Final Report

On EURAMET Key Comparison EURAMET.M.D-K2.1 (1522)

Key comparison on density determination of liquids by hydrostatic weighing

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Contents

Table of Figures

1. Introduction

This report presents the results of the EURAMET.M.D-K2.1 (1522) key comparison on the density of liquids determined by hydrostatic weighing. It was organized and carried out within the framework of the EMPIR project 17RPT02 “rhoLiq”.

The aim of this key comparison is to compare the results of the density determinations of liquid samples by hydrostatic weighing of the participating laboratories. Density measurements of liquids are mainly performed by laboratories calibrating or checking liquid density measuring instruments such as oscillation-type density meters. Another aim of this comparison is to establish traceability for liquid density measurements at emerging National Metrology Institutes (NMIs) to enable them to provide high-level measurement and calibration services, and to produce density reference materials for national stakeholders, e.g. food, chemical, pharmaceutical and petroleum industries. The results of this comparison can be used to claim calibration and measurement capabilities (CMCs).

BEV organized the comparison and acted as pilot, supported by PTB. The participating NMIs are listed in table 1.

For the comparison samples of deuterated ultra-pure water, tetrachloroethylene (TCE), and of an oil with a high viscosity (EF168) were measured by the hydrostatic weighing method using solid density standard. The chosen liquids represent a density interval from 700 kg/m^3 to 1 600 kg/m^3. The temperature range was from 5 °C to 20 °C. The measurements should have been carried out at atmospheric pressure. The reference values for this comparison were determined by BEV and PTB. BEV’s values were linked to EURAMET.M.D-K2 [1] and PTB’s values were linked to CCM.D-K2 [2]. These reference values were also used in EURAMET.M.D-K2.2 (1523) key comparison on density determination of liquids using oscillation type density meters.

The majority of European emerging NMIs participated in this project had not yet participated in a Regional Metrology Organisation (RMO) or in a *Comité Consultatif pour la Masse et les Grandeurs Apparentées* (CCM) comparison, or they obtained unsatisfactory results, or the uncertainty had a magnitude that was not fit for purpose.

In the presented comparison IPQ, BEV-PTP, INM, CMI, DMDM, GUM, IMBiH, JV, PTB, and UME participated. The results of ten hydrostatic weighing apparatuses (1 per partner) were compared against the reference values provided by the PTB’s and BEV’s hydrostatic weighing apparatuses.

The preparation of the samples started in January 2019 and the shipment of the samples was completed in March 2019. The corona pandemic caused delays in the originally proposed schedule of this key comparison. The final version of the technical protocol for the comparison procedure was issued by BEV-PTP in November 2021. Measurements were performed from March to June 2021.

2. Participants

Ten laboratories took part in the comparison and received samples.

Table 1: Participating laboratories, address and responsible person.

Laboratory (country)	Mailing address for the packages	Person responsible for the comparison
BEV-PTP (Austria)	Bundesamt für Eich- und Vermessungswesen Arltgasse 35 A-1160 Vienna Austria	Lukas Prochaska Tel.: +43 1 21110 826363 e-mail: lukas.prochaska@bev.gv.at
INM (Romania)	Institutul National de Metrologie Sos. Vitan-Bârzesti 11, Sector 4, RO-042122 Bucuresti, Romania	Florin Benga Tel.: +4021 3345060 Fax: +4021 3345345 e-mail: florin.benga@inm.ro
CMI (Czech Republic)	Cesky Metrologicky Institut Okružní 31, CZ-638 00 Brno, Czech Republic	Peter Bartos Tel: +545 555322 e-mail: pbartos@cmi.cz
DMDM (Serbia)	Direkcija za mere i dragocene metale Mike Alasa 14, 11000 Beograd	Jelena Bebic Tel: +381(11) 202 44 26 e-mail: jelenabebic@dmdm.rs
GUM (Poland)	Główny Urząd Miar Elektoralna 2 00-139 Warszawa Poland	Elżbieta Lenard Tel.: +48 22 581 9410, +48 22 581 9010 Fax: +48 581 93 80 e-mail: elzbieta.lenard@gum.gov.pl
IMBiH (Bosnia and Herzegovina)	Institut za mjeriteljstvo Bosne i Hercegovine Augusta Brauna 2 71000 Sarajevo	Sejla Alisic Azmir Alic Tel: +387(0) 33 568 920 Fax: +387 (0) 33 568 909 e-mail: sejla.alisic@met.gov.ba azmir.alic@met.gov.ba
IPQ (Portugal)	Instituto Português da Qualidade Rua António Gião 2 2829-513 CAPARICA Portugal	Andreia Furtado Tel.: +35 1212948164 Fax: +35 1212948188 e-mail: afurtado@ipq.pt

Laboratory (country)	Mailing address for the packages	Person responsible for the comparison
JV (Norway)	Justervesenet Fetveien 99 N-2007 Kjeller Norway	Pekka T Neuvonen Tel.: +47 64848484 Fax: +47 64848485 e-mail: ptn@justervesenet.no
PTB (Germany)	Physikalisch-Technische Bundesanstalt Bundesallee 100 38116 Braunschweig Germany	Jürgen Rauch Tel.: +49 531 592-3141 Fax: +49 531 592-3305 e-mail: juergen.rauch@ptb.de
UME (Türkiye)	Ulusal Metroloji Enstitüsü P.K. 54, 41470, Gebze – Kocaeli Türkiye	Gökce S. Sariyerli Ümit Y. Akcadag Tel.: + 90 (262) 679 50 00 Fax: + 90 (262) 679 50 01 e-mail: gokce.sariyerli@tubitak.gov.tr umit.akcadag@tubitak.gov.tr

3. Liquid Samples

For the purpose of this comparison the density of deuterated ultra-pure water (air saturated, mixture with ultrapure water), tetrachloroethylene (TCE) and an oil with a high viscosity (EF168) at 2 temperatures (5 °C, 20 °C) were determined. TCE was chosen for its large density, EF168 was chosen for its relatively high viscosity compared to the other two liquids. The density of the water was modified by the addition of heavy water. The measurements were carried out at atmospheric pressure by hydrostatic weighing of a solid density standard.

The necessary amount of the liquids was prepared by PTB. The liquids were sent to the laboratories as part of the diagnostic comparison within the EMPIR rhoLiq project 17RPT02. The deuterated water was a mixture of ultrapure tap water from PTB (Braunschweig/Germany) and of heavy water (D_2O) with a concentration of approximately 0.2 vol% (labelled as “water” in the subsequent text). The total volume of TCE and EF168 had been homogenized and refilled in 1 L bottles. Each liquid was distributed in 1 litre transport bottles and labelled according to a sample plan.

The samples were checked for homogeneity and stability. This process is described in detail in Chapter 4.

4. Results of check measurements

The stability and homogeneity of the prepared test liquids were checked by density measurements. The check measurements started at the time of the hydrostatic weighing measurements of the samples in March 2021. The final check measurements were carried out in June 2021.

The density meter used for the check measurements was a DMA5000 (Anton Paar) with a resolution of 0.001 kg/m^3. The uncertainty of the absolute density values of the DMA5000 is approximately between 0.01 kg/m^3 and 0.02 kg/m^3. The differences between density values were determined with uncertainties less than 0.002 kg/m^3.

Each time in between the check measurements, the density of ultrapure water was measured as a reference.

4.1. Drift or stability of the liquid density

From each of the three liquids under test 18 bottles of 1 L for hydrostatic weighing by the project partners were prepared. Two retention samples of 10 mL were taken from each 1 L-bottle before sealing. The 10 mL retention samples were labelled and stored at PTB. The labelling ensured a direct link form the 10 mL retention samples to the distributed 1 L-bottles. The total amount of retention samples for each sample were split into two ensembles. Each ensembles of retention samples represented the 18 times 1 L-bottles. The density values were determined with a certain time interval between the two ensembles of retention samples. The time interval represents at least the starting point and the end of the density measurements by all project partners.

The drift of the density values was estimated in the following way: The difference of the measured mean density values ($\Delta\rho$) between the two ensembles of retention samples was regarded as a rectangular distribution and the expanded (k=2) uncertainty (U_{drift}) of the mean value of that rectangular distribution is assumed to represent the drift or stability of the density value.

Sending the samples back to the pilot laboratory was not required by the technical protocol.

Table 2: Estimated values of the sample stability.

Samples	$\Delta\rho$	U_{drift} Drift/Stability
	kg m^{-3}	
Water	0	0
TCE	0.019	0.011
EF168	0	0

4.2. Homogeneity of the liquid density

For determination of the homogeneity of the three samples, the density measurements of the retention samples were used. Two times the standard deviation of a single measured density value served as the measure for the homogeneity of the test samples and was regarded as a rectangular distribution. The expanded (k=2) uncertainty (U_{hom}) of the mean value of that rectangular distribution is assumed to represent the homogeneity of the density value.

Table 3: Estimated homogeneity of the samples.

Samples	U_{hom} Homogeneity
	kg m^{-3}
Water	0.0081
TCE	0.073
EF168	0.064

5. Results of project partners and data analysis

5.1. General issues

Within a period of two months all measurements should had been performed according to the timetable of the technical protocol. The actual measurements were performed from March to June 2021. Due to the pandemic situation the reporting deadline was extended until November 2021. All partners except CMI sent their reports until the extended deadline. CMI delivered their reports in March 2022.

5.2. Reference values

In order to calculate the reference values the measurement results of the pilot laboratories were linked to CCM.D-K2 [2] for PTB and EURAMET.M.D-K2 [1] for BEV-PTP.

From the results of the link laboratories (X_i) the linked reference value of each pilot laboratory was calculated by

$$X_{Ri} = X_i - D_i \tag{1}$$

with the D_i originating from CCM.D-K2 and EURAMET.M.D-K2, respectively. The standard uncertainty of the linked reference values of each link laboratory was estimated by

$$u_{Ri} = \sqrt{u^2(D_i) + u^2(X_i) - 2 \cdot \mathrm{cov}(D_i, X_i) + u_{\mathrm{drift}}^2 + u_{\mathrm{hom}}^2} \tag{2}$$

with *u*(D_i) representing the standard uncertainty for D_i from CCM.D-K2 / EURAMET.M.D-K2 and *u*(X_i) the uncertainty of the results reported by the link laboratories. The correlation *cov*(D_i,X_i) between the measurements in this comparison, and the key comparisons CCM.D-K2 / EURAMET.M.D-K2, is not negligible because of the very similar circumstances and instruments used during the measurements. PTB estimated a correlation of 100 % (same apparatus and staff) while BEV-PTP estimated the correlation to be of 2.5 % due to the long time of around 15 years that passed since the last key comparison, changes in personnel and the slightly different liquid samples.

From these corrected values (X_{Ri}) the weighted average has been calculated:

$$X_{\mathrm{ref}} = \overline{X_{Ri}} = \frac{\sum(W_i \cdot X_{Ri})}{\sum W_i} \text{ with } W_i = \frac{1}{u_{Ri}^2} \tag{3}$$

The reference value standard uncertainty combining these effects is:

$$u_{\mathrm{ref}} = \frac{1}{\sqrt{\sum W_i}} \tag{4}$$

Table 4: Reference density values.

Liquids and temperatures		X_{ref}	U_{ref} (k=2)
		kg m^{-3}	
Water	20 °C	998.4205	0.0066
TCE	5 °C	1647.424	0.053
	20 °C	1622.598	0.053
EF168	20 °C	830.358	0.045

5.3. Degrees of equivalence

The degree of equivalence D_i of the project partners institute i with respect to the reference value X_{ref} is calculated by

$$D_i = x_i - X_{\mathrm{ref}} \tag{5}$$

where x_i is the reported density value. The expanded uncertainty for D_i of the participating laboratories is given by

$$U(D_i) = \sqrt{U_i^2 + U_{\mathrm{ref}}^2} \tag{6}$$

and for the linking laboratories by

$$U(D_i) = \sqrt{U_i^2 - U_{\mathrm{ref}}^2} \tag{7}$$

The minus sign in the equation above takes into account the correlation between the laboratory measurement standard uncertainty and the reference standard uncertainty that was calculated form the laboratory result.

The absolute normalised error E_n of the project partners institute i and of the linking laboratories is calculated with respect to the reference value X_{ref} by

$$E_n = \frac{|D_i|}{U(D_i)} \tag{8}$$

5.4. Deuterated Water

In this section the density measurement results of deuterated water (0.2 % D_2O in H_2O) at the temperature of 20 °C are presented. The density results ρ und its expanded uncertainties $U(\rho)$ reported by the project partners are summarised in Table 5 together with the degree of equivalence D_i and its expanded uncertainty $U(D_i)$, the degree of equivalence D_i given in ppm and the absolute normalised error E_n.

All reported uncertainties in Table 5 represent a confidence interval of 95 % (expansion factor k=2).

The density reference value is calculated as it is described in Chapter 5.2.

The expanded uncertainties $U(\rho)$ in Table 5 are given by the project partners and do not include contributions due to the drift or the inhomogeneity of the liquid samples. The normalised error E_n, of the laboratory i with respect to the reference value X_{ref} (Table 4) is calculated as in Chapter 5.2.

The expanded uncertainties $U(\rho)$ of the results of BEV-PTP and PTB providing the reference values are increased, due to the linking procedure after [1] and due to the sample inhomogeneities listed in Table 3.

Table 5: Results of deuterated water at 20 °C.

Project partner	ρ in kg m^{-3}	$U(\rho)$ in kg m^{-3}	D_i in kg m^{-3}	$U(D_i)$ in kg m^{-3}	E_n
BEV-PTP	998.425	0.011	0.0045	0.0093	0.49
INM	998.4336	0.0070	0.0131	0.0096	1.36
CMI	998.428	0.022	0.008	0.023	0.35
DMDM	998.4188	0.0084	-0.002	0.011	0.16
GUM	998.410	0.015	-0.011	0.016	0.65
IMBIH	998.429	0.012	0.009	0.013	0.66
IPQ_2nd	998.4309	0.0056	0.0104	0.0087	1.20
JV	998.392	0.080	-0.029	0.081	0.35
PTB	998.4240	0.0081	0.0035	0.0047	0.74
UME	998.4275	0.0082	0.007	0.011	0.66

The measured density values are displayed in Figure 1.

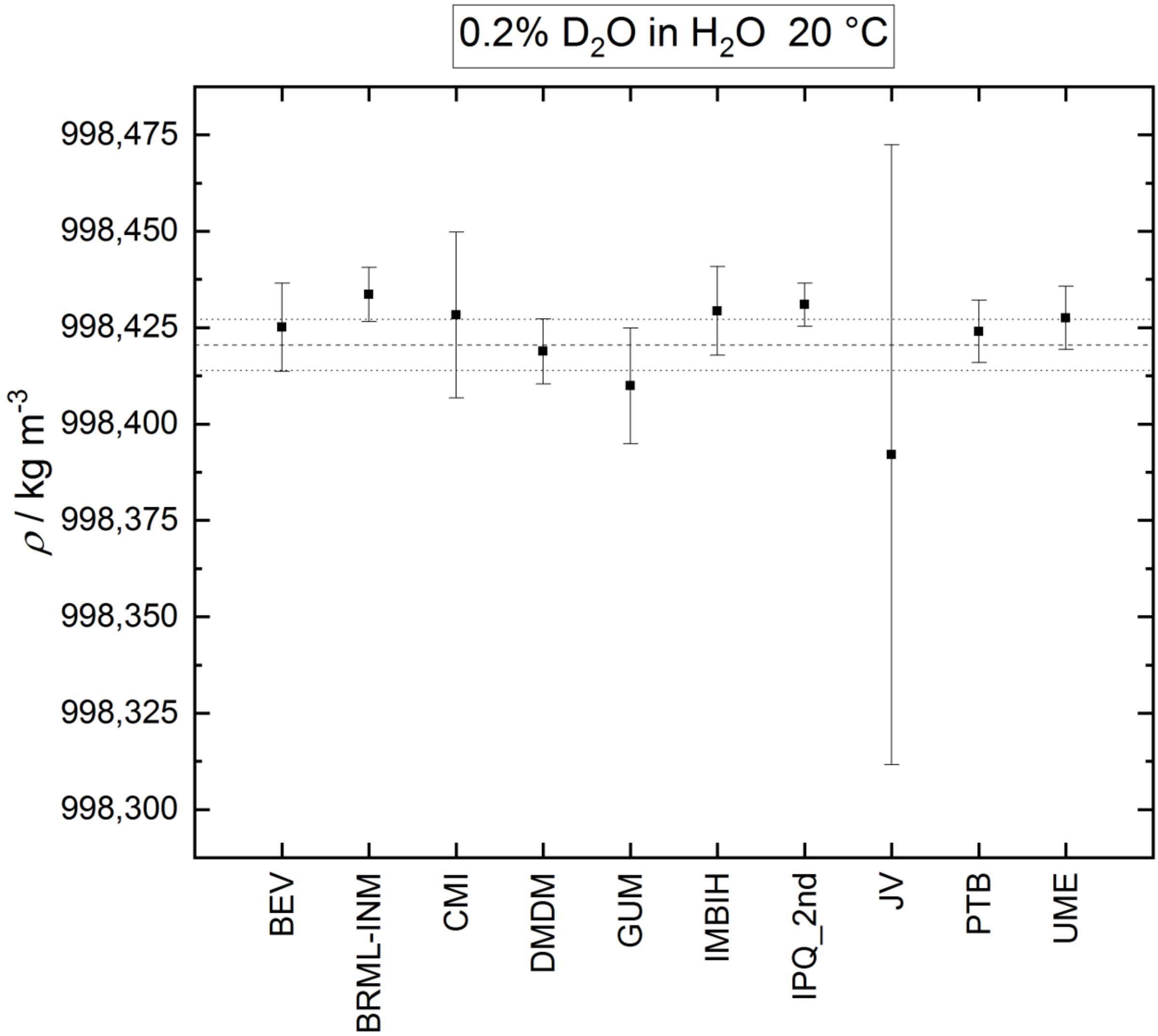

Figure 1: Water at 20 °C. Measured (Table 5) and reference density values (X_{ref}: dashed line; $X_{ref} \pm U_{ref}$: dotted lines; Table 4) with their expanded uncertainties (k=2).

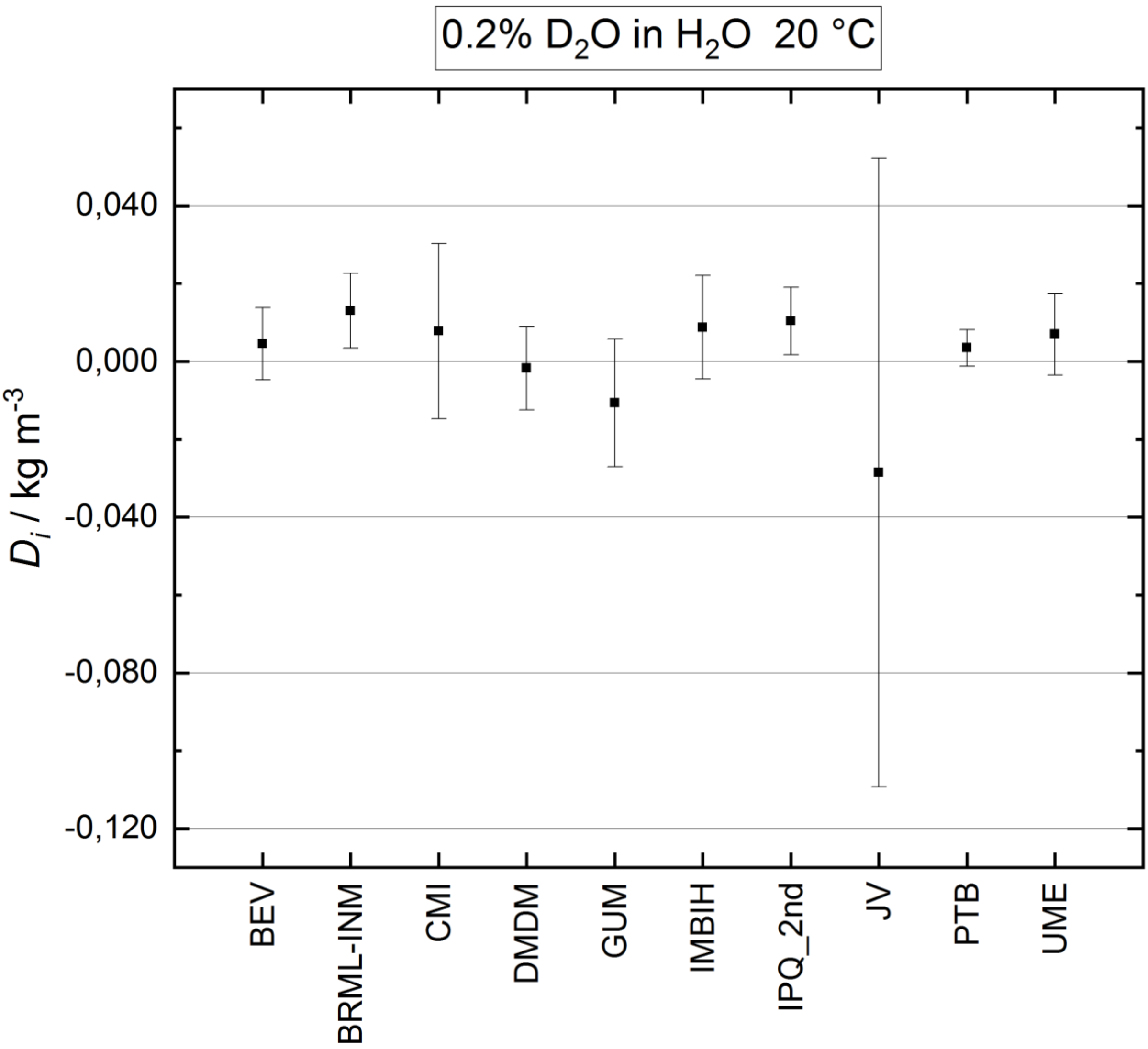

Figure 2: Water at 20 °C. Degree of equivalence D_i.

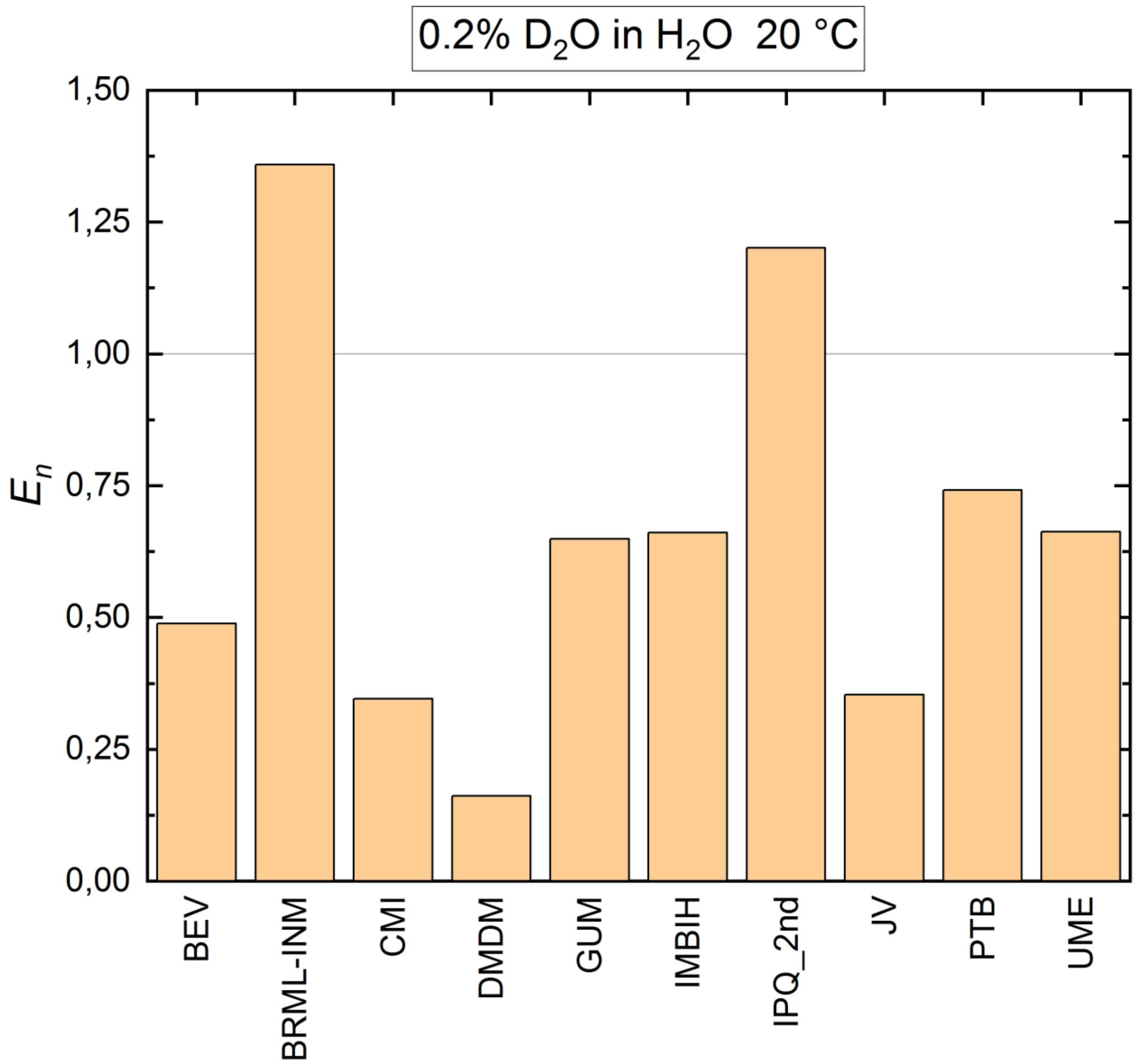

Figure 3: Water at 20 °C. Normalised error E_n.

5.5. Tetrachloroethylene (TCE)

5.5.1. TCE at 5 °C

In this section the density measurement results of tetrachloroethylene (TCE) at 5 °C are presented. The density results ρ und its expanded uncertainties $U(\rho)$ reported by the project partners are summarised in Table 6 together with the degree of equivalence D_i and its expanded uncertainty $U(D_i)$, the degree of equivalence D_i given in ppm and the absolute normalised error E_n.

All reported uncertainties in Table 6 represent a confidence interval of 95 % (expansion factor k=2).

The density reference value is calculated as it is described in Chapter 5.2.

The expanded uncertainties $U(\rho)$ given by the project partners in Table 6 do not include contributions due to the drift or the inhomogeneity of the liquid samples. The normalised error E_n, of the laboratory i with respect to the reference value X_{ref} (Table 4) is calculated as in Chapter 5.2.

The expanded uncertainties $U(\rho)$ of the results of BEV-PTP and PTB providing the reference values are increased, due to the linking procedure after [1] and due to the sample inhomogeneities listed in Table 3.

Table 6: Results TCE at 5 °C.

Project partner	ρ in kg m^{-3}	$U(\rho)$ in kg m^{-3}	D_i in kg m^{-3}	$U(D_i)$ in kg m^{-3}	E_n
BEV-PTP	1647.425	0.077	0.001	0.055	0.02
INM	1647.0747	0.0075	-0.350	0.054	6.53
CMI	1647.724	0.080	0.299	0.096	3.11
DMDM	1647.290	0.028	-0.135	0.060	2.25
GUM	1647.427	0.011	0.003	0.054	0.05
IMBIH	---	---	---	---	---
IPQ_2nd	1647.377	0.013	-0.047	0.055	0.87
JV	---	---	---	---	---
PTB	1647.428	0.074	0.004	0.051	0.07
UME	1647.445	0.019	0.020	0.057	0.36

IPQ submitted corrected results labelled 'IPQ_2nd' because there were some errors in the calculations.

IMBiH and JV did not deliver data for TCE at 5 °C.

The measured density values are displayed in Figure 4.

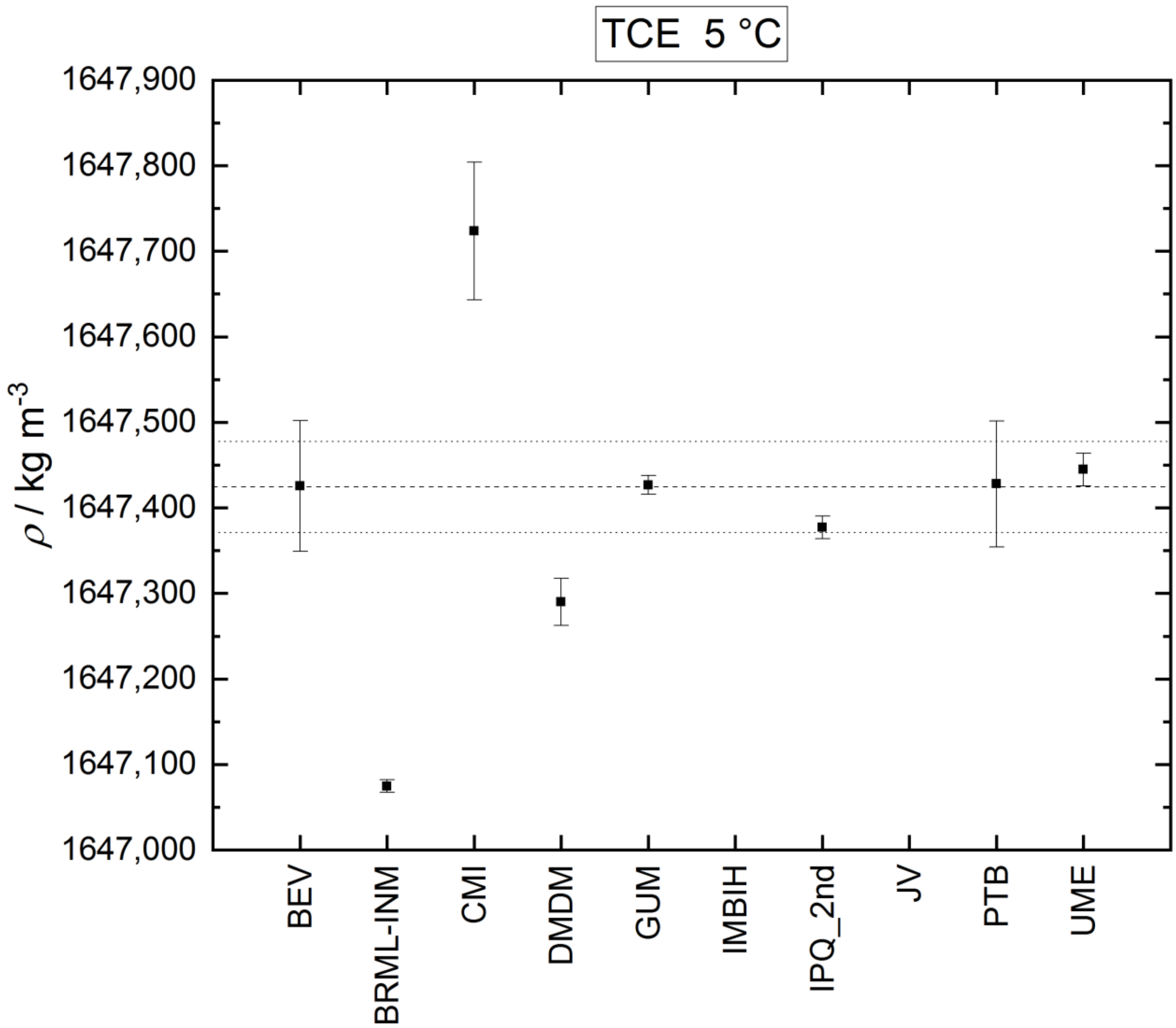

Figure 4: TCE at 5 °C. Measured (Table 6) and reference density values (X_{ref}: dashed line; $X_{ref} \pm U_{ref}$: dotted line; Table 4) with their expanded uncertainties (k=2).

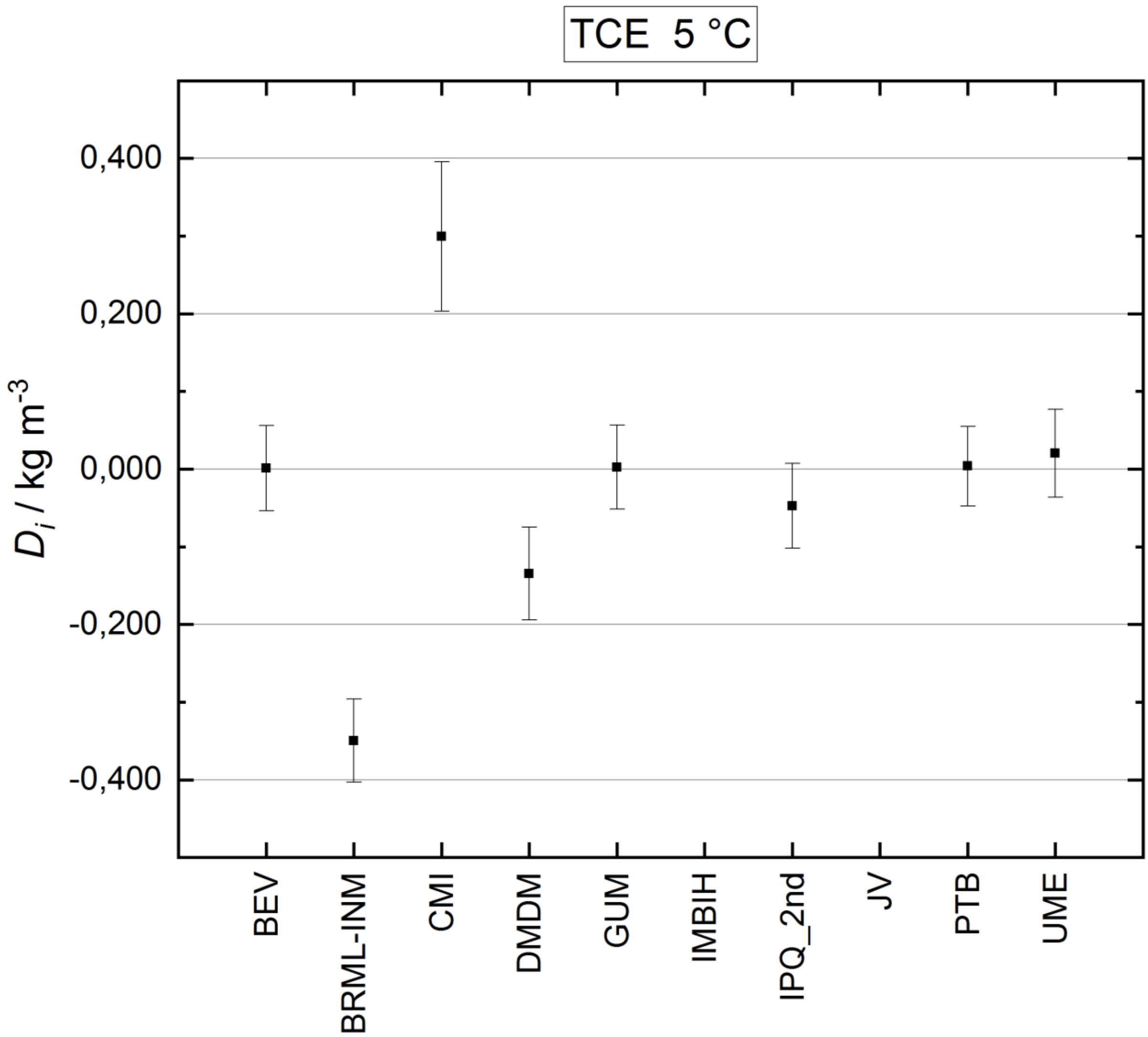

Figure 5: TCE at 5 °C: Degree of equivalence D_i.

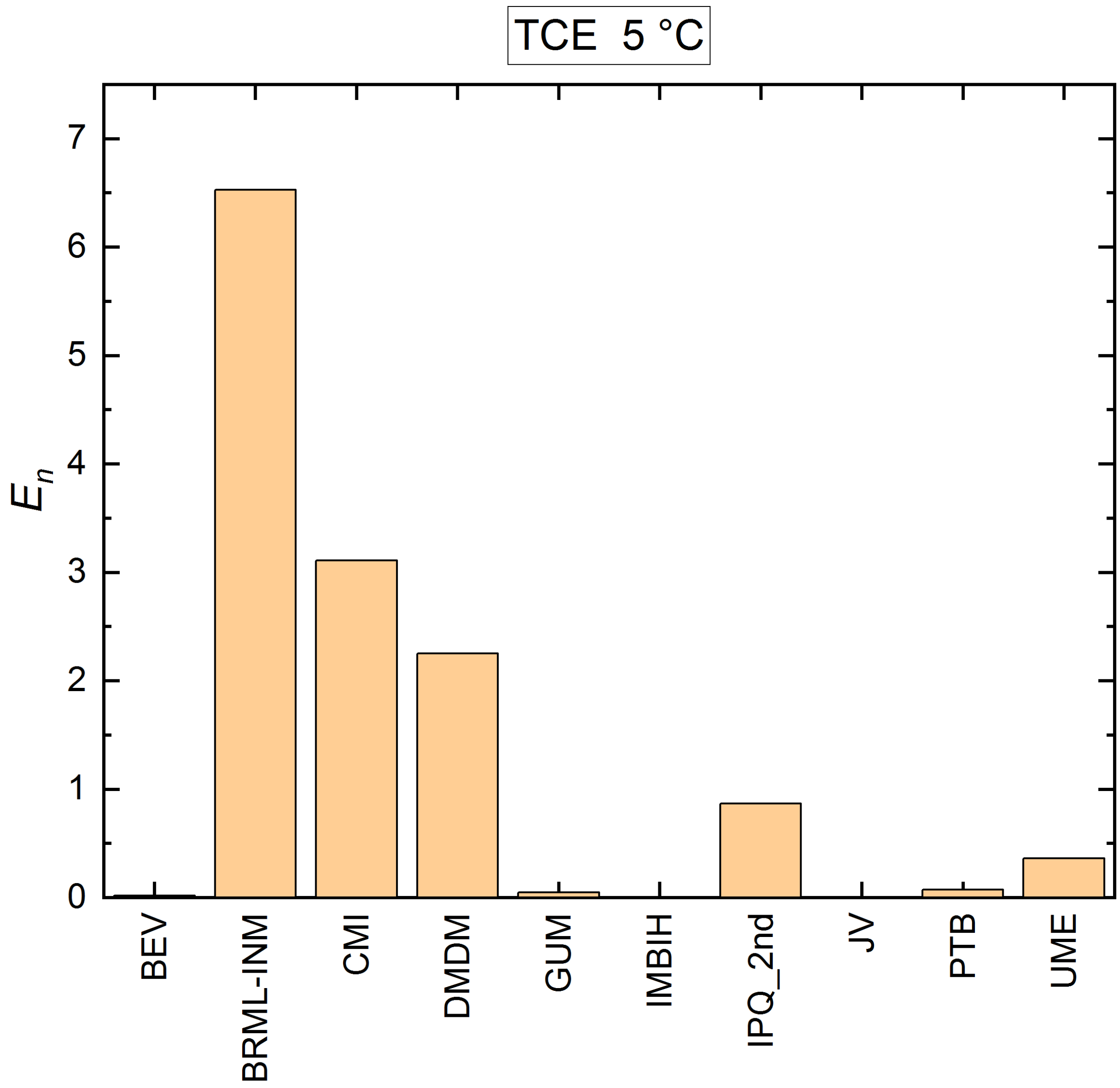

Figure 6: TCE at 5 °C: Normalised error E_n.

5.5.2. TCE at 20 °C

In this section the density measurement results of tetrachloroethylene (TCE) at 20 °C are presented. The density results ρ und its expanded uncertainties $U(\rho)$ reported by the project partners are summarised in Table 7 together with the degree of equivalence D_i and its expanded uncertainty $U(D_i)$, the degree of equivalence D_i given in ppm and the absolute normalised error E_n.

All reported uncertainties in Table 7 represent a confidence interval of 95 % (expansion factor k=2).

The density reference value is calculated as it is described in Chapter 5.2.

The expanded uncertainties $U(\rho)$ given by the project partners in Table 7 do not include contributions due to the drift or the inhomogeneity of the liquid samples. The normalised error E_n, of the laboratory i with respect to the reference value X_{ref} (Table 4) is calculated as in Chapter 5.2.

The expanded uncertainties $U(\rho)$ of the results of BEV-PTP and PTB providing the reference values are increased, due to the linking procedure after [1] and due to the sample inhomogeneities listed in Table 3.

Table 7: Results TCE at 20 °C.

Project partner	ρ in kg m^{-3}	$U(\rho)$ in kg m^{-3}	D_i in kg m^{-3}	$U(D_i)$ in kg m^{-3}	E_n
BEV-PTP	1622.595	0.075	-0.003	0.054	0.05
INM	1622.2640	0.0075	-0.334	0.053	6.27
CMI	1622.654	0.080	0.056	0.096	0.58
DMDM	1622.521	0.028	-0.077	0.060	1.29
GUM	1622.587	0.012	-0.011	0.054	0.21
IMBIH	---	---	---	---	---
IPQ_2nd	1622.487	0.013	-0.109	0.054	2.02
JV	1622.194	0.058	-0.404	0.078	5.18
PTB	1622.593	0.074	-0.005	0.052	0.09
UME	1622.609	0.019	0.011	0.056	0.20

IMBiH did not deliver data for TCE at 20 °C.

The measured density values are displayed in Figure 7.

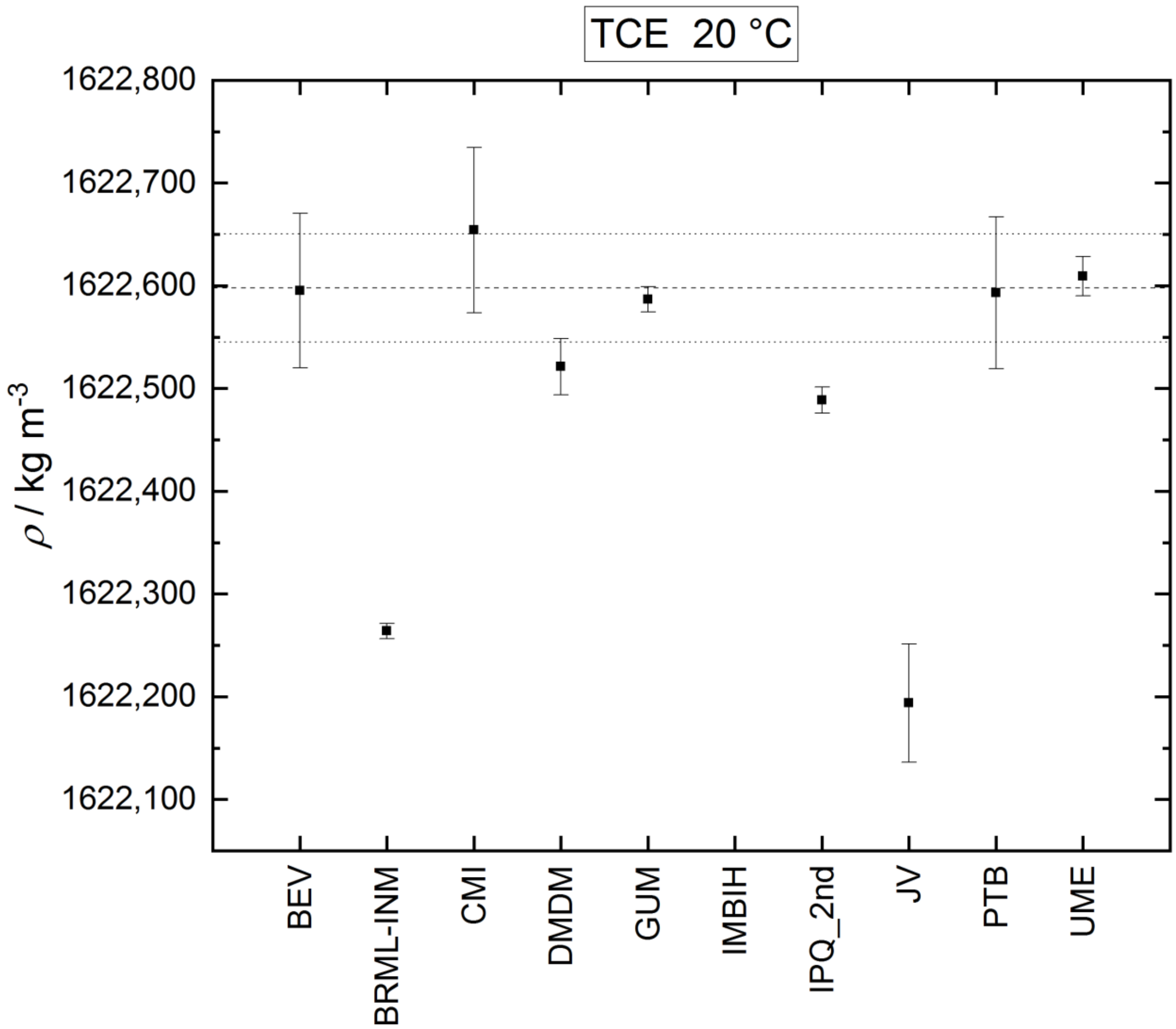

Figure 7: TCE at 20 °C. Measured (Table 7) and reference density values (X_{ref}: dashed line; X_{ref}±U_{ref}: dotted line; Table 4) with their expanded uncertainties (k=2).

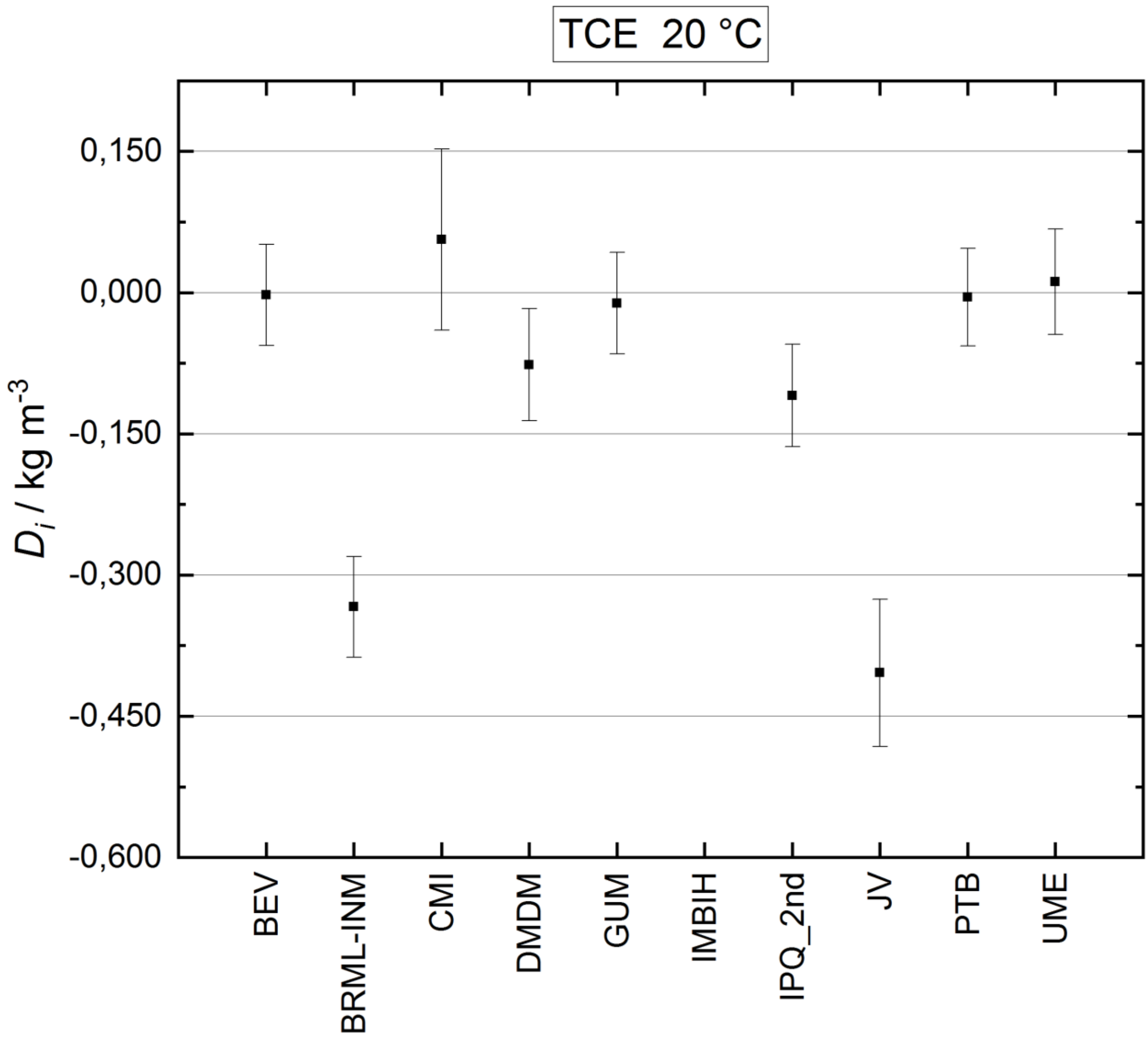

Figure 8: TCE at 20 °C: Degree of equivalence D_i.

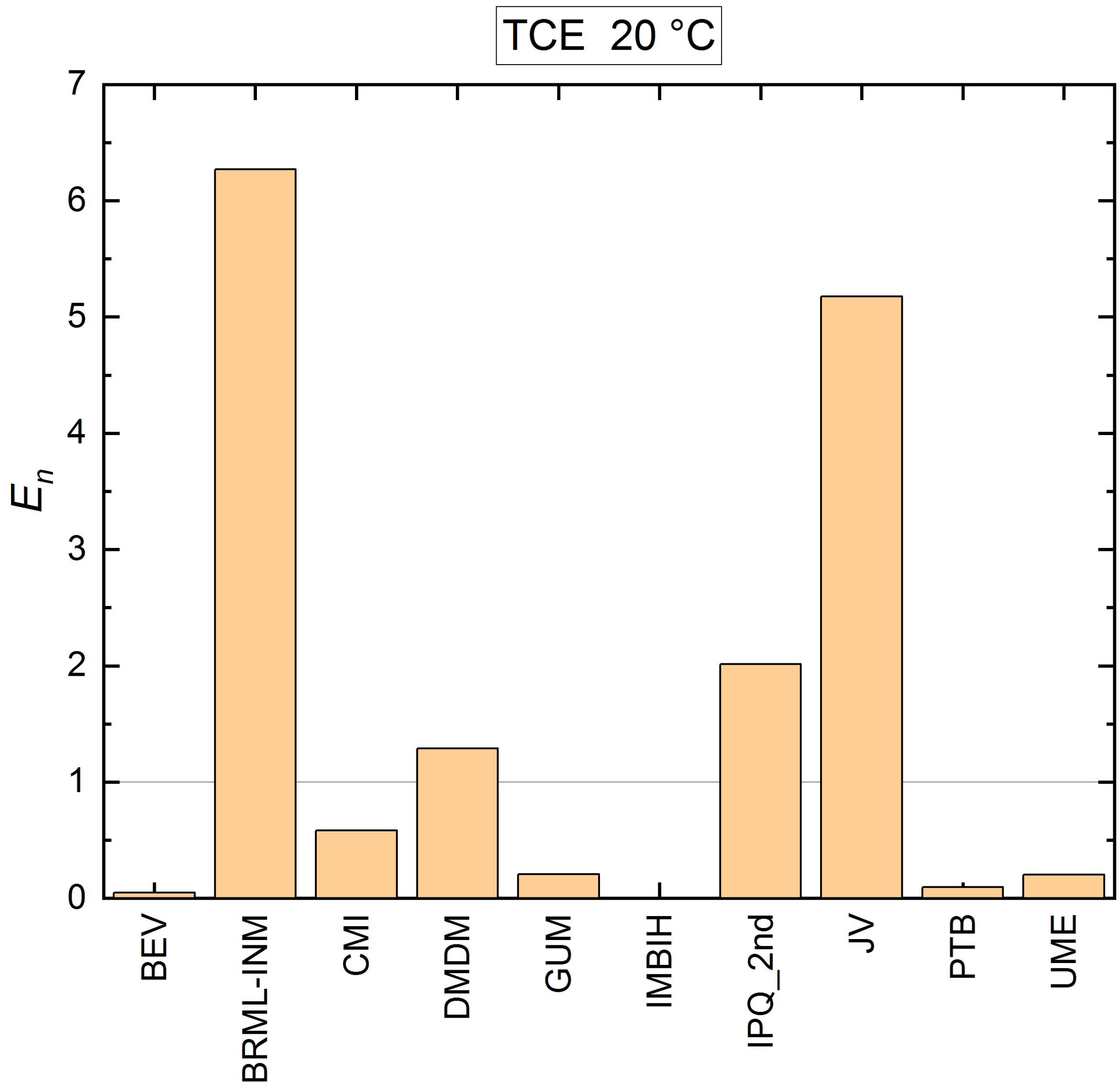

Figure 9: TCE at 20 °C: Normalised error E_n.

5.6. Viscosity oil EF168

In this section the density measurement results of EF168 at 20 °C are presented. The density results ρ und its expanded uncertainties $U(\rho)$ reported by the project partners are summarised in Table 8 together with the degree of equivalence D_i and its expanded uncertainty $U(D_i)$, the degree of equivalence D_i given in ppm and the absolute normalised error E_n.

All reported uncertainties in Table 8 represent a confidence interval of 95 % (expansion factor k=2).

The density reference value is calculated as it is described in Chapter 5.2.

The expanded uncertainties $U(\rho)$ given by the project partners in Table 8 do not include contributions due to the drift or the inhomogeneity of the liquid samples. The normalised error E_n, of the laboratory i with respect to the reference value X_{ref} (Table 4) is calculated as in Chapter 5.2.

The expanded uncertainties $U(\rho)$ of the results of BEV-PTP and PTB providing the reference values are increased, due to the linking procedure after [1] and due to the sample inhomogeneities listed in Table 3.

Table 8: Results EF168 at 20 °C.

Project partner	ρ in kg m^{-3}	$U(\rho)$ in kg m^{-3}	D_i in kg m^{-3}	$U(D_i)$ in kg m^{-3}	E_n
BEV-PTP	830.337	0.064	-0.021	0.046	0.46
INM	830.4131	0.0075	0.055	0.046	1.21
CMI	830.369	0.030	0.011	0.054	0.21
DMDM	830.555	0.010	0.197	0.046	4.26
GUM	830.3484	0.0078	-0.009	0.046	0.20
IMBIH	830.299	0.040	-0.059	0.060	0.97
IPQ_2nd	830.3783	0.0096	0.021	0.046	0.45
JV	830.368	0.032	0.010	0.055	0.18
PTB	830.391	0.064	0.033	0.045	0.74
UME	830.3586	0.0080	0.001	0.046	0.02

The measured density values are displayed in Figure 10.

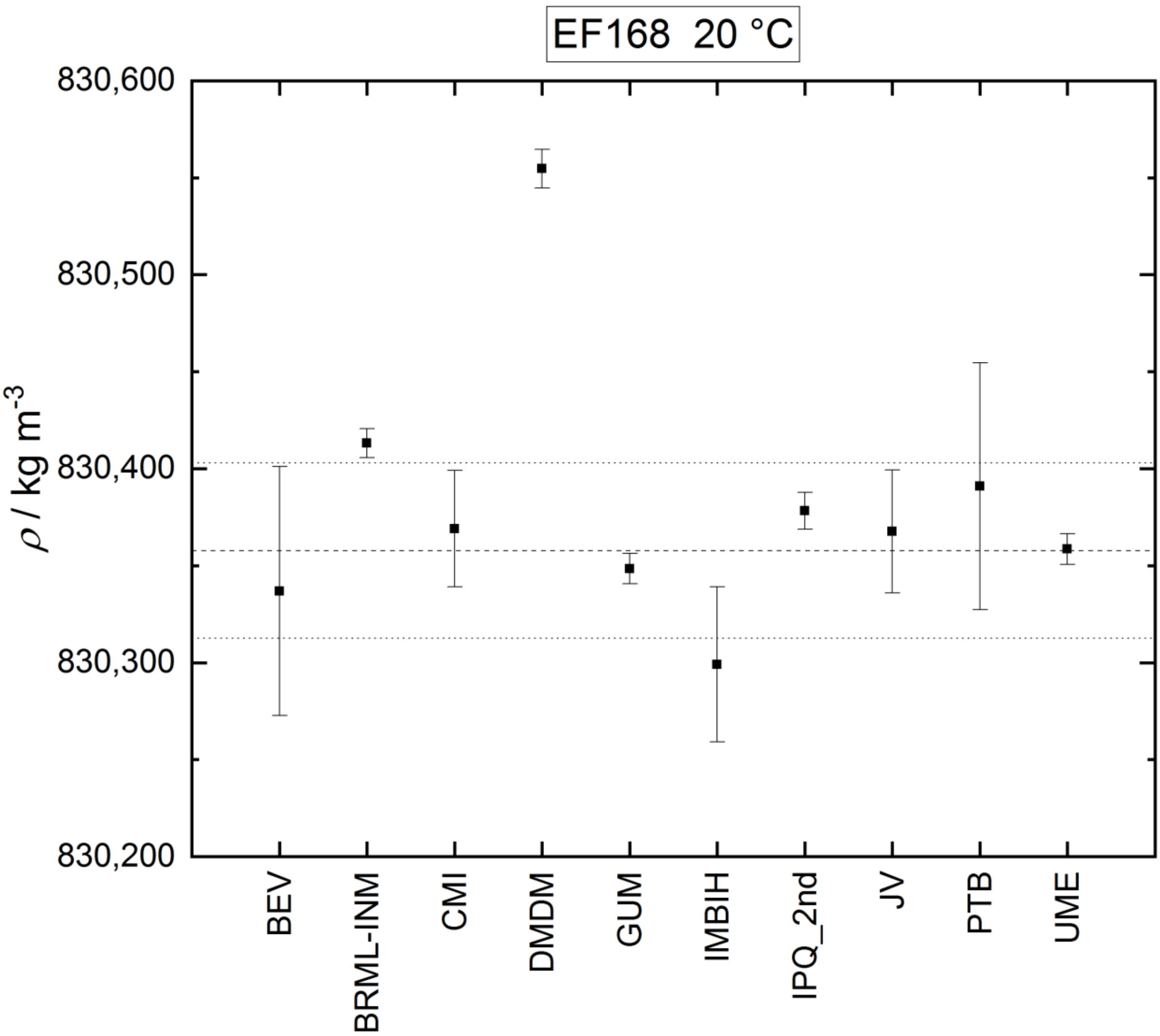

Figure 10: EF168 at 20 °C. Measured (Table 8) and reference density values (X_{ref}: dashed line; X_{ref}±U_{ref}: dotted line; Table 4) with their expanded uncertainties (k=2).

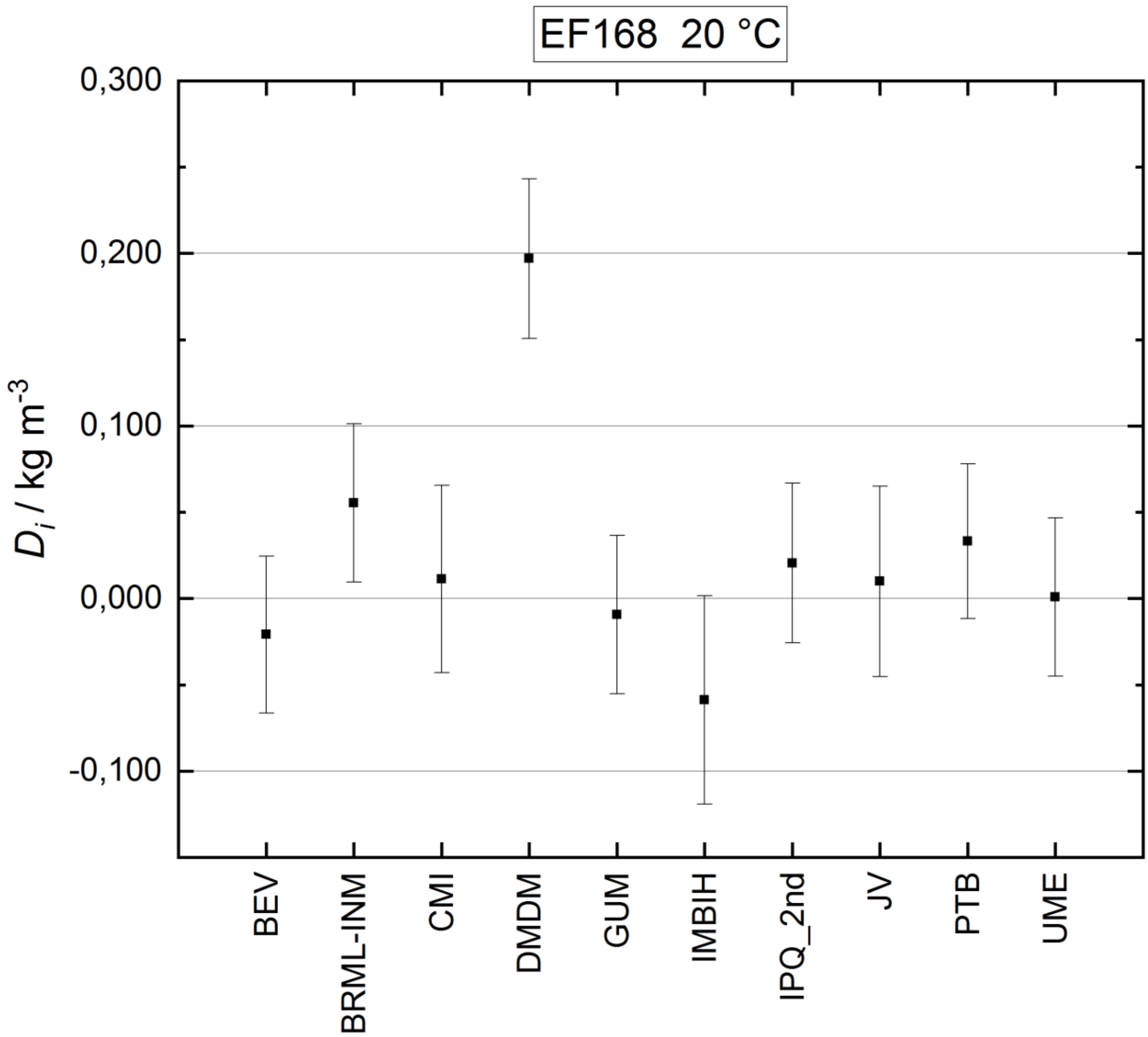

Figure 11: EF168 at 20 °C: Degree of equivalence D_i.

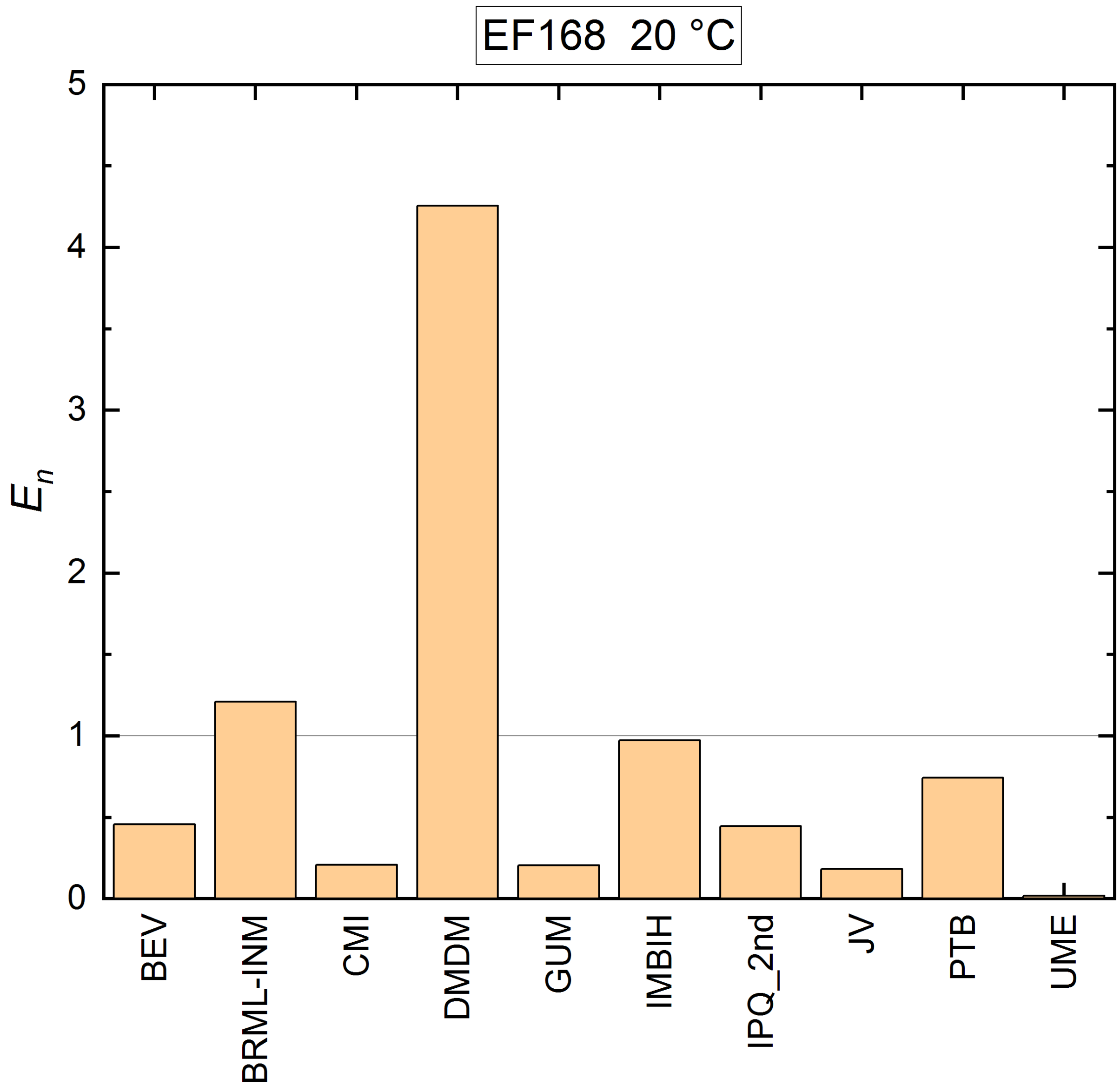

Figure 12: EF168 at 20 °C: Normalised error E_n.

6. Conclusions

Reference values for this comparison were determined by hydrostatic weighing using solid density standards at atmospheric pressure. The densities of three liquids (tetrachloroethylene (TCE), a viscosity oil (EF168) and a mixture of deuterated water) were investigated at 20 °C. Tetrachloroethylene was investigated at an additional temperature of 5 °C.

Uncertainty contributions due to a possible drift of the sample liquids were included in the uncertainty budget of the reference values.

The results of this comparison show that special care should be taken when handling the liquids. Contaminations can be introduced easily into samples and may cause deviations from reference values that are bigger than the stated uncertainties of the measurements. It is particularly valid for hydroscopic liquids like tetrachloroethylene. Participating institutes are encouraged to investigate their handling procedures.

In summary, more than half of the participants accomplished an E_n value of less than 1 with their measurements, enabling them to claim CMCs for the density of liquids determined by hydrostatic weighing.

Acknowledgements

The authors would like to acknowledge the kind assistance to all the colleagues in the participating laboratories for helping this comparison to run so smoothly despite the challenges the corona pandemic brought upon all of us.

References

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