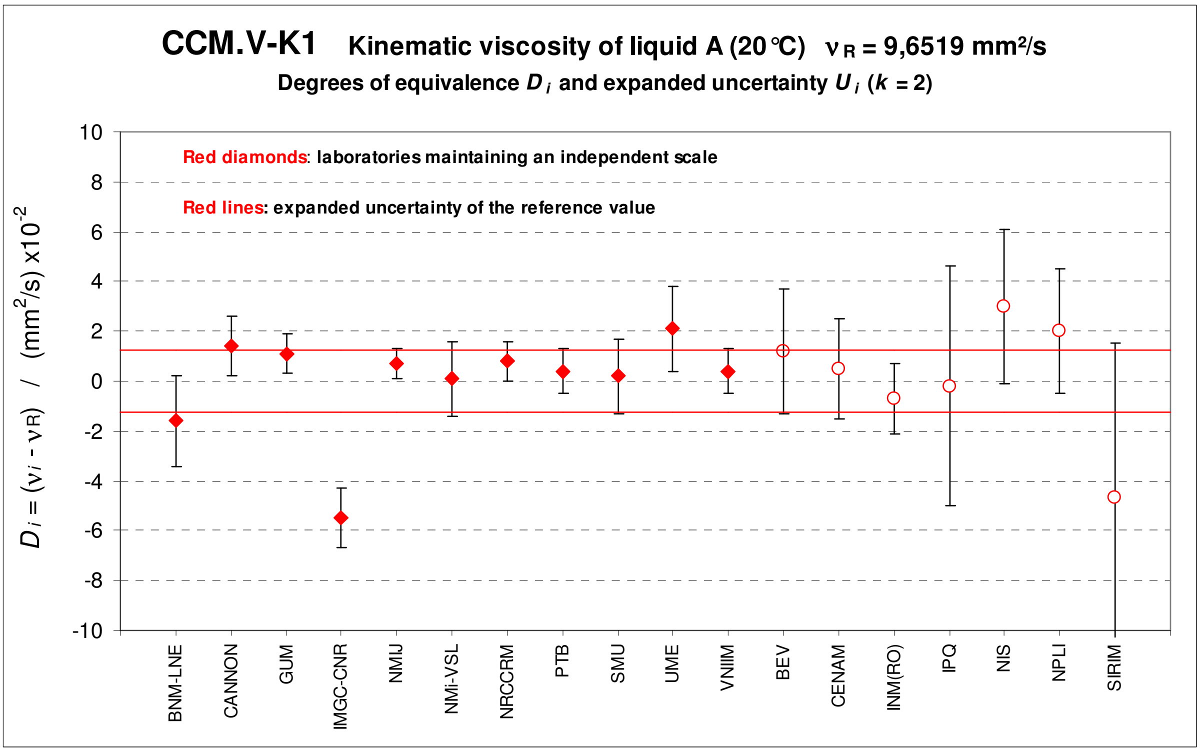

Figure 1: Liquid A at 20 °C

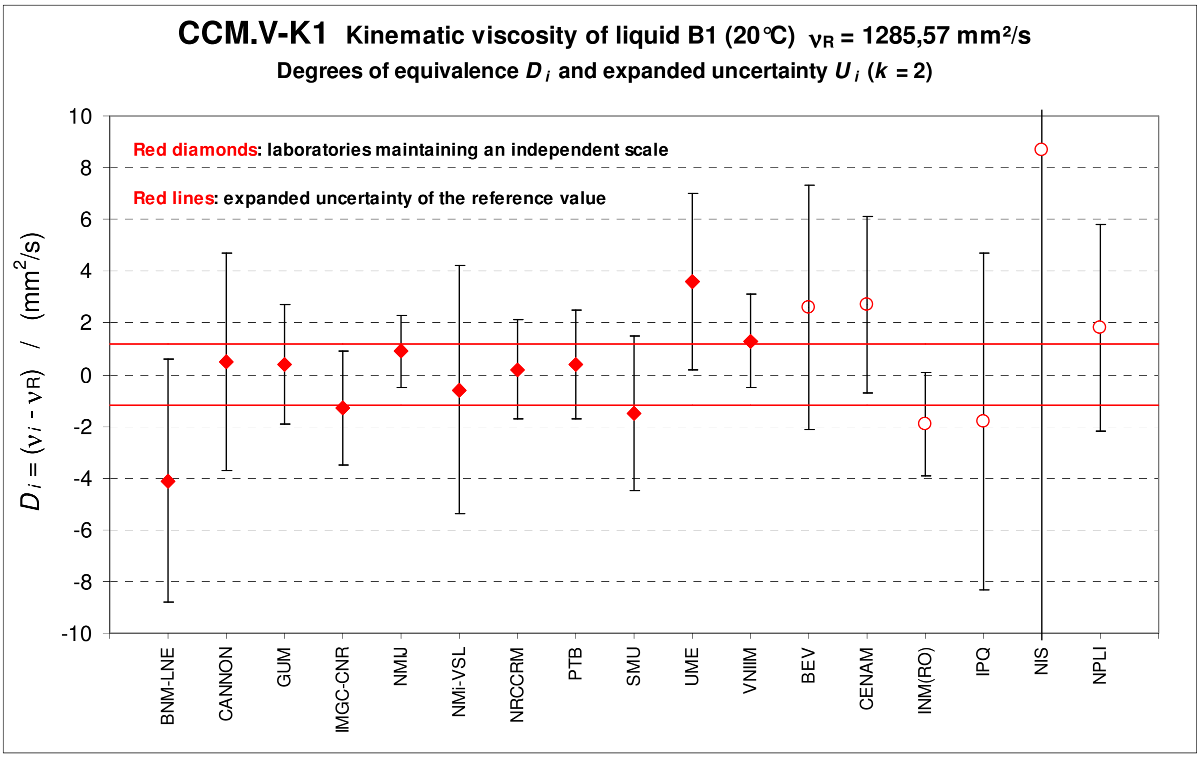

Figure 2: Liquid B1 at 20 °C

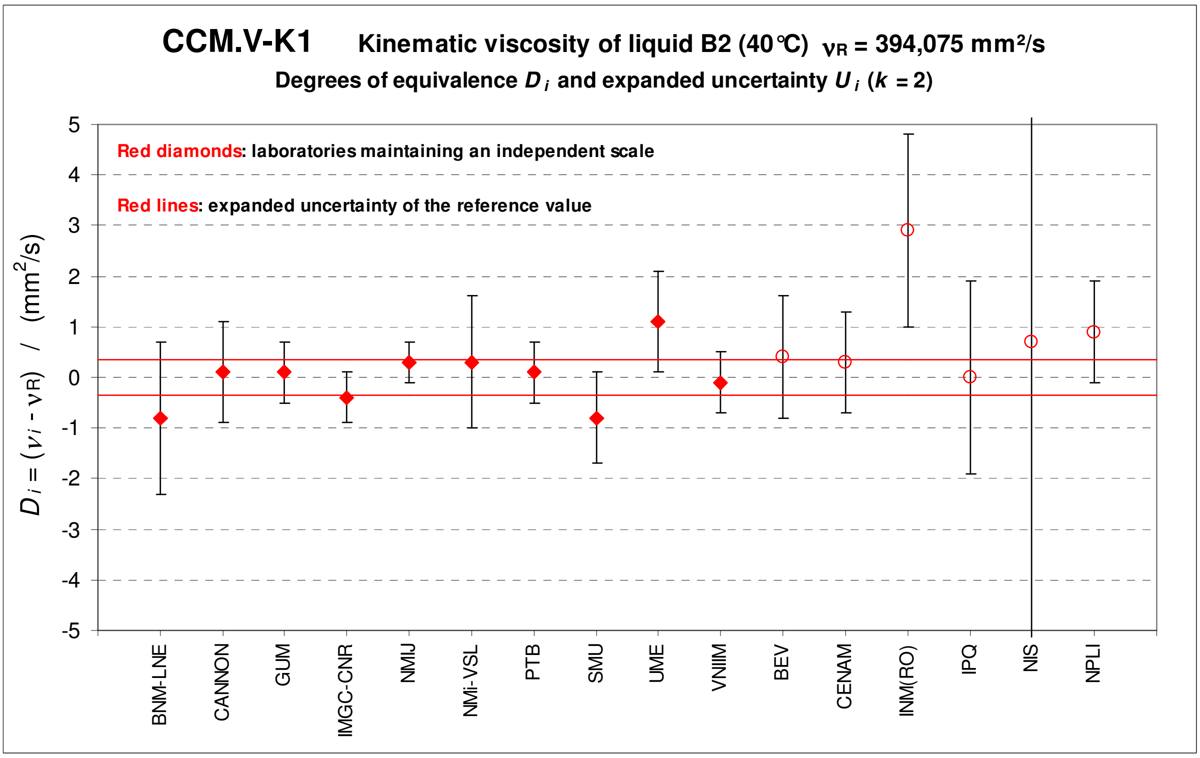

Figure 3: Liquid B2 at 40 °C

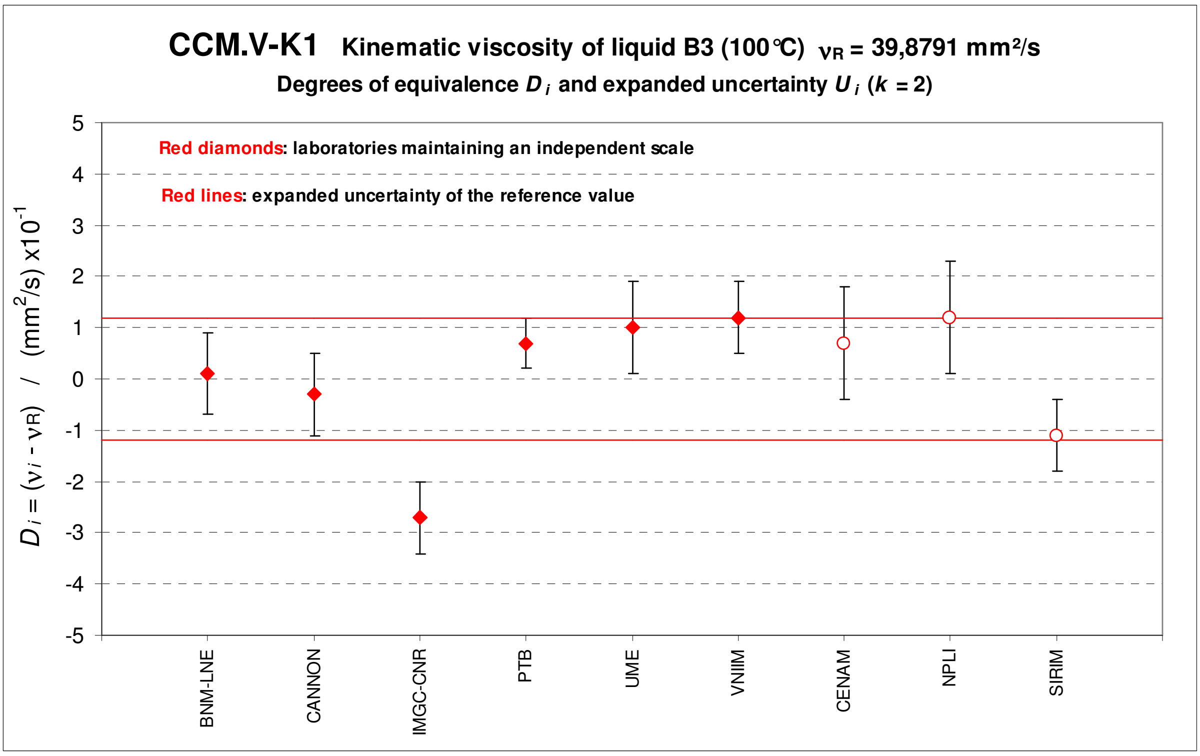

Figure 4: Liquid B3 at 100 °C

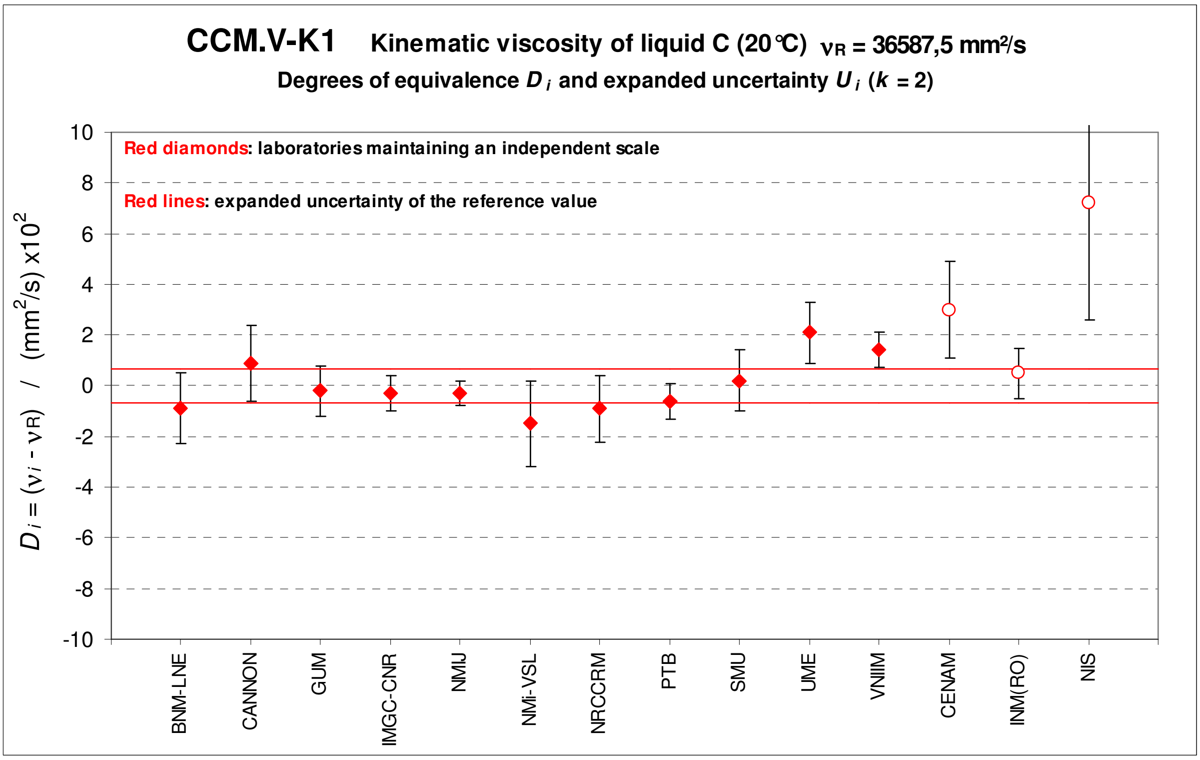

Figure 5: Liquid C at 20 °C

References

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[4] M. R. Hoover, R. E. Manning, R. F. Berg: Cannon Instrument Company's Viscosity Measurement Uncertainties (2002) Cannon, USA

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