#### **Final Report**

#### On EURAMET Key Comparison EURAMET.M.D-K2.2 (1523)

# Key comparison on density determination of liquids using oscillation type density meters

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#### 1. Introduction

This report presents the results of the EURAMET.M.D-K2.2 (1523) key comparison on the density of liquids determined by oscillation type density meters. It was organized and carried out within the framework of the EMPIR project 17RPT02 "rhoLiq".

The aim of this key comparison is to compare density determinations of liquid samples by oscillation type density meters. Density measurements of liquids are mainly performed by laboratories calibrating or verifying 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 oscillation type density meters. The chosen liquids represent a density interval from 700 kg/m<sup>3</sup> to 1 600 kg/m<sup>3</sup>. 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 using the hydrostatic weighing method of solid density standard within the key comparison EURAMET.M.D-K2.1 (1522). BEV's values were linked to EURAMET.M.D-K2 [1] and PTB's values were linked to CCM.D-K2 [2].

The majority of European emerging NMIs participating in this project have 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, INM-MD, PTB, and UME participated. The results of twelve oscillation type density meters (1 per partner, 2 for IMBiH) 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 January to August 2021.

# 2. Participants

Eleven laboratories took part in the comparison and received samples.

		1	
Laboratory	Mailing address	Person responsible	
(country)	for the packages	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 Național 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	
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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	
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Laboratory (country)	Mailing address for the packages	Person responsible for the comparison
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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
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#### 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 have already been sent to the laboratories as part of the diagnostic comparison within the EMPIR rhoLiq project 17RPT02. Arbitrary samples, chosen from the total amount of prepared 10 mL vials, were used as retention samples for check measurements. The homogeneity was confirmed by density measurements with a standard oscillation-type densitometer (first ensemble of 10 mL samples). After completion of the measurements by all participants, density measurements of the second ensemble of 10 mL samples, served to estimate the stability of the distributed samples.

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 done in June 2021.

The density meter used was a DMA5000 (Anton Paar) with a resolution of 0.001 kg/m<sup>3</sup>. The uncertainty of the absolute density values of the DMA5000 is approximately between 0.01 kg/m<sup>3</sup> and 0.02 kg/m<sup>3</sup>. The difference between density values can be determined with uncertainties less than 0.002 kg/m<sup>3</sup>.

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 10 mL retention samples were stored at PTB. The total amount of retention samples for each sample were split into two ensembles and 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 density values ( $\Delta \rho$ ) between the two ensembles of retention samples and was regarded as a rectangular distribution and the expanded (*k*=2) uncertainty ( $U_{\text{drift}}$ ) of the mean value of that rectangular distribution is assumed to represent the drift or stability of the density value.

A shipment of the samples back to the pilot laboratory was not requested by the technical protocol.

	Δρ	Udrift	
Samples		Drift/Stability	
	kg m <sup>-3</sup>		
Water	0.0032	0.0018	
TCE	0.026	0.015	
EF168	0.0170	0.0097	

#### Table 2: Estimated values of the sample stability.

## 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 serves as 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.

Samples	U <sub>hom</sub> Homogeneity	
	kg m <sup>-3</sup>	
Water	0.0068	
TCE	0.050	
EF168	0.055	

5. Results of project partners and data analysis

## 5.1. General issues

According to the timetable of the technical protocol all measurements should have been performed within a period of two months. 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.

After collecting data of all participants, it was realized that the liquids under test aged substantially during 2 years of storage. Therefore, some extra considerations were taken into account for the reference values in this comparison.

#### 5.2. Reference values

In order to calculate the reference values the measurement results of the link laboratories have been corrected according to the degrees of equivalence of CCM.D-K2 [2] for PTB and EURAMET.M.D-K2 [1] for BEV-PTP using the linking procedure described in [1].

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<sub>i</sub>* originating from CCM.D-K2 and EURAMET.M.D-K2, respectively. The uncertainty of the linked reference values of each link laboratory was estimated by

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

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

The reference value uncertainty combining these effects is:

$$u_{\rm ref,HW} = \frac{1}{\sqrt{\Sigma W_i}} \tag{4}$$

The expanded uncertainties  $U(\rho)$  of the reference values of BEV-PTP and PTB determined by hydrostatic weighing within EURAMET.M.D-K2.1 (1522) are increased, due to the linking procedure after [1] and due to the sample inhomogeneities listed in Table 3.

Liquids and tempe	ratures	$X_{ m ref,HW}$	U <sub>ref,HW</sub> (k=2)
	Tatules	kg m <sup>-3</sup>	
Water	20 °C	998.4205	0.0066
TCE	5 °C	1647.424	0.053
ICE	20 °C	1622.598	0.053
EF168	20 °C	830.358	0.045

Table 4: Reference density values from hydrostatic weighing.

Due to a temporal instability of the liquids in the 10 mL vials after 2 years of storage, a systematic drift of the measure density values of the 10 mL vials was recognised. Therefore, a correction (bias) for the reference values was calculated from the comparison of density in the 10 mL vials to the 1 L bottles. This correction  $\Delta_{\text{Bias}}$  was applied to the reference values of all three liquids, at every measurement temperature. The uncertainty  $U_{\text{Bias}}$  of the bias correction  $\Delta_{\text{Bias}}$  was estimated from the mean of the standard deviations of the 10 mL check measurements. The resulting values are presented in Tables 4 and 5.

Table 5: Bias correction	(10 mL checks vs. X <sub>ref</sub> ).
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Liquid	Т	Mean checks of HW	U <sub>Bias</sub> (k=2) (mean checks)	$\Delta_{ extsf{Bias}}$ (1 L vs. 10 mL)
	°C	kg m <sup>-3</sup>		
Water	20	998.4291	0.0024	-0.0086
TCE	20	1622.537	0.018	0.061
EF168	20	830.484	0.017	-0.126

The reference values in Table 6 were calculated by

$$X_{\rm ref} = X_{\rm ref, HW} - \Delta_{\rm Bias}$$
(5)

and their standard uncertainty was estimated by

$$u_{\rm ref} = \sqrt{u_{\rm ref,HW}^2 + u_{\rm drift}^2 + u_{\rm hom}^2 + u_{\rm Bias}^2}$$
 (6)

Liquids and tempe	ratures	X <sub>ref</sub>	U <sub>ref</sub> ( <i>k</i> =2)
		kg m <sup>-3</sup>	
Water	20 °C	998.429	0.010
TCE	5 °C	1647.367	0.082
	20 °C	1622.537	0.082
EF168	20 °C	830.484	0.081

Table 6: Reference density values after bias correction.

#### 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

$$D_i = x_i - X_{\rm ref} \tag{7}$$

with an assigned standard uncertainty of

$$U(D_i) = \sqrt{U_i^2 + U_{\text{ref}}^2} \tag{8}$$

where  $x_i$  is the reported density value and  $U(x_i)$  its expanded uncertainty. Due to the calibration model of the oscillation type densitometers (with air and ultrapure water) and the small uncertainty of the reference density value of ultrapure water [4] compared to the reported uncertainties of the participants, a correlation between the reference value and the participants' measurement data is neglected.

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

$$E_n = \frac{|x_i - X_{\text{ref}}|}{\sqrt{U_i^2 + U_{\text{ref}}^2}} = \frac{|D_i|}{U(D_i)}$$
(9)

#### 5.4. Deuterated Water

In this section the density measurement results of deuterated water (0.2 % D<sub>2</sub>O in H<sub>2</sub>O) at the temperature of 20 °C are presented. The density results  $\rho$  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  $U(D_i)$ , 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  $U(\rho)$  in Table 7 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.

	$\rho$ in	$U(\rho)$ in	D <sub>i</sub> in	U(D <sub>i</sub> ) in	_
Project partner	, kg m⁻³	kg m⁻³	kg m⁻³	kg m⁻³	En
BEV-PTP	998.4300	0.0077	0.001	0.013	0.07
INM	998.420	0.030	-0.009	0.032	0.29
CMI	998.428	0.025	-0.001	0.027	0.04
DMDM	998.414	0.049	-0.015	0.050	0.30
GUM	998.4252	0.0056	-0.004	0.012	0.34
IMBIH	998.461	0.026	0.032	0.028	1.15
DMA4500					
IMBIH	998.450	0.015	0.021	0.019	1.11
DMA5000					
IPQ_2nd	998.422	0.023	-0.007	0.025	0.28
INM-MD	998.437	0.036	0.008	0.037	0.22
JV					
PTB	998.428	0.011	-0.001	0.015	0.07
UME	998.414	0.021	-0.015	0.023	0.65

#### Table 7: Results of deuterated water at 20 °C.

All participants except INM-MD used water (0.2 vol%) from the in 1 L bottles used for EURAMET.M.D-K2.1 (1522). As INM-MD did not participate in the hydrostatic weighing key comparison, they received 10 mL vials of deuterated water.

JV did not deliver data for water.

The measured density values are displayed in Figure 1.

Remark from IMBiH:

IMBiH used water (0.2 vol%) from the in 1 L bottles, repacked into small 10 mL bottles and stored these bottles for 2 years.



Figure 1: Water at 20 °C. Measured (Table 7) 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<sub>i</sub>.



Figure 3: Water at 20 °C. Normalised error E<sub>n</sub>.

# 5.4.1. Comments of participants

IMBiH used water (0.2 vol%) from the 1 L bottles, repacked into small 10 mL bottles and stored these bottles for 2 years.

# 5.5. Tetrachloroethylene (TCE)

# 5.5.1. TCE at the temperature of 5 °C

In this section the density measurement results of tetrachloroethylene (TCE) at 5 °C are presented. The density results  $\rho$  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  $U(D_i)$ , 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.

Project partner	ho in kg m <sup>-3</sup>	<i>U</i> ( <i>ρ</i> ) in kg m⁻³	<i>D</i> i in kg m⁻³	<i>U(D</i> i) in kg m⁻³	En
BEV-PTP	1647.4200	0.0077	0.056	0.082	0.69
INM	1647.434	0.076	0.070	0.110	0.63
CMI	1647.422	0.054	0.058	0.098	0.60
DMDM	1647.273	0.053	-0.091	0.097	0.93
GUM	1647.363	0.022	-0.001	0.085	0.01
IMBIH DMA4500					
IMBIH DMA5000					
IPQ_2nd	1647.365	0.024	0.002	0.085	0.02
INM-MD	1647.012	0.037	-0.352	0.089	3.95
JV	1647.279	0.050	-0.085	0.096	0.88
PTB	1647.307	0.023	-0.057	0.085	0.67
UME	1647.308	0.051	-0.055	0.096	0.57

#### Table 8: Results TCE at 5 °C.

IPQ submitted corrected results labelled 'IPQ\_2nd' because there were some errors in the calculations.

IMBiH 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 8) and reference density values (X<sub>ref</sub>: dashed line; X<sub>ref</sub>±U<sub>ref</sub>: dotted line; Table 4) with their expanded uncertainties (k=2).









## 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  $\rho$  und its expanded uncertainties  $U(\rho)$  reported by the project partners are summarised in Table 9 together with the degree of equivalence  $D_i$  and its expanded uncertainty  $U(D_i)$ , and the absolute normalised error  $E_n$ .

All reported uncertainties in Table 9 represent a confidence interval of 95 % (expansion factor k=2).

The density reference value is calculated as it is described in Chapter 4.2.

The expanded uncertainties  $U(\rho)$  given by the project partners in Table 9 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 5) is calculated as in Chapter 4.2.

Project partner	ho in kg m <sup>-3</sup>	U( ho) in kg m <sup>-3</sup>	<i>D</i> i in kg m⁻³	<i>U(D</i> i) in kg m⁻³	En
BEV-PTP	1622.5680	0.0077	0.031	0.082	0.38
INM	1622.586	0.041	0.049	0.091	0.53
СМІ	1622.597	0.054	0.060	0.098	0.61
DMDM	1622.546	0.054	0.009	0.098	0.09
GUM	1622.540	0.022	0.003	0.084	0.03
IMBIH DMA4500	1622.310	0.073	-0.23	0.11	2.07
IMBIH DMA5000	1622.602	0.037	0.065	0.090	0.73
IPQ_2nd	1622.528	0.023	-0.009	0.085	0.11
INM-MD	1622.595	0.041	0.058	0.091	0.64
JV	1622.450	0.026	-0.087	0.085	1.02
PTB	1622.486	0.020	-0.051	0.084	0.61
UME	1622.476	0.051	-0.061	0.096	0.64

Table 9: Results	TCE at	20 °C.
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The measured density values are displayed in Figure 7.



Figure 7: TCE at 20 °C. Measured (Table 9) and reference density values (X<sub>ref</sub>: dashed line; X<sub>ref</sub>±U<sub>ref</sub>: dotted line; Table 4) with their expanded uncertainties (k=2).



Figure 8: TCE at 20 °C: Degree of equivalence D<sub>i</sub>.



Figure 9: TCE at 20 °C: Normalised error E<sub>n</sub>.

## 5.6. Viscosity oil EF168

In this section the density measurement results of EF168 at 20 °C are presented. The density results  $\rho$  und its expanded uncertainties  $U(\rho)$  reported by the project partners are summarised in Table 10 together with the degree of equivalence  $D_i$  and its expanded uncertainty  $U(D_i)$ , and the absolute normalised error  $E_n$ .

All reported uncertainties in Table 10 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 10 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.

	$\rho$ in	$U(\rho)$ in	$D_i$ in	U(D <sub>i</sub> ) in	_
Project partner	kg m <sup>-3</sup>	kg m <sup>-3</sup>	kg m⁻³	kg m <sup>-3</sup>	En
BEV-PTP	830.3350	0.0077	-0.023	0.081	0.28
INM	830.519	0.029	0.035	0.086	0.41
CMI	830.468	0.026	-0.016	0.085	0.19
DMDM	830.482	0.052	-0.002	0.096	0.02
GUM	830.483	0.020	-0.001	0.083	0.01
IMBIH DMA4500	830.510	0.027	0.026	0.085	0.31
IMBIH DMA5000	830.477	0.013	-0.007	0.082	0.09
IPQ_2nd	830.357	0.033	-0.001	0.087	0.00
INM-MD	830.564	0.030	0.080	0.086	0.93
JV	830.512	0.021	0.028	0.083	0.34
PTB	830.477	0.012	-0.007	0.082	0.09
UME	830.479	0.026	-0.005	0.085	0.06

Table	10:	Results	EF168	at	20	°C.
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IPQ mixed the content of the five viscosity oil ampoules and stored the liquid in a Duran flask with hard plastic cap. For this reason, the liquid did not age as described in Chapter 5.2.

BEV did use Duran flask with hard plastic cap for sample storage too, keeping the liquid from aging.

Therefore, data analysis for IPQ and BEV was done in respect of the unbiased reference values.

The measured density values are displayed in Figure 10.



Figure 10: EF168 at 20 °C. Measured (Table 10) and reference density values (X<sub>ref</sub>: dashed line; X<sub>ref</sub>±U<sub>ref</sub>: dotted line; Table 4) with their expanded uncertainties (k=2).



Figure 11: EF168 at 20 °C: Degree of equivalence D<sub>i</sub>.



Figure 12: EF168 at 20 °C: Normalised error E<sub>n</sub>.

#### 6. Conclusions

Reference values for this comparison of oscillation type density meters were determined by hydrostatic weighing of a solid density standard at atmospheric pressure and linked to the CCM.D-K2 key comparison for PTB and EURAMET.M.D-K2 key comparison for BEV. 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 drift of the sample liquids were included in the uncertainty budget of the reference values.

A long-term stability issue of the density of the viscosity oil samples was found after collecting the measurement data of all participants. Therefore, the aging effect of the liquid was considered by calculating a biased reference value.

The results of this comparison show that special care should be taken when handling liquid samples. 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. Packaging material, specifically the caps of bottles, have a big impact on long-term stability of liquid samples. The participating institutes are encouraged to investigate their handling procedures.

In summary, almost 90 % 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 oscillation type density meters.

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