EURO-ASIAN COOPERATION OF NATIONAL METROLOGICAL INSTITUTIONS COOMET	ЕВРО-АЗИАТСКОЕ СОТРУДНИЧЕСТВО ГОСУДАРСТВЕННЫХ МЕТРОЛОГИЧЕСКИХ УЧРЕЖДЕНИЙ КООМЕТ

RMO SUPPLEMENTARY COMPARISON

COOMET.M.D-S1

(COOMET 555/AZ/12)

COMPARISON OF LIQUID SAMPLES OF DENSITY

FINAL REPORT

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Abstract

The results are presented of the supplementary comparison COOMET.M.D-S1 (COOMET 555/AZ/12) that covered the measurements of density of four reference liquids (tridecane, distilled water, high-viscosity oil, and tetrachloroethylene) at 20 °C and 101325 Pa. laboratories of five national metrology institutes (NMIs) took part in the comparison. participating laboratories used the equipment approved in the participating countries as the state measurement standards of density. Measurements were carried out near 20 °C and at atmospheric pressure by two methods: method of hydrostatic weighting of reference measures of density and by using laboratory density meters DMA5000, manufactured by Anton Paar GmbH, Austria in the time interval from April 2, 2015 to August 28, 2017. Uncertainties of the measurement results obtained by the pilot laboratory were confirmed by the results of the CIPM key comparison CCM.D-K2 [1] with the D.I. Mendeleyev Institute for Metrology as a participant.

The components for a possible drift or inhomogeneity of the liquid are investigated for the final evaluation of the data. For this purpose, results of stability and homogeneity measurements of the pilot laboratory are used. The participants did not include in their uncertainty budget a possible drift of the liquid's density since no significant drift could be detected, and the influence of the drift and its uncertainty are negligible.

For this supplementary comparison, estimates of the density values of reference liquids obtained by the reference laboratory before sending samples to the participants (pilot laboratory, VNIIM, participant of the CIPM key comparison CCM.D-K2 [1]) were established as reference values.

With one exception, the results of water density measurements showed good agreement between the participants. For the highest and lowest density liquids, tetrachlorethylene and tridecane, abnormal results were reported by two laboratories. In the case of a high-viscosity oil, the results are clearly different.

The expanded uncertainties of all reference densities are below $1{,}3 \cdot 10^{-5}$ in relative terms. This satisfies the needs of all customers who wish to calibrate or check liquid density measuring instruments such as oscillation-type density meters. The results of the comparison can be used to entries in the calibration measurement capabilities table in the BIPM key comparison database.

Table of Contents

Introduction

This report presents the results of the RMO supplementary comparison of liquid samples of density COOMET.M.D-S1 (also known as COOMET 555/AZ/12). laboratories of five national metrology institutes (NMIs) took part in the comparison. In order to ensure that the supplementary comparison is carried out, density of the following transfer standards (reference liquids) was measured: tridecane, tetrachloroethylene, distilled water, and high-viscosity oil. The measurements were performed at atmospheric pressure and a temperature of 20 °C. participating laboratories used the equipment approved in the participating countries as the state measurement standards of density. Measurements were carried out in the period from April 2, 2015 to August 28, 2017. Uncertainties of the measurement results obtained by the pilot laboratory were confirmed by the results of the CIPM Key Comparison CCM.D-K2 [1] with the D.I. Mendeleyev institute for metrology as a participant; they are consistent with its published CMC.

One of five participants in these supplementary comparisons is not a member of the CIPM MRA (SCM). SCM results are presented in this report but are not included in the calculation of the degree of equivalence.

1 Participating laboratories

Table 1. Participating laboratories, representatives of the participating laboratories, and measurement dates

participating Laboratory	Acronym	Contact person	Measurement Dates
D.I. Mendeleyev Institute for Metrology	VNIIM	Alexey Domostroyev	June 6, 2015 – August 18, 2015 August 17, 2017 – August 28, 2017
Azerbaijan Institute of Metrology	AzMI	Emma Nabieva	October 22, 2015 – December 9, 2015
Center for Standardization and Metrology under the Ministry of Economy of the Kyrgyz Republic	CSM	Olga Tabullo	October 23, 2015 – December 21, 2015
National Institute of Metrology of the Republic of Moldova	INM	Anna Chubara	November 6, 2015 – January 29, 2016
Kazakh Institute of Metrology RSE	KazInMetr	Ulan Moldaganapov	October 22, 2015 – January 12, 2016

2 Samples for the Comparison

In order to ensure the Supplementary Comparison, the Pilot Laboratory purchased and prepared at least 20 dm^3 of reference samples of liquid tridecane, tetrachloroethylene, distilled water, and high-viscosity oil with nominal dynamic viscosity of 1100 mPa s (at 20 °C). Nominal density values of the liquid samples used in this Comparison correspond to the nominal density values of liquid samples used in CCM.D-K2 [1] with a maximum deviation of no more than 5 % (high-viscosity mineral oil). Tridecane (in CCM.D-K2 n-pentadecane was used) was chosen due to its better accessibility while maintaining similar stable physical properties (difference between the nominal densities of tridecane and n-pentadecane is no more than 2 %). Density of distilled water was slightly altered by the addition of triatomic alcohol $C_3H_5(OH)_3$ (glycerin).

Table 2. Physical properties of liquid samples

Liquid sample	Chemical formula	Temperature coefficient of volumetric expansion and its uncertainty	Coefficient of isothermal compressibility and its uncertainty	Surface tension and its uncertainty	Nominal density at atmospheric pressure and at 20 °C
		kg/(m^{3}K)	10^{-11}/Pa	mN/m	kg/m^3
Tridecane	$C_{13}H_{28}$	0.70 0.05	85 5	27	769
Distilled water	H_2O	0.21 0.02	46 2	73	998
Mineral oil	–	0.60 0.05	was not measured	31	846
Tetrachloroethylene	C_2Cl_4	1.66 0.05	73 5	32	1622

The Pilot Laboratory carried out measurements of reference liquids, which were each mixed in a separate container. After the measurements, a control sample of 5000 cm^3 was taken from each reference sample and put into glass bottles with sealed covers. Bottles with control samples were then labeled and stored in the Pilot Laboratory for testing the stability of its properties in time. Reference liquids intended for measurements were put in glass bottles with nominal volumes of 250 cm^3 and 2500 cm^3, and then shipped to the participating laboratories. All glass bottles and plastic containers were labeled with an index of the liquid sample and its nominal viscosity at 20 °C. Each participating laboratory got a cardboard box with four plastic containers of liquid samples with nominal volumes of 250 cm^3. Glass bottles with nominal volumes of 2500 cm^3 were additionally placed in a foam container inside the cardboard box to ensure their safety during transportation.

Boxes with liquid samples were completed with a passport for each liquid sample containing names of the chemical component(s) used to prepare the sample, sample index and its nominal density at 20 °C, a list of contents with the number of bottles and indexes of liquids, as well as safety procedures and package's weight and dimensions. This information was also sent to participating laboratories beforehand. Amount of liquid sample (250 cm^3 or 2500 cm^3) required to carry out density measurements depended on the standard equipment used and was agreed upon with each participating laboratory individually.

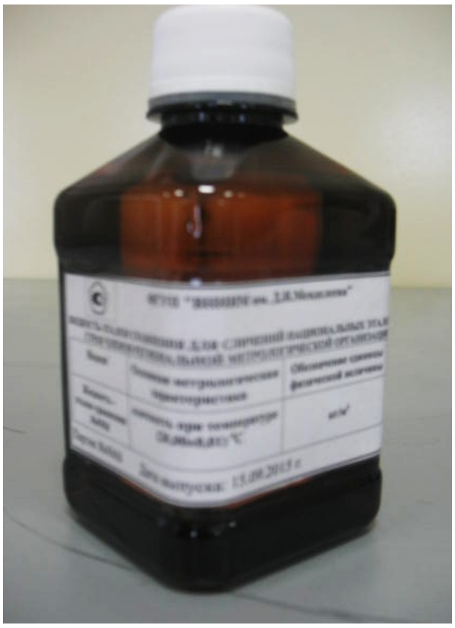

Figure 1. Liquid sample for the Comparison in a plastic container with a nominal volume of 250 cm^3.

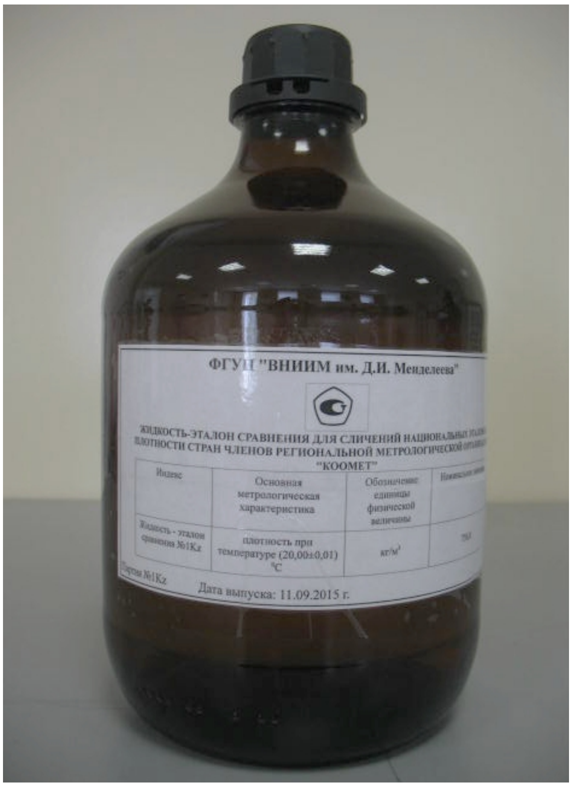

Figure 2. Liquid sample for the Comparison in a glass bottle with a nominal volume of 2500 cm^3.

After the participating laboratories completed their measurements, liquid samples were sent back to the Pilot Laboratory for repeat measurements to determine possible change of samples' viscosity during transportation and measurement processes.

3 Equipment and methods of measurement

Participating laboratories carried out density measurements of the liquid samples using equipment approved in the participating country as the State Measurement Standard of density.
Types and main characteristics of the measuring equipment used are given in the Table 3.

Table 3. Types and main characteristics of the measuring equipment

Participating Laboratory	Method of measurement	Measuring equipment	Traceability
VNIIM	Hydrostatic weighing	Hydrostatic weighing setup UGV-1, Standard silica sphere	VNIIM Mass: GET 3-2008
AzMI	Direct measurements	Density analyzer DMA 5000, Anton Paar GmbH, No. 80460374 0 – 3 g/cm^3 d = 1·10^{-6} g/cm^3	PTB (through reference materials prepared by ZMK Analytik GmbH)
CSM	Hydrostatic weighing	Hydrostatic weighing setup UPA-01, OOO Sibir-complekt (Russia), Glass viscosity measure No. 8 m = 126,2476 g V = 122,2879 cm^3	VNIIM Mass: GET 3-2008 Viscosity: GET 18-2000
INM	Direct measurements	Density analyzer DMA 5000, Anton Paar GmbH, No. 80460374 0 – 3 g/cm^3 d = 1·10^{-6} g/cm^3	H&D Fitzgerald Ltd.
KazInMetr	Hydrostatic weighing	Hydrostatic weighing setup (VNIIM), Glass viscosity measure No. 11 m = 137,0878 g V = 107,9051 cm^3	VNIIM Mass: GET 3-2008 Viscosity: GET 18-2000

At the time of the measurements, State Measurement Standards of density of Center for Standardization and Metrology under the Ministry of Economy of the Kyrgyz Republic and Kazakh Institute of Metrology RSE were traceable to the State Measurement Standard of the Russian Federation GET 18-2000. When processing the measurement results, correlation due to adoption of the unit of density was taken into account.

Uncertainty of the measurement results obtained by the participating laboratories had to be calculated in accordance with [2].

4 Symbols used

x_i	–	results of the supplementary comparison;
$u(x_i)$	–	declared standard uncertainties of the participants;
N	–	number of participating laboratories;
x_{ref}	–	supplementary comparison reference value;
$u(x_{ref})$	–	standard uncertainty of the supplementary comparison reference value;
$cov(x_i, x_{ref})$	–	covariance of measurement results of the i-th NMI and the supplementary comparison reference value due to adopting the unit of density;
CMC	–	Calibration and Measurement Capabilities.

5 Results of the samples stability measurements

In accordance with the technical protocol of the comparison, after performing the measurements each participating Laboratory had to send the samples back to the Pilot Laboratory for repeated measurements of density in order to assess the stability of density values. The samples were shipped back using the same glass bottles and plastic containers that the samples arrived in. Each participating laboratory was required to undertake the necessary steps to preserve purity of the samples. Certain amount of liquid samples was irretrievably lost in the measurement process due to the measurement techniques used, and therefore could not be sent back to the pilot laboratory. Since the participating laboratories received different amounts of liquid samples in accordance with their respective requirements, stability testing by hydrostatic method could only be performed for samples contained in 2500 cm^3 glass bottles returned from Center for Standardization and Metrology under the Ministry of Economy of the Kyrgyz Republic and Kazakh Institute of Metrology RSE. Therefore, the stability measurements were carried out using Density analyzer DMA 5000, Anton Paar GmbH, No. 80460374, traceable to the State Measurement Standard of Density GET 18-2004.

Results of the stability measurements of the samples received by the pilot laboratory are given in Table 4.

Table 4. Results of the stability measurements of the samples

Liquid sample	Density of the sample measured by the Pilot at 20 °C before shipping to the participating Laboratory ρ_1, kg/m^3	participating Laboratory	Density of the sample measured by the Pilot at 20 °C after receiving it from the participating Laboratory ρ_2, kg/m^3	Deviation of density before shipping and after receiving the samples back by the Pilot $\Delta\rho_{1\text{-}2}$, kg/m^3
Tridecane	756,990	AzMI	756.952	– 0.038
		CSM	757.000	0.010
		KazInMetr	756.991	0.009
		INM	756.938	– 0.052
Distilled water	998,201	AzMI	998.204	0.003
		CSM	998.199	– 0.002
		KazInMetr	998.202	0.001
		INM	998.208	0.007
Mineral oil	890,540	AzMI	890.501	– 0.039
		CSM	890.522	– 0.018
		KazInMetr	890.509	– 0.030
		INM	890.491	– 0.049
Tetrachloroethylene	1615,43	AzMI	1615.52	0.09
		CSM	1615.34	– 0.09
		KazInMetr	–	–
		INM	1615.47	0.05

At the final stage of the measurements (August 17, 2017 – August 28, 2017), the pilot laboratory carried out density measurements of reference liquid samples stored in sealed packaging and not subjected to transportation and measurements in order to verify stability of their properties. Those control samples were stored in the pilot laboratory and were not shipped to the participating laboratories for measurements.

Results of the stability measurements of control samples stored in the pilot laboratory are given in Table 5.

Table 5. Results of the stability measurements of control samples

Liquid sample	Density of the control sample measured by the Pilot at 20 °C before shipping to the Participants ρ_1, kg/m^3	Density of the control sample measured by the Pilot at 20 °C after measurements by the Participants $\rho_к$, kg/m^3	Deviation of density before shipping and after receiving the samples back by the Pilot $\Delta\rho_{1\text{-k}}$, kg/m^3
Tridecane	756.990	756.995	0.005
Distilled water	998.201	998.198	– 0.003
Mineral oil	890.540	890.528	– 0.012
Tetrachloroethylene	1615.432	1615.441	0.009

The results from Table 5 show that density of the control samples has not changed significantly during storage in sealed bottles from June 2015 to August 2017. The largest deviation of – 0.012 kg/m^3 occurs in the results for high-viscosity mineral oil density measurements.

Analysis of the results of repeated measurements (Table 4) shows that systematic decrease of density is true only for high-viscosity mineral oil. The same is not observed for the other three reference liquids. By comparing the data from Tables 4 and 5, it can be seen that the result of the density measurements of high-density mineral oil control sample is less than the first measurement result by 0.012 kg/m^3. However, this deviation is within the expanded uncertainty of mineral oil density measurements obtained by the participating Laboratory, therefore there is no basis to suspect a systematic decreasing of high-viscosity oil density during measurements. These changes in density are most likely caused by a possible ingress of solvent traces in the oil from cleaning the equipment and storage containers and are not associated with changes in the properties of the reference liquid.

Taking into account that change in density of the control samples during storage did not exceed the standard uncertainties of density measurements of corresponding liquids obtained by the Pilot Laboratory, results of the participating laboratories were not corrected for the density change during measurements.

6 Measurement results and analysis data

This section contains measurement results submitted by the participating laboratories.

Standard uncertainty for the reported results of density measurements is calculated by dividing the submitted expanded uncertainty for 95 % probability by 2.

For all measuring results of KazInMetr and density measurements results for tridecane, water, and mineral oil of CSM, there is a covariance between these participating laboratories and the pilot laboratory VNIIM**,** due to traceability to the pilot laboratory, which is the reference value at the same time. This covariance is taken into account when calculating degrees of equivalence of the laboratories (see Appendix A).

6.1 Tridecane

Density measurements of tridecane were performed once. The results were normalized to a temperature of 20 °C and atmospheric pressure of 101.3 kPa.

Results of tridecane density measurements and its expanded uncertainties with confidence factor P = 0.95 submitted by the participating laboratories are given in Table 6.

Table 6. Results of tridecane density measurements and its expanded uncertainties

participating laboratory	Tridecane density at 20 °C and atmospheric pressure of 101.3 kPa, kg/m^3 *(Xi)*	Expanded uncertainty P = 0.95, kg/m^3 *U(Xi)*
VNIIM	756.990	0.012
AzMI	756.988	0.032
CSM	756.938	0.020
KazInMetr	756.910	0.100
INM	757.471	0.120

Results of tridecane density measurements obtained by all participating laboratories, their uncertainties and line of the reference value for density are shown in Figure 3.

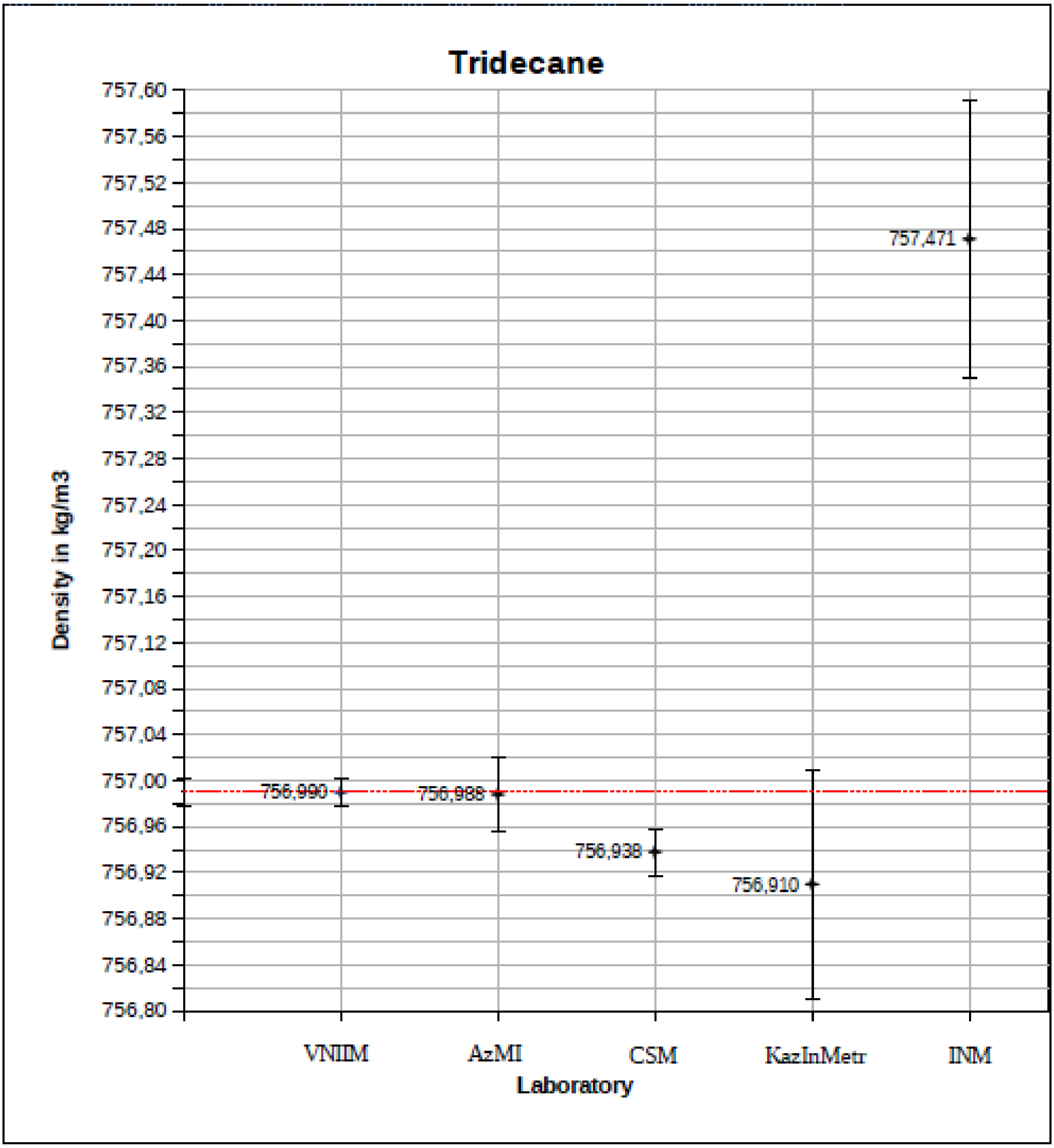

Figure 3. Reported density results of the participants for tridecane at 20 °C and atmospheric pressure of 101.3 kPa and the reference value (red dashed line). The uncertainties are for a confidence level of 95%

6.2 Distilled water

Density measurements of distilled water were performed once. The results were normalized to a temperature of 20 °C and atmospheric pressure of 101.3 kPa.

Results of distilled water density measurements and its expanded uncertainties with confidence factor P = 0.95 submitted by the participating laboratories are given in Table 7.

Table 7. Results of distilled water density measurements and its expanded uncertainties

Participating Laboratory/Country code	Distilled water density at 20 °C and atmospheric pressure of 101.3 kPa, kg/m^3 (X_i)	Expanded uncertainty P = 0.95, kg/m^3 $U(X_i)$
VNIIM/RU	998.201	0.010
AZMI/AZ	998.201	0.015
CSM ME/KG	998.222	0.020
KazInMetr/KZ	998.202	0.027
INM-MD/MD	998.201	0.130

Results of distilled water density measurements obtained by all participating laboratories, their uncertainties and line of the reference value for density are shown in Figure 4.

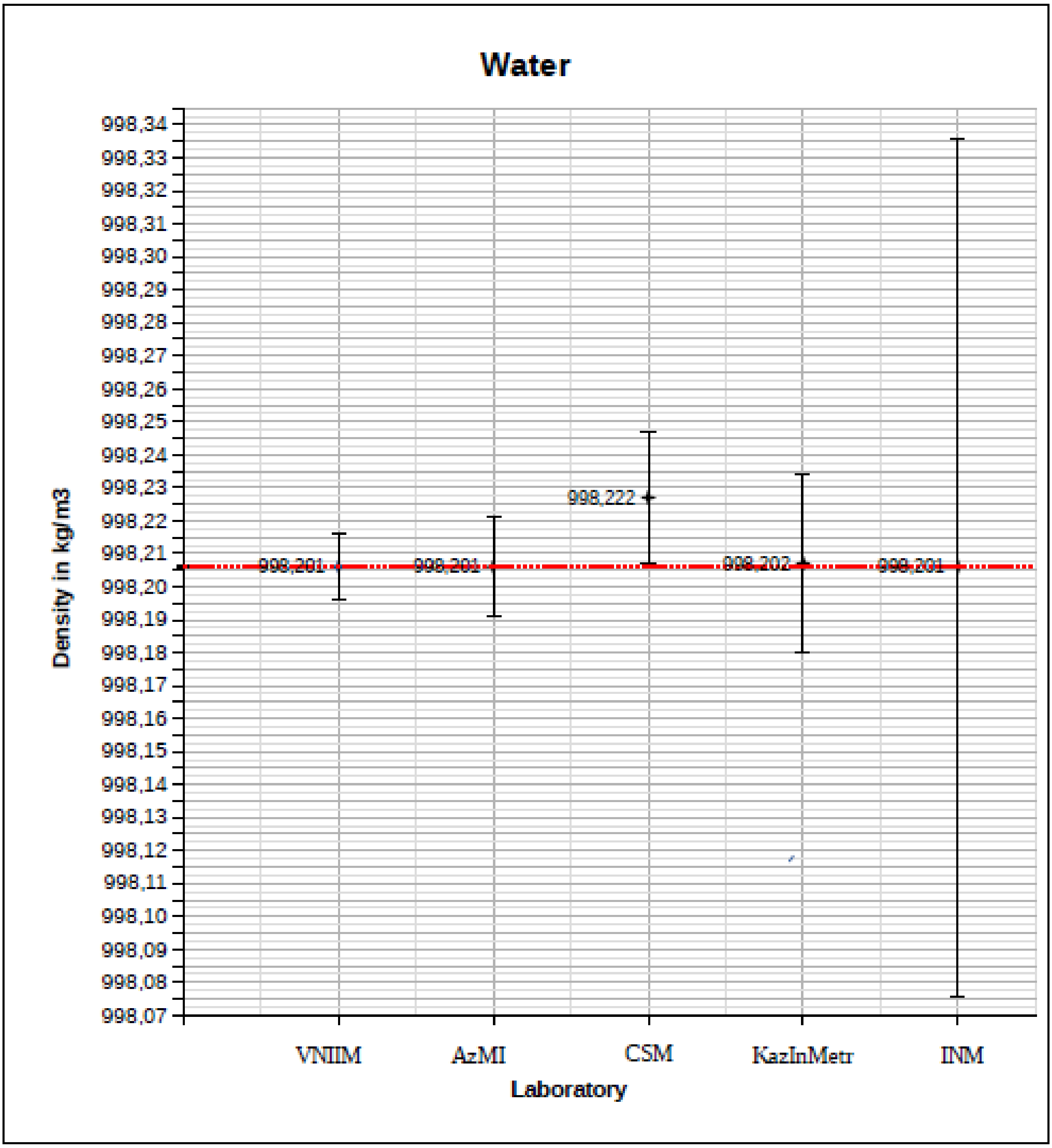

Figure 4. Reported density results of the participants for distilled water at 20 °C and atmospheric pressure of 101.3 kPa and the reference value (red dashed line). The uncertainties are for a confidence level of 95%

6.3 High-viscosity mineral oil

Density measurements of high-viscosity mineral oil were performed once. The results were normalized to a temperature of 20 °C and atmospheric pressure of 101.3 kPa.

Results of high-viscosity mineral oil density measurements and its expanded uncertainties with confidence factor P = 0.95 submitted by the participating laboratories are given in Table 8.

Table 8. Results of high-viscosity mineral oil density measurements and its expanded uncertainties

participating Laboratory/Country code	High-viscosity mineral oil density at 20 °C and atmospheric pressure of 101.3 kPa, kg/m^3 (X_i)	Expanded uncertainty P = 0.95, kg/m^3 $U(X_i)$
VNIIM/RU	890.540	0.018
AZMI/AZ	890.572	0.036
CSM ME/KG	890.562	0.020
KazInMetr/KZ	890.590	0.020
INM-MD/MD	890.634	0.120

Results of high-viscosity mineral oil density measurements obtained by all participating laboratories, their uncertainties and line of the reference value for density are shown in Figure 5.

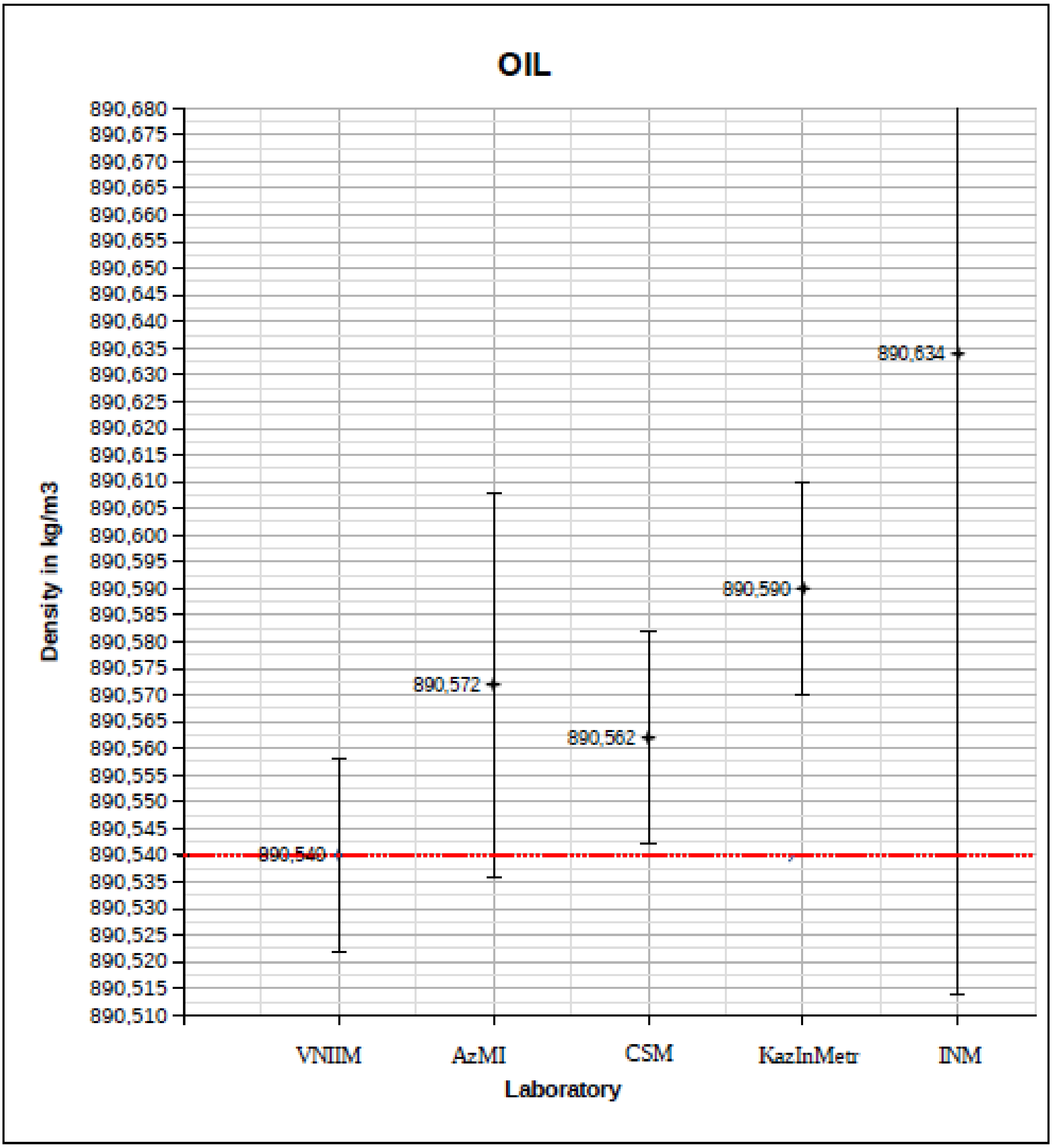

Figure 5. Reported density results of the participants for high-viscosity mineral oil at 20 °C and atmospheric pressure of 101.3 kPa and the reference value (red dashed line). The uncertainties are for a confidence level of 95%

6.4 Tetrachloroethylene

Density measurements of tetrachloroethylene were performed once. The results were normalized to a temperature of 20 °C and atmospheric pressure of 101.3 kPa.

Results of tetrachloroethylene density measurements and its expanded uncertainties with confidence factor P = 0.95 submitted by the participating laboratories are given in Table 9.

Table 9. Results of tetrachloroethylene density measurements and its expanded uncertainties

participating Laboratory/Country code	Tetrachloroethylene density at 20 °C and atmospheric pressure of 101.3 kPa, kg/m^3 (X_i)	Expanded uncertainty P = 0.95, kg/m^3 $U(X_i)$
VNIIM/RU	890.540	0.018
AZMI/AZ	890.572	0.036
CSM ME/KG	890.562	0.020
KazInMetr/KZ	890.590	0.020
INM-MD/MD	890.634	0.120

Results of tetrachloroethylene density measurements obtained by all participating laboratories, their uncertainties and line of the reference value for density are shown in Figure 6.

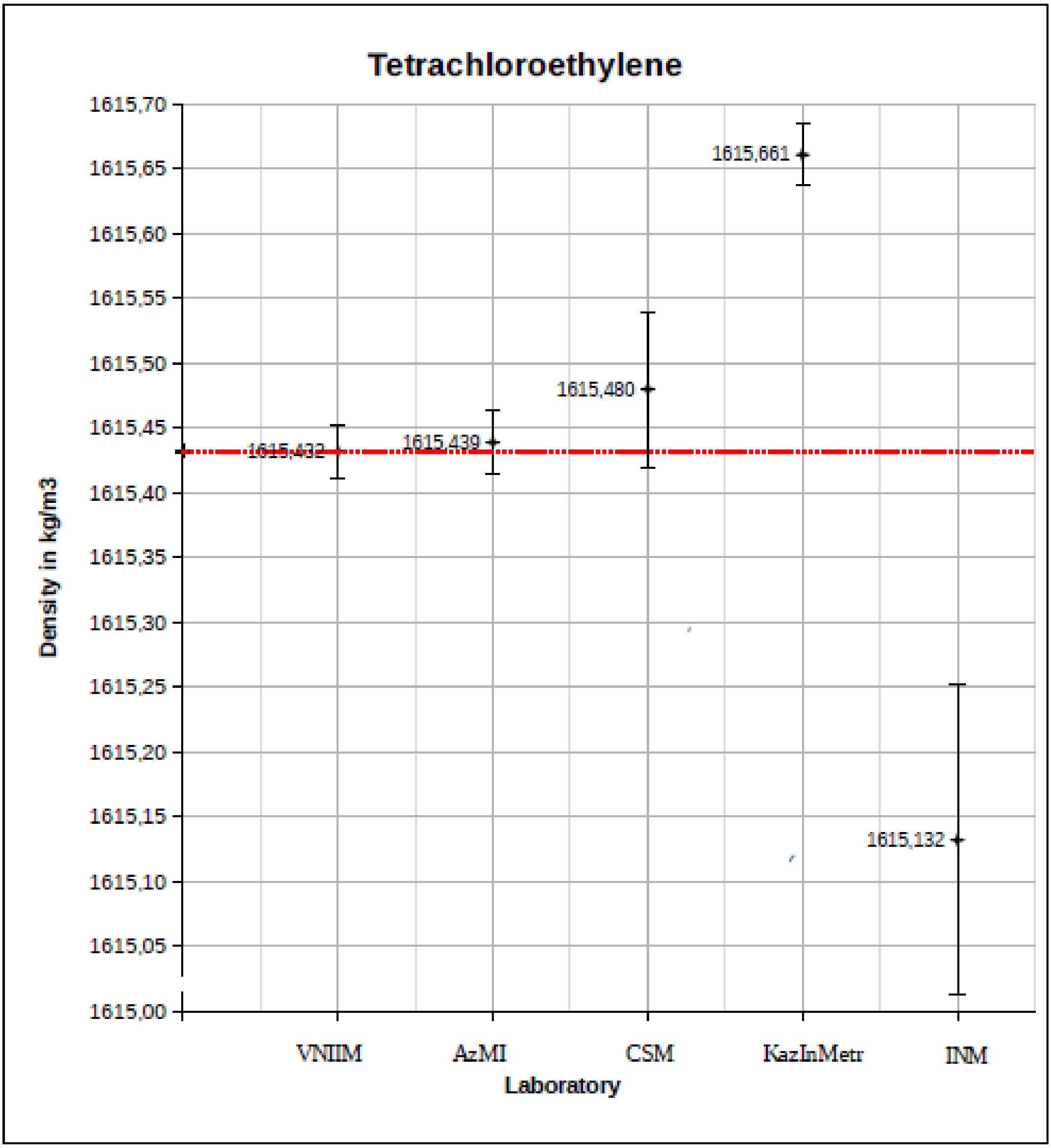

Figure 6. Reported density results of the participants for tetrachloroethylene at 20 °C and atmospheric pressure of 101.3 kPa and the reference value (red dashed line). The uncertainties are for a confidence level of 95%

7 Reference value of Supplementary Comparison

Participant laboratories of Key Comparison (KC) offers to other participant laboratories traceability to reference values to CCM KC trough their participations. The participation of such NMIs in the CIPM KC is problematic, since the circle of CIPM KC participants is limited primarily by primary national standards, which have approximately the same level of accuracy, as well as by measurement methods, used in key comparisons. To carry out supplementary comparisons of this type, it is necessary to involve a reference laboratory, which would be a participant in key comparisons in this type measurements. The task of this laboratory is to determine the reference values of supplementary comparison. In accordance with [3], reference values of supplementary comparison are established by a reference laboratory based on their measurement results. The reference laboratory was the pilot laboratory, VNIIM, a participant of the CIPM Key Comparison CCM.D-K2 [1]. For this supplementary comparison, the density values estimated for the reference liquids (transfer standards) and corresponding uncertainties obtained by the reference laboratory before shipping the samples to the participants are established as the reference values X_{ref}, kg/m^3. The uncertainties of the reference laboratory are consistent with the published CMCs of VNIIM.

The estimated density values of standard liquids established as reference values of the Supplementary Comparison and corresponding standard uncertainties are given in Table 10.

Table 10. The estimated density values of standard liquids established as reference values of the Supplementary Comparison and corresponding standard uncertainties.

Liquid sample	Reference density values of liquid samples at 20 °C and atmospheric pressure of 101.3 kPa X_{ref}, kg/m^3	Standard uncertainties of reference density values of liquid samples $u(X_{ref})$, kg/m^3
Tridecane	756.990	0.006
Distilled water	998.201	0.005
Mineral oil	890.540	0.009
Tetrachloroethylene	1615.432	0.010

There is a covariance between the density measurement results of the pilot laboratory VNIIM/RU and participating laboratories CSM and KazInMetr due to the density traceability to the Pilot, which is at the same time the reference value. CSM and KazInMetr density measurements of tridecane, distilled water, high-viscosity oil, and tetrachloroethylene were carried out using standard glass density measures (KazInMetr only; CSM measured density of tetrachloroethylene using laboratory density meter DMA5000), the volumes of which were determined by the pilot laboratory VNIIM by hydrostatic weighting in a comparator liquid. VNIIM’s standard silica sphere with a nominal mass of 1 kg was used as a reference.

Standard uncertainty of the VNIIM's standard silica sphere volume, $u_0 = 9 \cdot 10^{-4}$ cm^3, is a uniform and constant component of uncertainty budget of the participating laboratories. The covariance was calculated according to the following formula:

$$cov\left(x_i, x_{ref}\right)=u_0^2\left(x_{ref}\right)=\left(\frac{M_{stref}}{V_{stref}^2}\cdot u\left(V_{stref}\right)\right)^2, \quad (1)$$

where M_{stref} is the mass of the VNIIM's standard silica sphere, kg;

V_{sti} is the volume of the VNIIM's standard silica sphere, m^3;

$u(V_{\text{stref}})$ = is the standard uncertainty of the volume of VNIIM's standard sphere, m^3.

For KazInMetr and CSM the covariance was:
$cov(x_{\text{i}}, x_{\text{ref}}) = 3.25 \cdot 10^{-5}$ kg^2/m^6

Due to the fact that the CSM is not a member of the CIPM MRA, further processing and calculation of the degrees of equivalence of the CSM results were not performed.

8 Degrees of equivalence

The degree of equivalence d_{i} of the result X_{i} of the i-th laboratory in relation to the reference value X_{ref} was calculated according to the following formula:

$$d_i=X_i-X_{ref} \text{ , kg/m}^3 \quad (2)$$

For a participating laboratory that does not have covariance with the reference laboratory, the expanded uncertainty $U(d_{\text{i}})$ of the degree of equivalence was calculated using formula 3:

$$U\left(d_i\right)=2\sqrt{u^2\left(X_i\right)+u^2\left(X_{ref}\right)} \text{ , kg/m}^3, \quad (3)$$

where $u(X_{\text{i}})$ and $u(X_{\text{ref}})$ are the standard uncertainties of density measurement results of a participating laboratory and the reference liquid density value respectively.

For a participating laboratory that has covariance with the reference laboratory, the expanded uncertainty $U(d_{\text{i}})$ of the degree of equivalence was calculated using formula 4:

$$\widetilde{U}\left(d_i\right)=2\sqrt{u^2\left(X_i\right)+u^2\left(X_{ref}\right)-2\,cov\left(x_i, x_{ref}\right)} \text{ , kg/m}^3 \quad (4)$$

9 Confirmation of CMC data

For a participating laboratory that does not have covariance with the reference laboratory, confirmation of CMC is based on the E_{n} criteria determined by the following formula:

$$E_n=\frac{\left|X_i-X_{\text{ref}}\right|}{2\sqrt{u^2\left(X_i\right)+u^2\left(X_{\text{ref}}\right)}} \ . \quad (5)$$

If the condition (6) is met

$$E_n < 1 \quad , \tag{6}$$

the minimum standard uncertainty that can be declared by a participating Laboratory as CMC is

$$u(CMC) = u(X_i) \tag{7}$$

If the condition (6) is not met, a participating laboratory does not confirm their declared uncertainty.

For a participating laboratory that has covariance with the reference laboratory, confirmation of CMC is based on E_n criteria determined by the following formula:

$$E_n = \frac{|X_i - X_{\text{ref}}|}{2\sqrt{u^2(X_i) + \text{u}^2(X_{\text{ref}}) - 2\,\text{cov}\,(x_i, \text{x}_{\text{ref}})}} \quad . \tag{8}$$

If the condition (9) is met

$$E_n < 1 \quad , \tag{9}$$

the minimum standard uncertainty that can be declared by a participating laboratory as CMC is determined in accordance with (7).

If the condition (9) is not met, a participating laboratory does not confirm their declared uncertainty.

Since the participating laboratories have to make decision whether to exclude their inaccurate measurements results, and to analyze the reasons for the underestimation, approving increased uncertainties, no further processing of the measurement results during Report B stage was carried out during the Report A review stage, if conditions (6) and (9) were not met.

Measurement results X_i, standard uncertainties $u(X_i)$ submitted by the participating laboratories; calculated degrees of equivalence d_i in relation to the reference value of the supplementary Comparison X_{ref}; their expanded uncertainties $U(d_i)$; covariance $cov(x_i, x_{ref})$; criteria values $E_n(E_n)$; and expanded uncertainties U(CMC) of the participating laboratories are given in Tables 11, 12, 13, and 14.

Table 11. Tridecane

Tridecane, 20 °C								
	X_{ref}, kg/m^3	$u(X_{ref})$, kg/m^3						
	756.990	0.006						
Laboratory	$X_{i,}$ kg/m^3	$u(X_i)$, kg/m^3	$cov(x_i,x_{ref})$, kg^2/m^6	d_i, kg/m^3	$U(d_i)$, kg/m^3	E_n (E_n)	u(CMC), kg/m^3	U(CMC), kg/m^3
AzMI	756.988	0.016	–	-0.002	0.034	0.1	0.016	0.032
KazInMetr	756.910	0.050	$3.25 \cdot 10^{-5}$	-0.080	0.099	0.8	0.050	0.100
INM	757.471	0.060	–	+0.481	0.121	4.0	-	–

Table 12. Distilled water

Water, 20 °C								
	X_{ref}, kg/m^3	$u(X_{ref})$, kg/m^3						
	998.201	0.005						
Laboratory	$X_{i,}$ kg/m^3	$u(X_i)$, kg/m^3	$cov(x_i,x_{ref})$, kg^2/m^6	d_i, kg/m^3	$U(d_i)$, kg/m^3	E_n (E_n)	u(CMC), kg/m^3	U(CMC), kg/m^3
AzMI	998.201	0.008	–	0.000	0.018	0.0	0.008	0.016
KazInMetr	998.202	0.0135	$3.25 \cdot 10^{-5}$	+0.001	0.024	0.0	0.0135	0.027
INM	998.201	0.065	–	0.000	0.130	0.0	0.065	0.130

Table 13. High-viscosity oil

High-viscosity oil, 20 °C								
	X_{ref}, kg/m^3	$u(X_{ref})$, kg/m^3						
	890.540	0.009						
Laboratory	$X_{i,}$ kg/m^3	$u(X_i)$, kg/m^3	$cov(x_i,x_{ref})$, kg^2/m^6	d_i, kg/m^3	$U(d_i)$, kg/m^3	E_n (E_n)	u(CMC), kg/m^3	U(CMC), kg/m^3
AzMI	890.572	0.019	–	+0.032	0.042	0.8	0.019	0.038
KazInMetr	890.590	0.010	$3.25 \cdot 10^{-5}$	+0.050	0.022	2.3	-	–
INM	890.634	0.060	–	+0.094	0.121	0.8	0.060	0.120

Table 14. Tetrachloroethylene

Tetrachloroethylene, 20 °C								
	X_{ref}, kg/m^3	$u(X_{ref})$, kg/m^3						
	1615.432	0.011						
Laboratory	$X_{i,}$ kg/m^3	$u(X_i)$, kg/m^3	$cov(x_i,x_{ref})$, kg^2/m^6	d_i, kg/m^3	$U(d_i)$, kg/m^3	E_n (E_n)	u(CMC), kg/m^3	U(CMC), kg/m^3
AzMI	1615.439	0.013	–	+0.007	0.033	0.2	0.13	0.026
KazInMetr	1615.661	0.012	$3.25 \cdot 10^{-5}$	+0.229	0.028	8.1	-	–
INM-MD	1615.132	0.060	–	-0.300	0.122	2.5	-	–

The participating laboratories degrees of equivalence in relation to the reference values and corresponding expanded uncertainties for all four standard liquids are given in Figures 7, 8, 9, and 10.

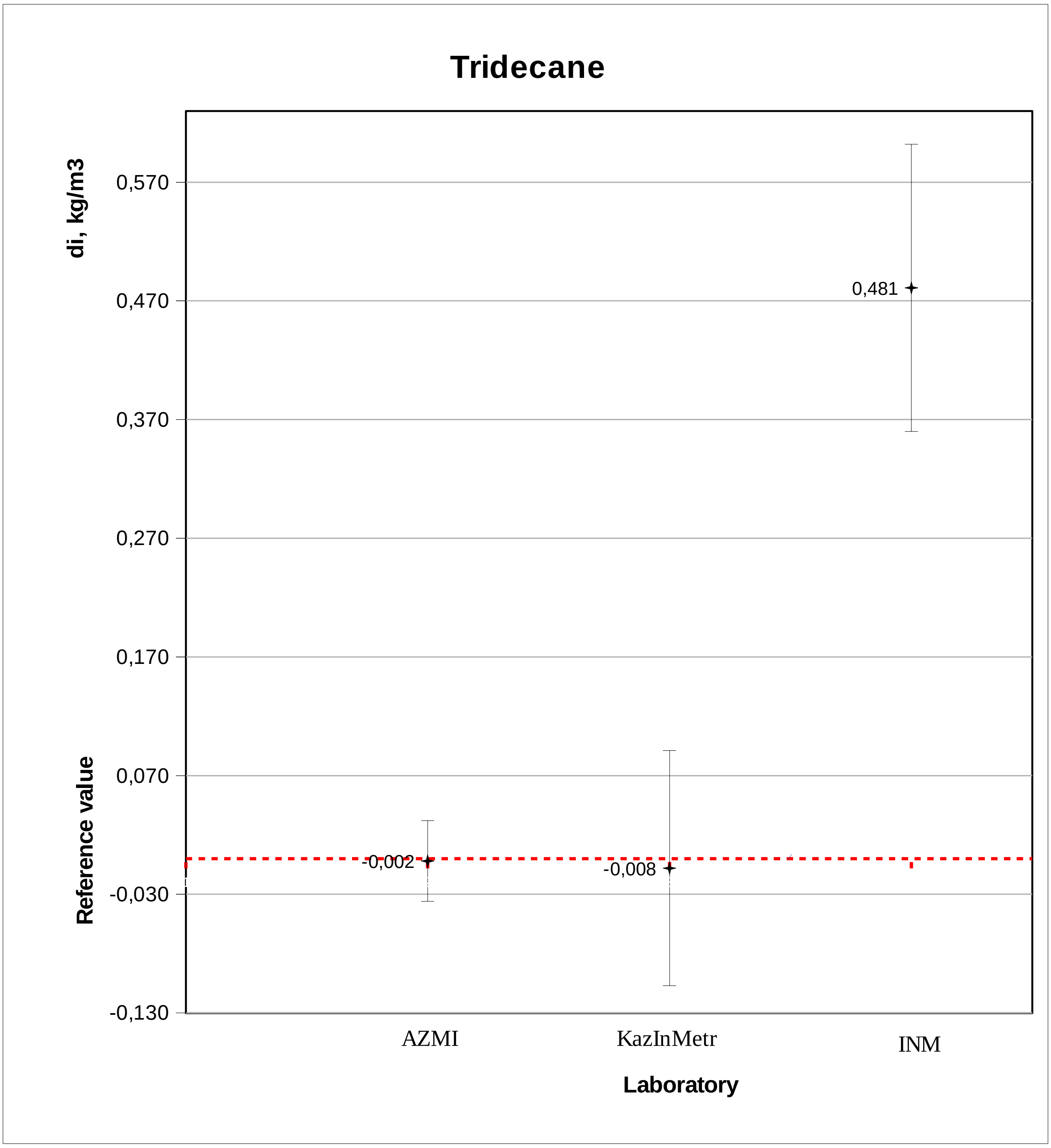

Figure 7. The participating laboratories degrees of equivalence in relation to the reference values and corresponding expanded uncertainties for tridecane density measurements

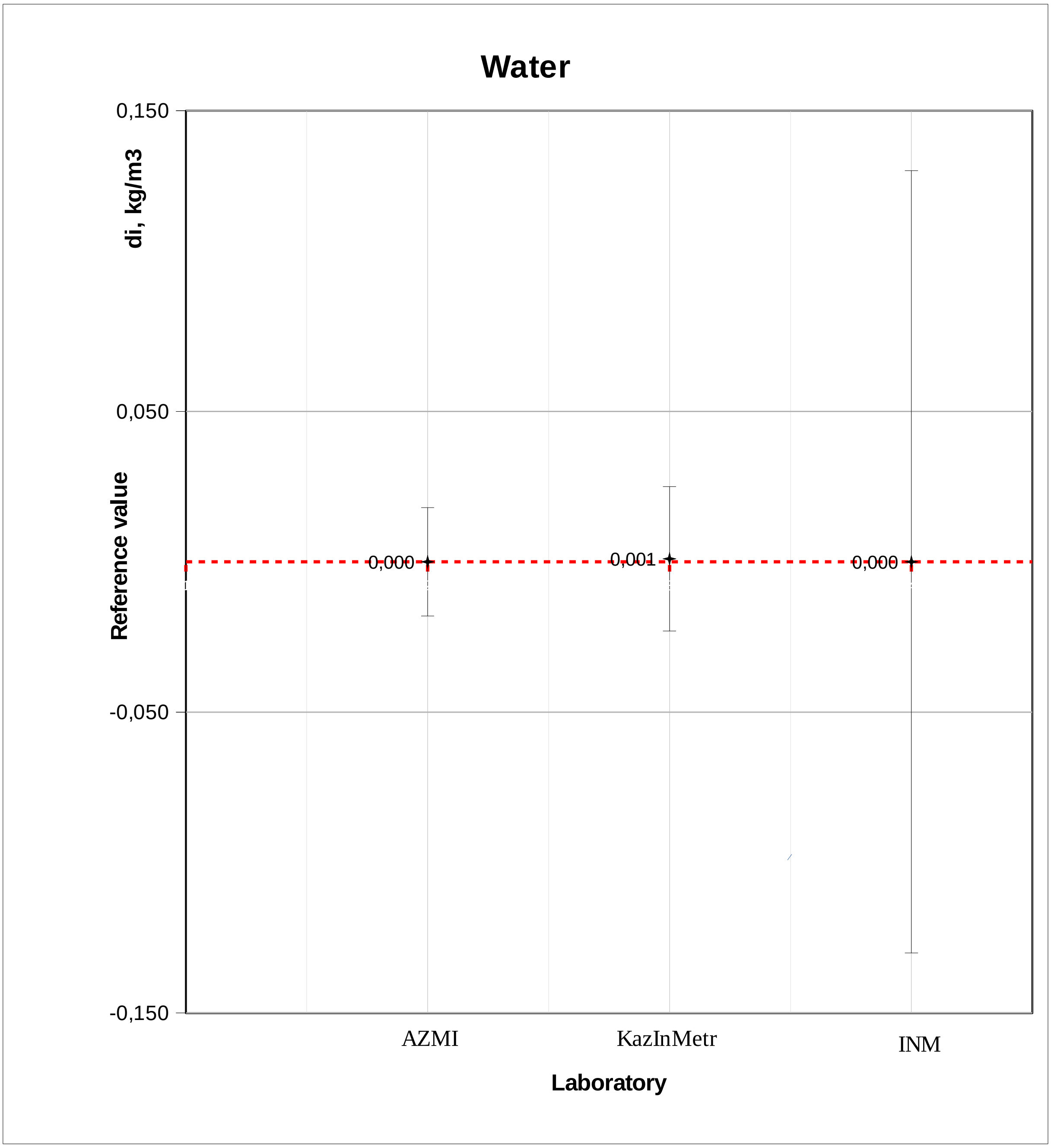

Figure 8. The participating laboratories degrees of equivalence in relation to the reference values and corresponding expanded uncertainties for distilled water density measurements

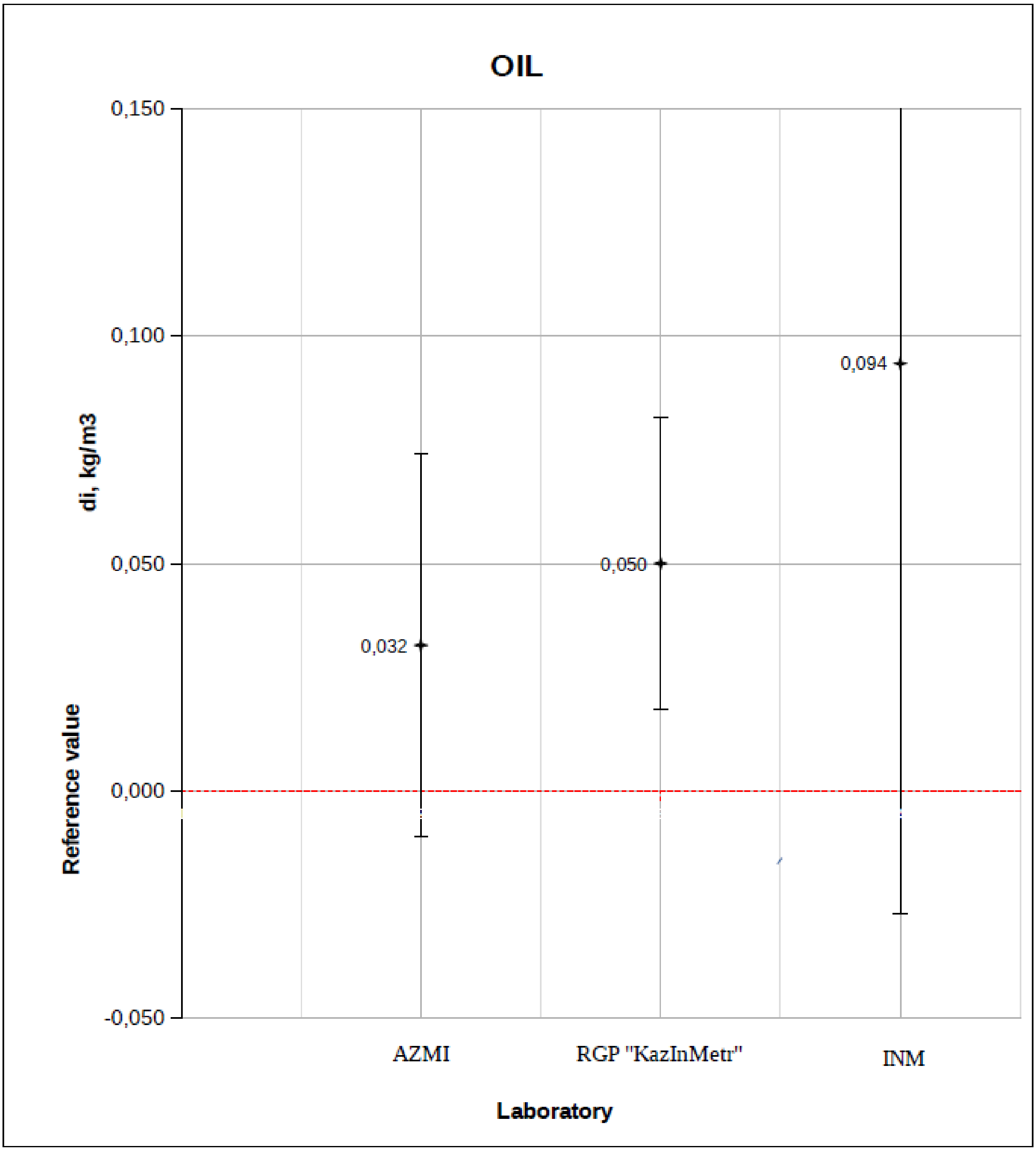

Figure 9. The participating laboratories degrees of equivalence in relation to the reference values and corresponding expanded uncertainties for high-viscosity oil density measurements

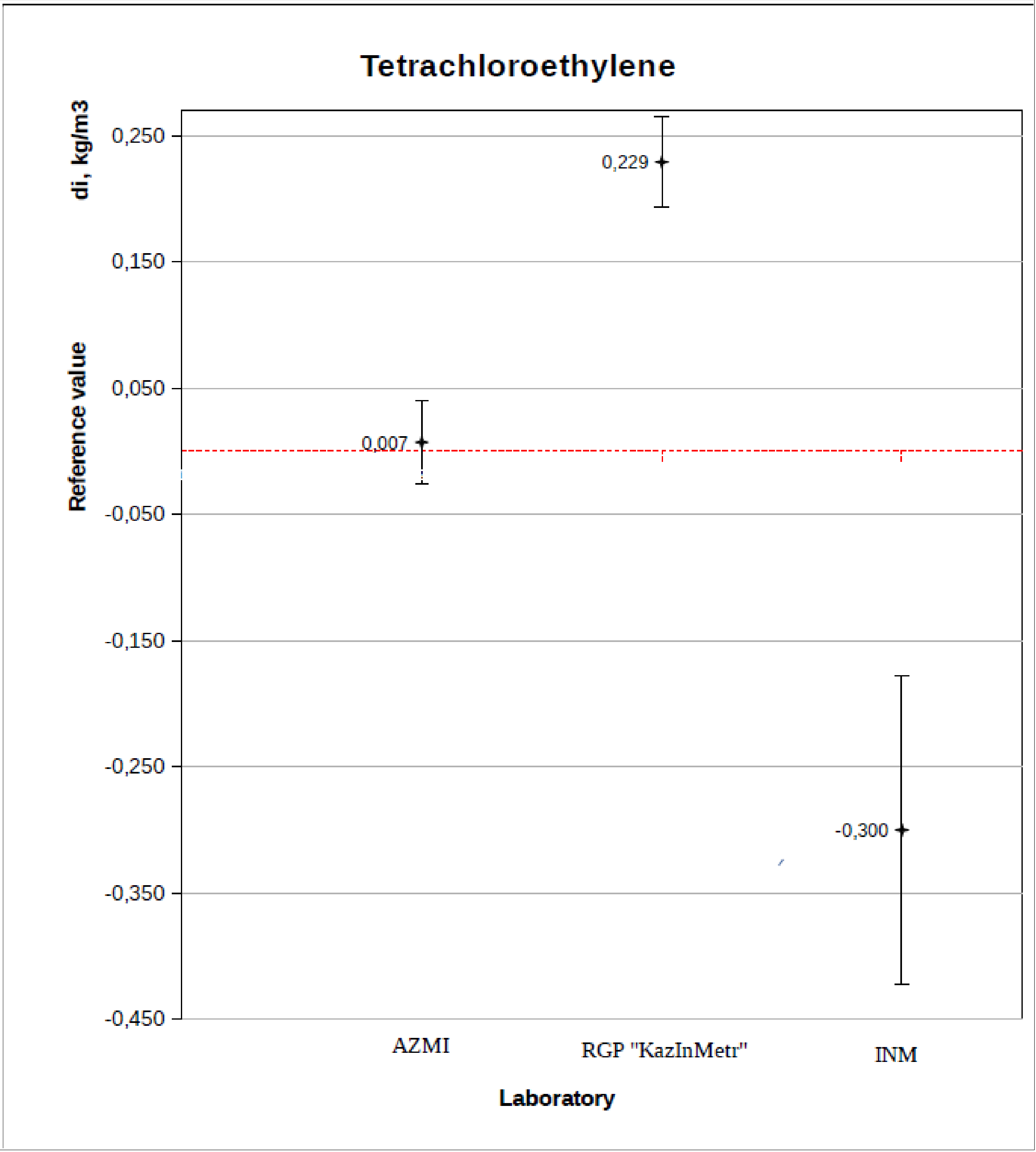

Figure 10. The participating laboratories degrees of equivalence in relation to the reference values and corresponding expanded uncertainties for tetrachloroethylene density measurements

10 Conclusion

During the RMO supplementary comparison, densities of four reference liquids (tridecane, distilled water, high-viscosity oil, and tetrachloroethylene) were determined at 20 °C. Measurements were performed at atmospheric pressure by two methods: method of hydrostatic weighting of reference measures of density and by using laboratory density meters DMA5000, manufactured by Anton Paar GmbH, Austria.

Components for a possible density drift or liquid inhomogeneity were not included in the final calculations, taking into consideration that deviations of density values of liquids stored in sealed containers during the Comparison determined by the Pilot Laboratory do not exceed the uncertainties declared by the Pilot Laboratory.

The results closest to the control value were obtained when measured in distilled water. When measuring the density of distilled water, all three participating laboratories, members of the CIPM MRA, confirmed their inaccuracies.

The most abnormal are the results obtained for the most difficult liquid to measure, high-viscosity mineral oil. All the results of oil density measurements submitted by the participant laboratories exceed the reference value obtained by the pilot laboratory. When testing the stability of control samples, density measurements of high-viscosity oil demonstrated the greatest density decrease of 0.012 kg/m^3 during storage. Due to the inconsistency of experimental data from stability testing, which did not confirm increasing of high-viscosity oil density value during its transportation and storage and taking into account the measurement results obtained by the participating laboratories, and as the density deviation of the control sample during storage did not exceed the uncertainty of the pilot laboratory's result, it was not possible to correct the reference value for density of high-viscosity oil. KazInMetr results do not seem to be abnormal in relation to the results of the other participating laboratories, but KazInMetr did not confirm their uncertainty because if its low value.

For the liquid with the lowest density value, tridecane, the most abnormal result was obtained by INM.

For the liquid with the highest density value, tetrachloroethylene, the most abnormal results were obtained by INM and KazInMetr/KZ.

The expanded uncertainty of reference density values of all the reference liquids does not exceed $2 \cdot 10^{-2}$ kg/m^3 or $1.3 \cdot 10^{-5}$ in relative terms. It satisfies the needs of calibration laboratory customers to calibrate density measuring instruments such as density gages of different types and laboratory-grade vibration density analyzers. The participating laboratories can use the Comparison results to confirm their CMCs when performing measurements and calibrations.

11 References

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