

Final Report
on
EUROMET Key Comparison
EUROMET.M.D-K2 (EUROMET 627)

Comparison of density determinations
of liquid samples

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Abstract

The results of the key comparison EUROMET 627 (EUROMET.M.D-K2) are presented. This project covered the density measurements of three liquids: dodecane, water and an oil of high viscosity measured at 15 °C, 20 °C and 40 °C. Seven European metrology laboratories and the South African laboratory CSIR-NML (now: NMISA) measured the densities at atmospheric pressure by hydrostatic weighing of solid density standards between 04 October 2001 and 18 December 2001. The stability and homogeneity of the liquids were investigated by the pilot laboratory PTB.

The results generally show good agreement among the participants. Only for the simple Mohr-Westphal balances do the uncertainties seem to be underestimated by the laboratories. Furthermore, the measurement of high-viscosity oil was difficult for some laboratories.

Nevertheless, the five laboratories PTB/DE, BNM/FR (now: LNE/FR), OMH/HU (now: MKEH/HU), IMGCI/IT (now: INRIM/IT) and GUM/PL agree with each other for stated uncertainties of 0.05 kg/m³ or less. This satisfies the current needs of customers who wish to calibrate or check liquid density measuring instruments such as oscillation-type density meters.

No reference values were calculated since the subsequent CCM key comparison CCM.D-K2 had a different scope and the EUROMET 627 comparison was soon superseded by the EURAMET 1019 (EURAMET.M.D-K2) comparison.

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1 Introduction

Hydrostatic density determinations for liquids are mainly performed by laboratories to provide a means for calibrating or checking liquid density measuring instruments such as oscillation-type density meters [1]. The aim of the EUROMET Project 627 "Comparison of density determinations of liquid samples" is to compare the results of the density determinations by the participating laboratories. The comparison was proposed and agreed at the 13th EUROMET Mass and Derived Quantities Contact Persons Meeting held in February 2001 at the Instituto Português da Qualidade (IPQ) in Lisbon, Portugal.

The comparison should support entries for the CMC tables in this sub-field. It was also intended to be a regional key comparison in accordance with the Mutual Recognition Arrangement [2].

The comparison EUROMET 627 follows the EUROMET Project 339 "Inter-comparison of volume standards by hydrostatic weighing." The final report for that project was published in August 2000 [3] and pointed out that the maximum relative density difference for the 1 kg sphere was only 2.2 ppm for the participants who used solid density standards. A similar CIPM key comparison (CCM.D-K1) started in 2001 and was finished in 2006.

For the EUROMET comparison 627 samples of dodecane, water and an oil of high viscosity were measured at 15 °C, 20 °C and 40 °C. The measurements were carried out at atmospheric pressure by hydrostatic weighing of a solid density standard. Apparatuses intended only to calibrate hydrometers or solid density standards are checked in different comparisons and thus were excluded from this EUROMET project although they cover liquid density determination. Oscillation-type density meters were also excluded since they are calibrated with liquids that are measured hydrostatically.

2 Comparison

2.1 Participants

Seven European laboratories and the South African laboratory CSIR-NML took part in the comparison (see table 1). The PTB was the Pilot Laboratory and the

laboratories of GUM (PL) and OMH (HU) helped the Pilot Laboratory prepare the Technical Protocol.

Table 1: Participating laboratories, persons responsible and dates of measurement.

Laboratory (acronym)	Country code	Person responsible	Date of measurement
Physikalisch-Technische Bundesanstalt (PTB)	DE	Horst Bettin	10 Oct. to 26 Oct. 2001
Centre for Metrology and Accreditation (MIKES)	FI	Martti Heinonen	09 Oct. to 18 Oct. 2001
National Metrology Laboratory (BNM-LNE)	FR	André Gosset	11 Oct. to 30 Oct. 2001
Országos Mérésügyi Hivatal (OMH)	HU	Zoltán Zelenka	11 Nov. to 30 Nov. 2001
Istituto di Metrologia G. Colonnetti (IMGC-CNR)	IT	Salvatore Lorefice	16 Oct. to 02 Nov. 2001
Norwegian Metrology & Accreditation Service (JV)	NO	Kristen Hellerud	30 Oct. to 31 Oct. 2001
Central Office of Measures (GUM)	PL	Hanna Durlik	15 Oct. to 02 Nov. 2001
National Metrology Laboratory of the CSIR (CSIR-NML)	ZA	Werner Jordaan, Ireen Field	18 Dec. 2001

2.2 Liquid samples

For the comparison three liquids with a large range of properties were chosen. The hydrostatic density measurement for water is difficult since water has a large and

very unstable surface tension. Thus, any meniscus effect on the wire becomes apparent.

In contrast to this, the surface tension of n-dodecane ($C_{12}H_{26}$) is low and usually does not pose any problems, so sinker volume and expansion can easily be checked. The main difficulty of this liquid is its rather large thermal expansion.

As the third liquid an oil with a high viscosity was chosen, since the indication of oscillation-type density meters shows a great influence on the viscosity of the liquid. Therefore, liquids with viscosities in the range 5 mPas to 10000 mPas are used to calibrate or check these instruments. For the comparison a viscosity oil named "VO-1" with a viscosity of approximately 2900 mPas at 20 °C (4700 mPas at 15 °C, 600 mPas at 40 °C) was chosen. In addition to the high viscosity, this liquid also posed other problems, since it is nearly opaque and no values for compressibility and surface tension could be given in the Technical Protocol. The value of the surface tension was made available to the participants only after all reports were received.

Before the comparison the stability of the liquids was checked. The density of a 1 litre sample was measured at 20 °C. After the liquid had been stored for four weeks in one of the bottles used for the liquid transportation, the density was measured again. The results proved that the liquids are suitable for the comparison (see table 2). Only the drift of the viscosity oil is (slightly) significant. The samples used for the stability check were not used for the comparison.

Table 2: Density at 20 °C at the beginning and at the end of the four-week check interval. The uncertainty ($k = 2$) of the difference takes correlations into account.

Liquid	Density at the beginning in kg/m^3	Density after 4 weeks in kg/m^3	Density increase and uncertainty ($k = 2$) in kg/m^3
Water (air saturated)	998.2006	998.2017	0.0011 ± 0.0040
n-dodecane	748.8491	748.8500	0.0009 ± 0.0040
Viscosity oil VO-1	911.4257	911.4318	0.0061 ± 0.0055

For the comparison the water sample was prepared anew. The stability check was repeated during the comparison (for results, see chapter 4). The density of this water sample was slightly varied by adding 27.8 g of 99.8% deuterated water (deuterium

oxide D₂O) to 19.22 kg of distilled and purified tap water. The density variation was calculated by the formula of Menaché et al. [4, 5]: 0.1385 kg/m³.

The formula for the density of de-aerated water of Tanaka et al. [6] was used to calculate the density of SMOW water at 15 °C, 20 °C and 40 °C. For the tap water at PTB a density value 3.4 ppm lower than the density of SMOW water was estimated [7]. The uncertainty of the calculated density of the mixture is estimated at 0.0021 kg/m³ for a confidence level of 95% (coverage factor $k = 2.1$).

Approximate values for the cubic thermal expansions and for the compressibilities of the liquids were listed in the Technical Protocol, see table 4. They were used by most of the participants. GUM/PL calculated the expansion coefficients from the measurements. The compressibility of VO-1 could be (and was) neglected by most of

Table 3: Calculated density of the deuterated water (uncertainty: 95% confidence level)

Temperature	Density (SMOW) [6] in kg/m ³	Density (tap) in kg/m ³	Calculated density of the mixture in kg/m ³
15 °C	999.1026	999.0992	999.2377 ± 0.0021
20 °C	998.2067	998.2033	998.3418 ± 0.0021
40 °C	992.2152	992.2118	992.3503 ± 0.0021

Table 4: Cubic thermal expansion and compressibility of the liquids

Liquid	Cubic thermal expansion in kg/(m ³ K)	Uncertainty ($k = 1$) in kg/(m ³ K)	Compressibility in 10 ⁻¹¹ Pa ⁻¹	Uncertainty ($k = 1$) in 10 ⁻¹¹ Pa ⁻¹
Dodecane	0.73	0.05	80	10
Water at 15 °C	0.15	0.02	47	2
at 20 °C	0.21	0.02	46	2
at 40 °C	0.38	0.02	44	2
Viscosity oil VO-1	0.61	0.05	unknown	

the participants. PTB/DE used $80 \cdot 10^{-11} \text{ Pa}^{-1}$ with a standard uncertainty of $30 \cdot 10^{-11} \text{ Pa}^{-1}$ and OMH/HU estimated the compressibility from literature values: $58 \cdot 10^{-11} \text{ Pa}^{-1}$ at 15 °C, $60 \cdot 10^{-11} \text{ Pa}^{-1}$ at 20 °C, and $73 \cdot 10^{-11} \text{ Pa}^{-1}$ at 40 °C with a standard uncertainty of $10 \cdot 10^{-11} \text{ Pa}^{-1}$.

Nominal values of surface tension and density were also given, see table 5. These values could be used to estimate the mass of the meniscus. This is most important for the Mohr-Westphal balances of JV/NO and CSIR-NML/ZA. Nevertheless, CSIR-NML/ZA neglected the meniscus mass (and the associated uncertainty) for the calculation of the density of VO-1.

Table 5: Nominal surface tension and nominal density values

Liquid	Nominal surface tension in mN/m	Nominal density in kg/m ³
Dodecane at 20 °C	25	749
Water at 15 °C	73	999
Water at 20 °C	73	998
Water at 40 °C	70	992
Viscosity oil VO-1 at 20 °C	32*	911

*) value was transmitted to the laboratories after all reports were received.

2.3 Measurements

The laboratories were asked to keep the liquids at the laboratory for at least two days after receipt and to open the bottles only for the measurements. The water sample should be degassed by the participating laboratory, but at temperatures not higher than 70 °C (see chapter 5.1). It was proposed using the following sample sequence: water, dodecane, viscosity oil. The temperature sequence for each liquid should be: 20 °C, 15 °C, 40 °C, 20 °C. The last measurement at 20 °C served to check whether the density had changed during the measurements. JV/NO and CSIR-NML/ZA could measure at 20 °C only. BNM/FR measured all liquids at 20 °C, then all liquids at 15 °C and so on. For each liquid and temperature, at least ten weighing sequences

had to be performed. In one measurement of JV/NO and GUM/PL, only nine single determinations were performed, which is of no significance. The density at the target temperature and at 101325 Pa was reported as final result.

The temperature of 20 °C was chosen since it is the usual reference temperature for density standards. The temperature of 15 °C is the reference temperature for petroleum liquids and liquefied petroleum gases [8, 9]. In order to check the expansion coefficients of the sinkers, it was decided to measure also at 40 °C, which turned out to be the highest temperature all laboratories could use.

2.4 Organisation of the comparison

The comparison started on September 3, 2001, by agreement to the Technical Protocol.

The first stability checks by hydrostatic weighing at 20 °C were performed from August 08 to September 17. These samples were not used for the comparison.

For the comparison, volumes of 18 to 20 litre of n-dodecane ($C_{12}H_{26}$), water and the viscosity oil "VO-1" were mixed in large containers. From September 14 to 18, the liquids were filled into the 1 litre transport bottles which were consecutively numbered. The use of the bottles is given in table 5. Bottle 18 of the new water was used to check the stability during the comparison by hydrostatic weighing at 20 °C from September 19 to November 19, 2001. Small samples were taken from all bottles and compared with an oscillating density meter to check the homogeneity (for results, see chapter 4).

The bottles were sent to the participants on September 24, 2001. Unfortunately, no ATA carnet was prepared for the package of the OMH/HU. This package therefore had to be re-shipped with a carnet on October 30.

The liquids should be sent back to the Pilot Laboratory as soon as possible after the measurements had been completed but 28 days after receipt of the liquids at the latest. By mistake, JV/NO first returned only the part of the liquid which had not been measured. CSIR-NML/ZA waited more than two months until it performed the measurements.

After the return of the liquids, the Pilot Laboratory checked whether the density of the samples had changed during the comparison. The samples of GUM/PL and OMH/HU, which were measured with a very low uncertainty, were checked at 20 °C in the hydrostatic weighing apparatus. All samples were compared using an oscillating density meter (for results, see chapter 4).

The participant forwarded their reports to the Pilot Laboratory between November 27, 2001, and January 17, 2002.

Table 6. Use of the transport bottles

Bottle No.	Use	Bottle No.	Use
1	(stability test at PTB) (water: non-deuterated)	10	IMGC (dodecane and viscosity oil: not used)
2	PTB	11	JV
3	MIKES	12	GUM
4	BNM	13	GUM
5	OMH	14	GUM
6	OMH	15	CSIR-NMI
7	OMH	16	stand-by (PTB)
8	IMGC (water: not used)	17	stand-by (PTB)
9	IMGC	18	water: stability check (PTB) of deuterated water, viscosity oil: stand-by (PTB)

3 Apparatuses and Methods

The participants used a great variety of apparatuses; the quoted uncertainties ranged from 0.003 kg/m³ to 0.4 kg/m³ for a coverage factor of 2. JV/NO and CSIR-NML/ZA employed an apparatus according to the Mohr-Westphal balance, first weighing sinker and suspension in air and then sinker and suspension in the liquid. All other laboratories weighed the suspension alternately with and without the sinker in the liquid.

Table 7 gives a survey of the main features of the apparatuses of the laboratories.

Table 7. Main features of the apparatuses of the participating laboratories

Institute/ country	Solid density standard (sinker)	Wire: diameter, material	Thermostat system	Thermometer for the liquid temperature	Meniscus effect
PTB/DE	Silicon sphere, 100 cm ³ , calibrated at PTB	Ø 0.1 mm, Pt-Ir	Tamson, 70 litre	25 Ohm PRT, ASL F17A	measured
MIKES/FI	Silicon sphere, 22 cm ³ , calibrated in water at MIKES	Ø 0.25 mm, tantalum	double-walled glass vessel	100 Ohm PRT, ASL F250	measured
BNM/FR	Hollow Pyrex glass cylinder, 100 cm ³ , calibrated in water at BNM	Ø 0.25 mm, Pt-Ir	Tamson, 70 litre	100 Ohm PRT, HP34420	estimated
OMH/HU	Hollow Pyrex glass sphere, 90 cm ³ , volume calibrated at PTB, mass calibrated at OMH	Ø 0.2 mm, Pt-Ir	Tamson, 70 litre	Tinsley 5187 SA	measured
IMGC/IT	Zerodur sphere, 100 cm ³ , calibrated at IMGC	Ø 0.3 mm, stainless steel	double-walled glass vessel	100 Ohm PRT, ASL F17	estimated
JV/NO	Glass cylinder, 10 cm ³ , calibrated in water at JV	Ø 0.2 mm, stainless steel	temperature of air- conditioned room	100 Ohm PRT, FPH 4000	estimated
GUM/PL	Silicon prism, 66 cm ³ , calibrated at PTB	Ø 0.12 mm, molybdenum	Tamson, 70 litre	Tinsley 5187 SA, ASL F700B	estimated
CSIR- NML/ZA	Glass cylinder, 10 cm ³ , calibrated in water at CSIR-NML	Ø 0.08 mm, stainless steel	room temperature	Hg glass thermometer	estimated

Table 8 lists the lowest quoted standard uncertainties of the main uncertainty contributions in the comparison, i. e.

volume of sinker (volume or density standard),

temperature of liquid on sinker,

meniscus mass difference for the measurements of water. (During the weighing with sinker the meniscus usually differs from the meniscus during weighing without sinker, which is due to the elongation of the wire or a rise of the liquid surface level.)

Also listed in table 8 are the lowest experimental standard deviation of the mean density, which usually is negligible, and the lowest standard uncertainty ($k = 1$) of the result.

JV/NO added a contribution to the prepared list of the Technical Protocol taking account of the wetting of the wire.

Table 8. Lowest standard uncertainties of the main components and lowest relative standard uncertainty of the liquid density

Institute/ country	Volume of sinker in $10^{-6} V_{20}$	Temperature of liquid in mK	Meniscus (for water) in mg	Standard deviation of mean density in 10^{-3} kg/m^3	Uncertainty ($k = 1$) of liquid density ρ_l in $10^{-6} \rho_l$
PTB/DE	1.0	4	0.04	0.06	1.8
MIKES/FI	23	22	0.65	0.9	40
BNM/FR	5	11	0.05	0.33	6
OMH/HU	1.9	1.0	0.05	0.022	2.0
IMGC/IT	0.6	10	0.10	0.16	3.1
JV/NO	21	50	0.47	6.4	40
GUM/PL	1.1	12	0.1	0.4	6
CSIR- NML/ZA	40*	200*	0.5*	20	60

*) CSIR-NML/ZA apparently stated expanded uncertainties in their report.

The two tables again show the large variety of apparatuses and uncertainties. The sinkers of OMH/HU, GUM/PL and PTB/DE are traceable to the primary density standards of the PTB. This leads only to a small maximal correlation of 14% between OMH/HU and PTB/DE, since the sinker volumes were determined with different apparatuses and the overall uncertainties quoted by these laboratories (see table 8) are far higher than the uncertainty of the PTB primary standards (relative uncertainty $0.7 \cdot 10^{-6}$ for $k = 1$). Similarly, the maximal correlation coefficient of OMH/HU and GUM/PL amounts to 4%. The sinkers of GUM/PL and PTB/DE were calibrated in the flotation apparatus of the PTB. The maximal correlation coefficient can be calculated from the uncertainties of the sinker volumes and the minimal uncertainty of the liquid density determination yielding a value of 11%.

4 Results of check measurements

a) Inhomogeneity and changes of the liquid densities during comparison

A density meter of the oscillation type was used to compare the liquid samples in the transport bottles before and after measurement by the participants. The density meter used, a DMA58 of Anton Paar, has a resolution of 0.001 kg/m^3 (if the density is calculated from the oscillation frequency). Although the standard uncertainty of the density values of the DMA58 is approximately 0.05 kg/m^3 , comparisons of similar liquids can be performed with standard uncertainties less than 0.010 kg/m^3 .

From each bottle a 50 ml sample was drawn and measured twice. From the standard deviation s_D of the difference between these two measurements of each bottle the standard deviation of a single measurement can be calculated: $s_1 = s_D/\sqrt{2}$. Comparing this standard deviation with the standard deviation of the density determinations of all bottles gives an estimate of the standard deviation s_H due to inhomogeneity of the liquid: $s_H = \sqrt{(s_B^2 - s_1^2/2)}$, where s_B is the standard deviation of the mean density values for all bottles. Although the uncertainty of the estimated standard deviation s_H is high, it is clear that the inhomogeneity of the liquids is smaller than a few in 10^{-6} in relative terms. Table 9 lists the standard deviations and Fig. 1 to Fig. 3 show the results of the measurements.

The contents of the three bottles from OMH/HU were mixed with one another for the hydrostatic check measurement before the check with the density meter. Therefore, only one sample was drawn for the DMA58 measurements.

JV/NO first returned only the parts of the liquids which had not been measured. So results are available for two JV/NO samples for each liquid for the time after the measurements at JV/NO.

Table 9: Calculation of the standard deviations due to inhomogeneity of the liquids. The values from November are without the bottles from CSIR/ZA, JV/NO (measured sample), and OMH/HU, which arrived later.

Liquid	Date of measurement	Standard deviation		
		s_1 of differences of single bottles in kg/m^3	s_B of density of all bottles in kg/m^3	due to inhomogeneity in kg/m^3
Water	19 Sept. 2001	0.0028	0.0022	0.0017
Water	14 Nov. 2001	0.0031	0.0031	0.0027
Dodecane	17 Sept. 2001	0.0059	0.0029	0
Dodecane	15 Nov. 2001	0.0068	0.0023	0
Viscosity oil VO-1	18 Sept. 2001	0.0051	0.0036	0.0026
Viscosity oil VO-1	29 Nov. 2001	0.0109	0.0065*	0.0035*

*) Without the value for bottle 4, the density for which had changed significantly

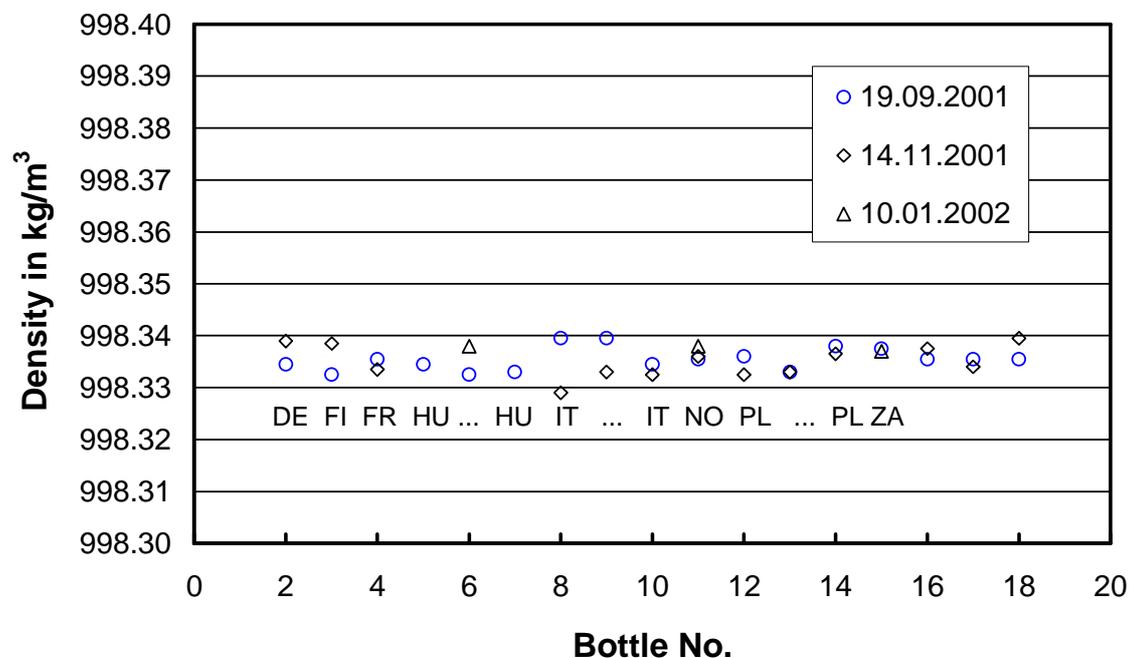


Fig. 1: Comparison of the densities of the water samples before and after the measurements by the participants. Bottles Nos. 16 and 17 are stand-by bottles. Bottle No. 18 was used for the stability test (see table 6).

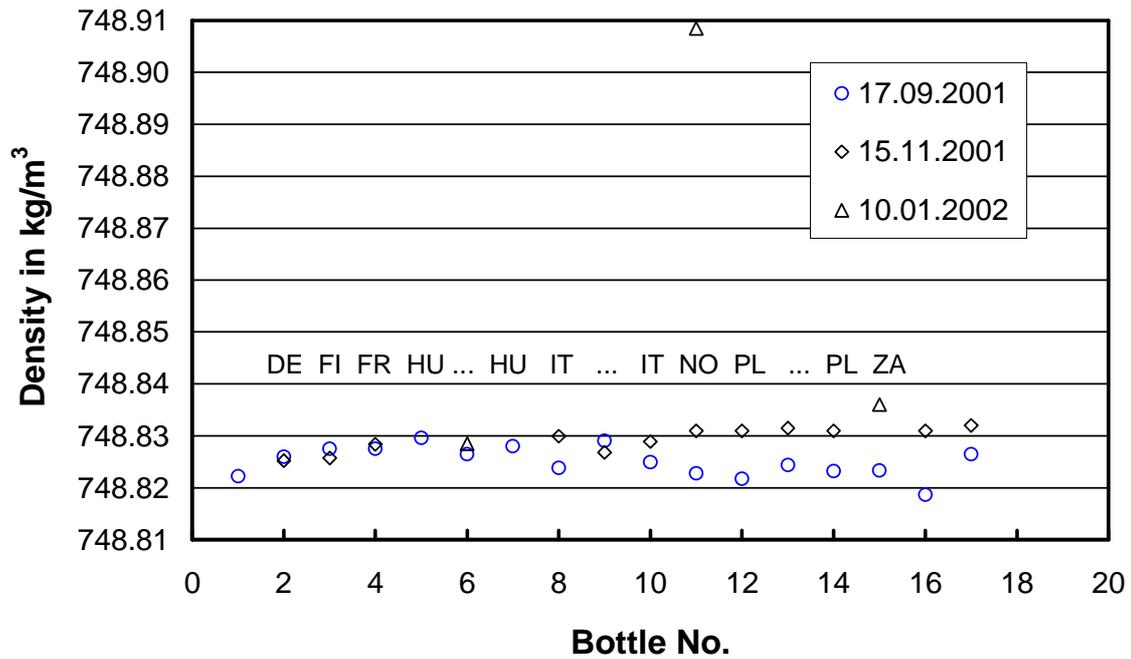


Fig. 2: Comparison of the densities of the dodecane samples before and after the measurements by the participants. Bottles Nos. 16 and 17 are stand-by bottles. Bottle No. 1 was used for the stability test (see table 6). The density of the measured part of bottle 11 had changed significantly during the comparison.

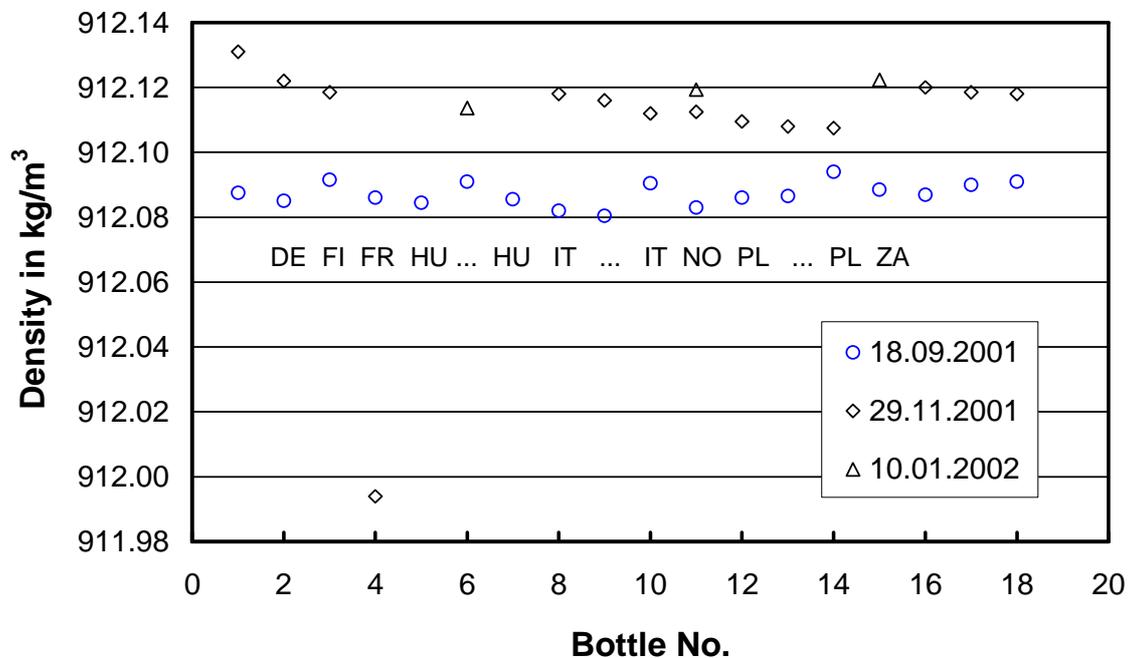


Fig. 3: Comparison of the densities of the viscosity oil VO-1 samples before and after the measurements by the participants. Bottles Nos. 16 to 18 are stand-by bottles. Bottle No. 1 was used for the stability test (see table 6). The sample of bottle 4 had changed its density during the measurement at BNM/FR.

The measured part of the dodecane sample of JV/NO had changed its density significantly. The variation may have happened after the measurement by JV/NO. The change of 0.08 kg/m^3 is smaller than the uncertainty quoted by JV/NO (0.14 kg/m^3 for $k = 2$).

As the viscosity oil VO-1 was measured without a viscosity correction for the density meter, the values in Fig. 3 differ considerably from the values determined hydrostatically. The difference between the values from September and the later values is probably mainly due to differences in the adjustment of the density meter (and partly due to the drift of the liquid).

The viscosity oil sample for BNM/FR changed its density during the measurement at BNM (see chapter 5.3).

b) Hydrostatic check measurements

At the PTB, the samples returned by OMH/HU and GUM/PL were hydrostatically measured at $20 \text{ }^\circ\text{C}$ because

- 1) the density of the samples might have changed during the transport to the participants. The density meter is not able to detect this with the desired accuracy, since these laboratories state very small uncertainties.
- 2) the drift of the density can be determined more accurately than in the four-week check interval due to the longer time interval.

Table 9 lists all results obtained at the PTB by hydrostatic weighing of the liquids. This table also contains the results of the stability check of the deuterated water with bottle No. 18. No significant deviation was found for the liquid samples of GUM/PL or OMH/HU. From these measurements the following drift coefficients can be calculated (uncertainties for a confidence level of 95%):

Deuterated water: $(-6 \pm 85) \cdot 10^{-6} \text{ kg}/(\text{m}^3 \text{ day})$

Dodecane: $(3 \pm 56) \cdot 10^{-6} \text{ kg}/(\text{m}^3 \text{ day})$

Viscosity oil VO-1: $(126 \pm 87) \cdot 10^{-6} \text{ kg}/(\text{m}^3 \text{ day})$

(The uncertainties take correlations into account. The reproducibility of the PTB hydrostatic weighing apparatus can be described by a standard deviation of 0.0015 kg/m^3 for water and dodecane and 0.0019 kg/m^3 for the viscosity oil.)

Table 9: Hydrostatic measurements at 20 °C to determine the density drift of the liquids.

Liquid	Bottle No.	Date	Density at 20 °C in kg/m ³
Deuterated water	18	21 Sept. 2001	998.3386
Deuterated water	2	10 Oct. 2001	998.3407
Deuterated water	2	15 Oct. 2001	998.3405
Deuterated water	18	20 Nov. 2001	998.3382
Deuterated water	12-14	22 Nov. 2001	998.3358
Deuterated water	5-7	17 Dec. 2001	998.3411
Dodecane	1	14 Aug. 2001	748.8491
Dodecane	1	13 Sept. 2001	748.8500
Dodecane	2	16 Oct. 2001	748.8504
Dodecane	2	19 Oct. 2001	748.8531
Dodecane	12-14	23 Nov. 2001	748.8475
Dodecane	5-7	19 Dec. 2001	748.8510
Viscosity oil VO-1	1	16 Aug. 2001	911.4258
Viscosity oil VO-1	1	18 Sept. 2001	911.4318
Viscosity oil VO-1	2	23 Oct. 2001	911.4331
Viscosity oil VO-1	2	26 Oct. 2001	911.4317
Viscosity oil VO-1	12-14	27 Nov. 2001	911.4437
Viscosity oil VO-1	5-7	21 Dec. 2001	911.4401

5 Results of participants

In this chapter the results reported by the participants are given. The uncertainties do not contain contributions due to inhomogeneity or drift of the liquids.

Also calculated are median, mean value and weighted mean value to give a preliminary characterisation of the results. The values for 20 °C were calculated using the mean of the two values of each laboratory, thus taking into account the high correlation between the measurements of one laboratory. Correlations between different laboratories were not taken into account.

No link was performed to the CCM key comparison CCM.D-K2 and, thus, no reference values for this comparison were calculated, because CCM.D-K2 had a different scope and the EUROMET 627 comparison was soon superseded by the EURAMET 1019 comparison.

5.1 Water

The participants were asked to degas the water samples using temperatures up to 70 °C in order to reduce problems due to the formation of air bubbles during heating up to 40 °C. The density effect of dissolved air is less than $3 \cdot 10^{-6}$ relatively for temperatures higher than 15 °C. IMG/IT did not degas the water sample. BNM/FR degassed the sample not before the measurement at 40 °C. CSIR-NML/ZA measured only at 20 °C and did not degas the sample.

The results for the deuterated water approximately agree within the combined uncertainties, even without taking into account drift or inhomogeneity of the liquid. The calculated values (see table 3 in chapter 2.2) agree with the results and the weighted mean values.

The normalised deviation E_n is defined by

$$E_n = \frac{\rho_1 - \rho_2}{\sqrt{U^2(\rho_1) + U^2(\rho_2)}}$$

where ρ_1 and ρ_2 are the densities of laboratories 1 and 2, respectively, and U is the expanded uncertainty for a confidence level of 95%.

The maximal normalised deviation for water is $E_n = 1.1$.

Table 10: Reported results of the participants for water at 20 °C; for the calculated values, see table 3 in chapter 2.2. The uncertainties are for a confidence level of 95% and do not include contributions due to drift or inhomogeneity of the liquid.

Institute/ country	Density at 20 °C (1) in kg/m ³	Uncert. (95%) in kg/m ³	Effective degrees of freedom	Density at 20 °C (2) in kg/m ³	Uncert. (95%) in kg/m ³	Effective degrees of freedom
PTB/DE	998.3407	0.0037	133	998.3405	0.0040	373
MIKES/FI	998.286	0.0781	460	998.263	0.0803	516
BNM/FR	998.340	0.012	103	998.341	0.014	148
OMH/HU	998.3396	0.0041	70	998.3404	0.0041	73
IMGC/IT	998.34099	0.0100	95	998.3380	0.0142	112
JV/NO	998.3737	0.0843	80			
GUM/PL	998.350	0.0194	68	998.354	0.012	82
CSIR- NML/ZA	998.40	0.10	118			
median	998.3408	0.0075		998.3405	0.0025	
mean	998.3464	0.0231		998.3295	0.0304	
weighted	998.3404	0.0026		998.3410	0.0027	
calculated	998.3418	0.0021	36	998.3418	0.0021	36

Table 10a: Reported results of the participants for water at 15 °C and 40 °C; for the calculated values, see table 3 in chapter 2.2. The uncertainties are for a confidence level of 95% and do not include contributions due to drift or inhomogeneity of the liquid.

Institute/ country	Density at 15 °C in kg/m ³	Uncert. (95%) in kg/m ³	Effective degrees of freedom	Density at 40 °C in kg/m ³	Uncert. (95%) in kg/m ³	Effective degrees of freedom
PTB/DE	999.2334	0.0038	78	992.3512	0.0050	136
MIKES/FI	999.170	0.0927	914	992.282	0.0954	713
BNM/FR	999.234	0.014	98	992.345	0.027	111
OMH/HU	999.2354	0.0043	83	992.3463	0.0063	26
IMGC/IT	999.2348	0.0062	78	992.3316	0.0263	120
JV/NO						
GUM/PL	999.242	0.0137	83	992.341	0.0319	64
CSIR- NML/ZA						
median	999.2344	0.0017		992.3430	0.0098	
mean	999.2249	0.0221		992.3329	0.0210	
weighted	999.2346	0.0025		992.3486	0.0038	
calculated	999.2377	0.0021	36	992.3503	0.0021	36

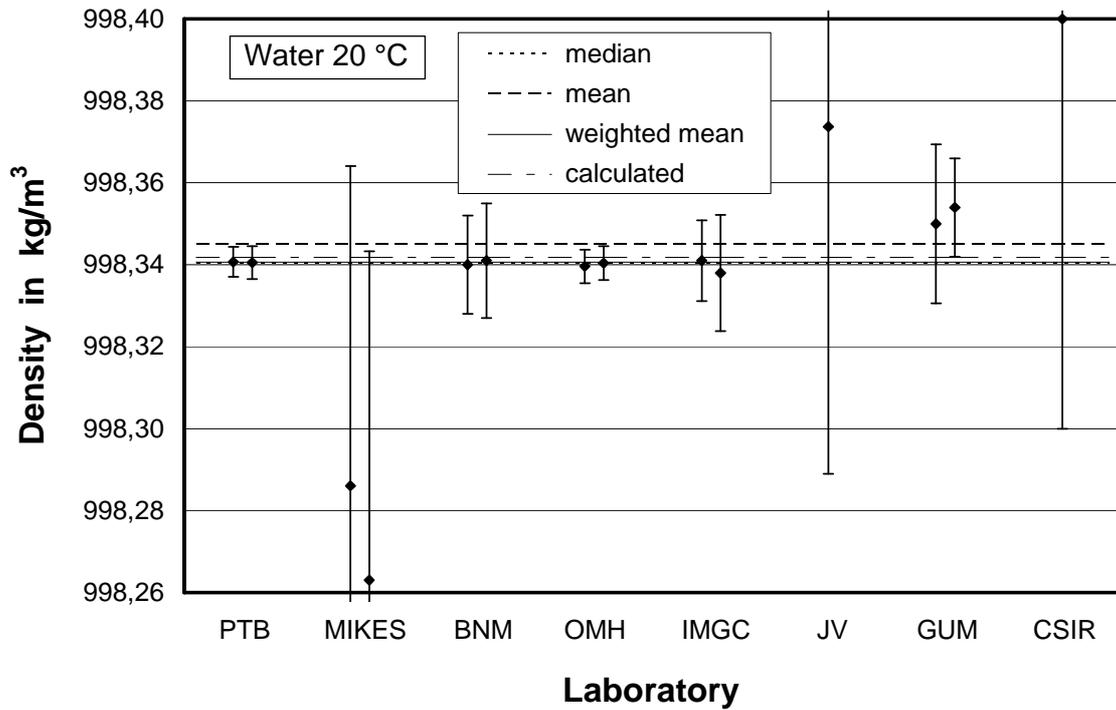


Fig. 4: Reported results of the participants for water at 20 °C. Left point of each laboratory: first measurement at 20 °C. The uncertainties (confidence level 95%) do not include contributions due to drift or inhomogeneity of the liquid. (Median and weighted mean are equal.)

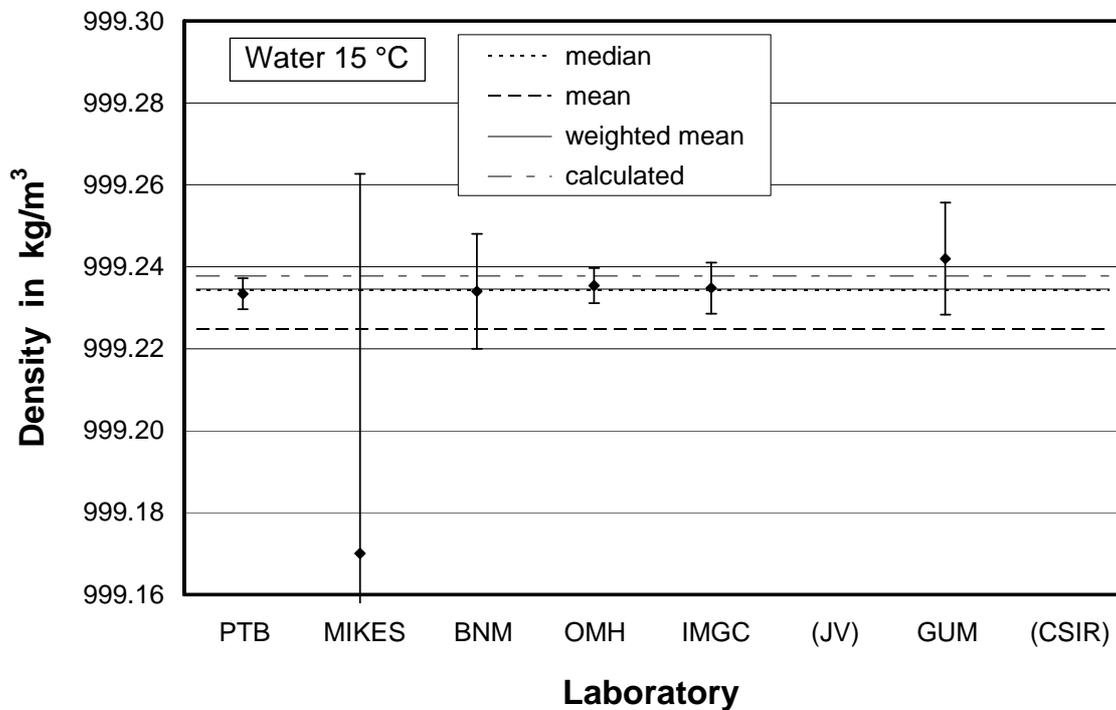


Fig. 5: Reported results of the participants for water at 15 °C. The uncertainties (confidence level 95%) do not include contributions due to drift or inhomogeneity of the liquid. (Median and weighted mean are nearly equal.)

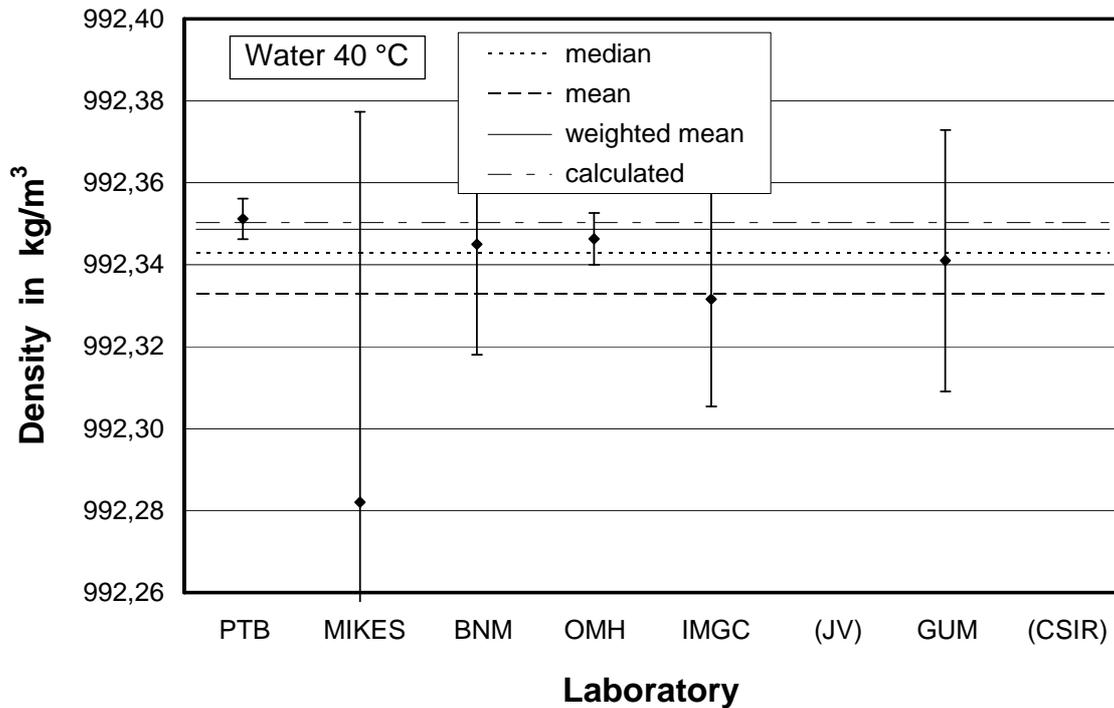


Fig. 6: Reported results of the participants for water at 40 °C. The uncertainties (confidence level 95%) do not include contributions due to drift and inhomogeneity of the liquid.

5.2 Dodecane

With two exceptions, the results for dodecane approximately agree within the combined uncertainties, even without taking drift or inhomogeneity of the liquid into account.

The maximal normalised deviation from the results of most other laboratories is $E_n = 1.6$ for the measurement by CSIR/ZA, which indicates that the CSIR/ZA value is discrepant. Inhomogeneity or drift of the liquid density cannot explain this deviation.

The normalised deviation for the measurement by JV/NO from most other laboratories is $E_n = 1.4$. The density variation observed by the Pilot Laboratory after the sample had been returned cannot explain the deviation of the JV/NO result, since it is in the wrong direction. Neither can inhomogeneity or drift of the liquid density explain this deviation.

Table 11: Reported results of the participants for dodecane at 20 °C. The uncertainties are for a confidence level of 95% and do not include contributions due to drift or inhomogeneity of the liquid.

Institute/ country	Density at 20 °C (1) in kg/m ³	Uncert. (95%) in kg/m ³	Effective degrees of freedom	Density at 20 °C (2) in kg/m ³	Uncert. (95%) in kg/m ³	Effective degrees of freedom
PTB/DE	748.8504	0.0064	75	748.8531	0.0064	75
MIKES/FI	748.929	0.2135	157	748.865	0.2128	157
BNM/FR	748.849	0.018	85	748.861	0.025	130
OMH/HU	748.8457	0.0035	119	748.8458	0.0033	104
IMGC/IT	748.8411	0.0173	106	748.8428	0.0238	80
JV/NO	748.6479	0.1387	143			
GUM/PL	748.853	0.0186	64	748.850	0.0204	57
CSIR- NML/ZA	748.54	0.19	21			
median	748.8474	0.0085		748.8516	0.0123	
mean	748.7945	0.0921		748.8530	0.0071	
weighted	748.8467	0.0029		748.8475	0.0029	

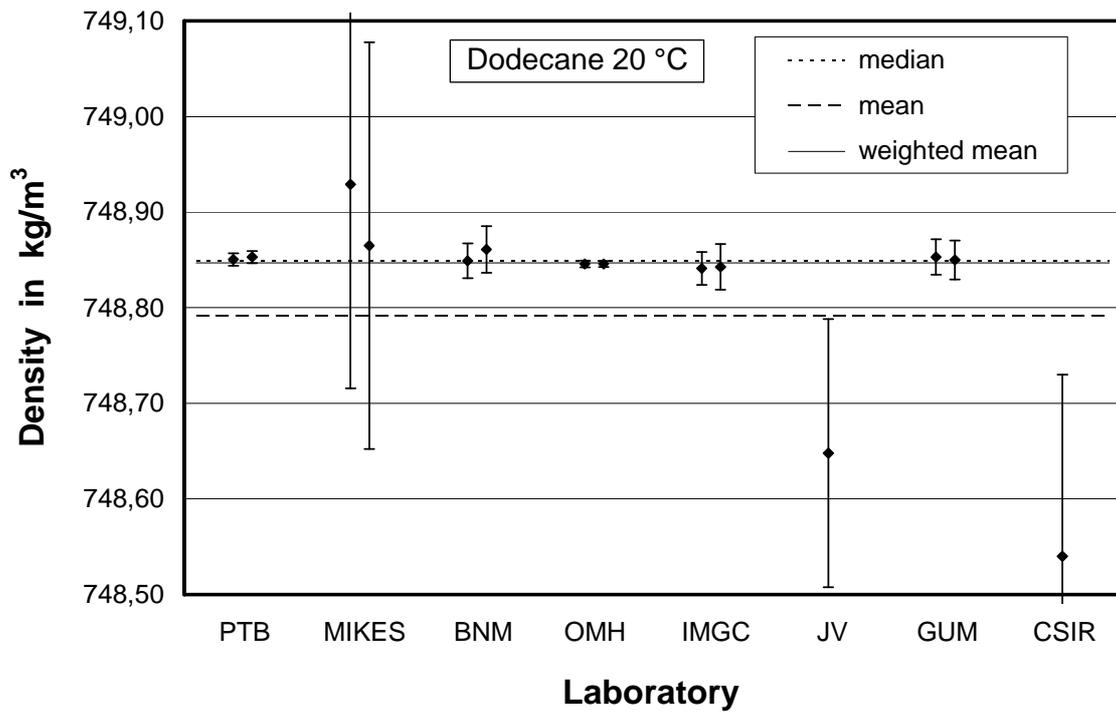


Fig. 7: Results of the participants for dodecane at 20 °C. Left point of each laboratory: first measurement at 20 °C. The uncertainties (confidence level 95%) do not include contributions due to drift or inhomogeneity of the liquid.

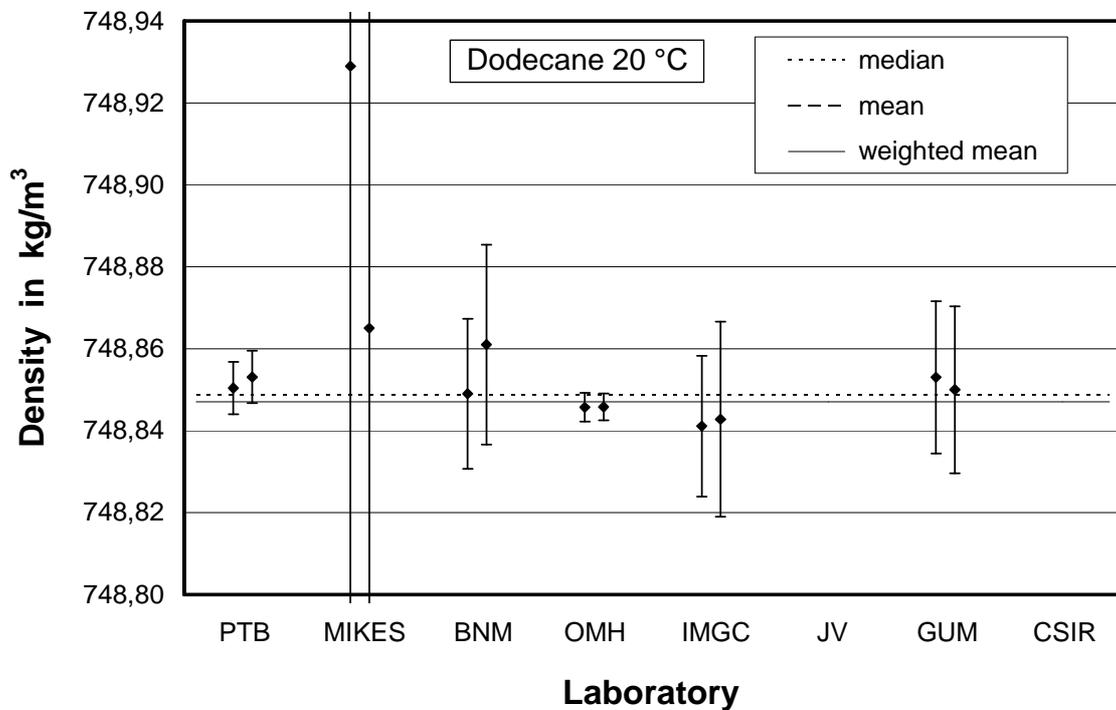


Fig. 7a: Same as Fig. 7, but with expanded scale.

Table 11a: Reported results of the participants for dodecane at 15 °C and 40 °C. The uncertainties are for a confidence level of 95% and do not include contributions due to drift or inhomogeneity of the liquid.

Institute/ country	Density at 15 °C in kg/m ³	Uncert. (95%) in kg/m ³	Effective degrees of freedom	Density at 40 °C in kg/m ³	Uncert. (95%) in kg/m ³	Effective degrees of freedom
PTB/DE	752.4779	0.0065	78	734.3143	0.0078	68
MIKES/FI	752.577	0.2149	163	734.157	0.2125	156
BNM/FR	752.484	0.030	84	734.304	0.040	70
OMH/HU	752.4700	0.0038	161	734.3043	0.0050	36
IMGC/IT	752.4693	0.0228	58	734.2913	0.0272	62
JV/NO						
GUM/PL	752.476	0.0203	63	734.278	0.0469	54
CSIR- NML/ZA						
median	752.4770	0.0119		734.2977	0.0198	
mean	752.4924	0.0341		734.2748	0.0482	
weighted	752.4722	0.0032		734.3065	0.0041	

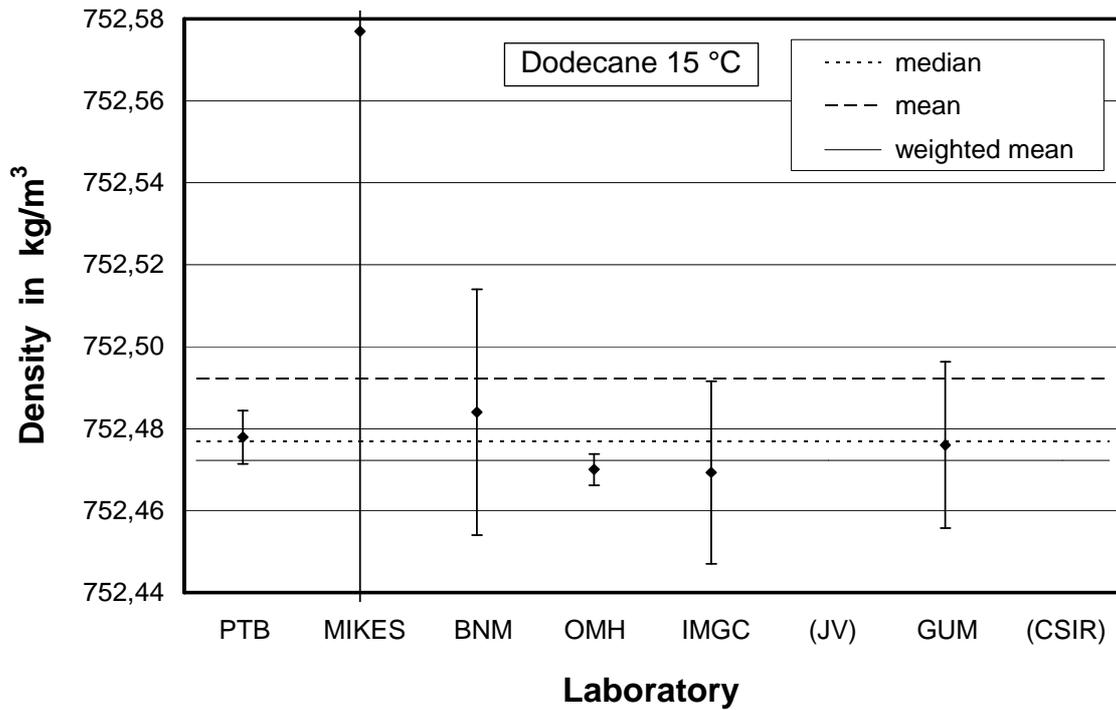


Fig. 8: Results of the participants for dodecane at 15 °C. The uncertainties (confidence level 95%) do not include contributions due to drift or inhomogeneity of the liquid.

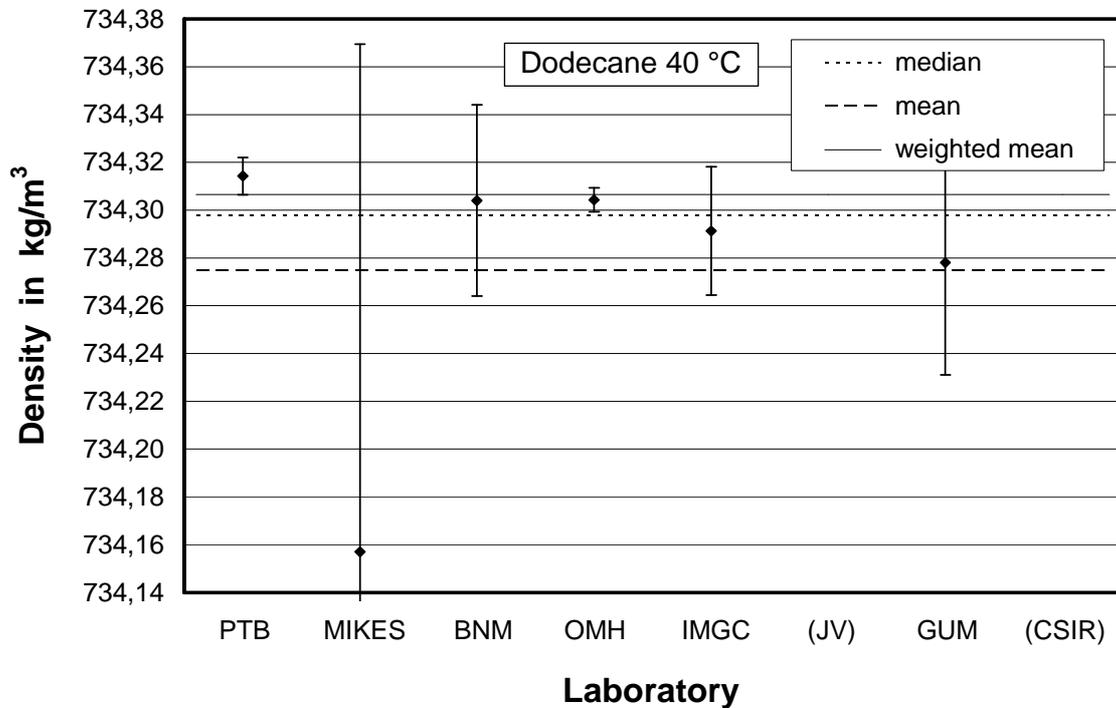


Fig. 9: Results of the participants for dodecane at 40 °C. The uncertainties (confidence level 95%) do not include contributions due to drift and inhomogeneity of the liquid.

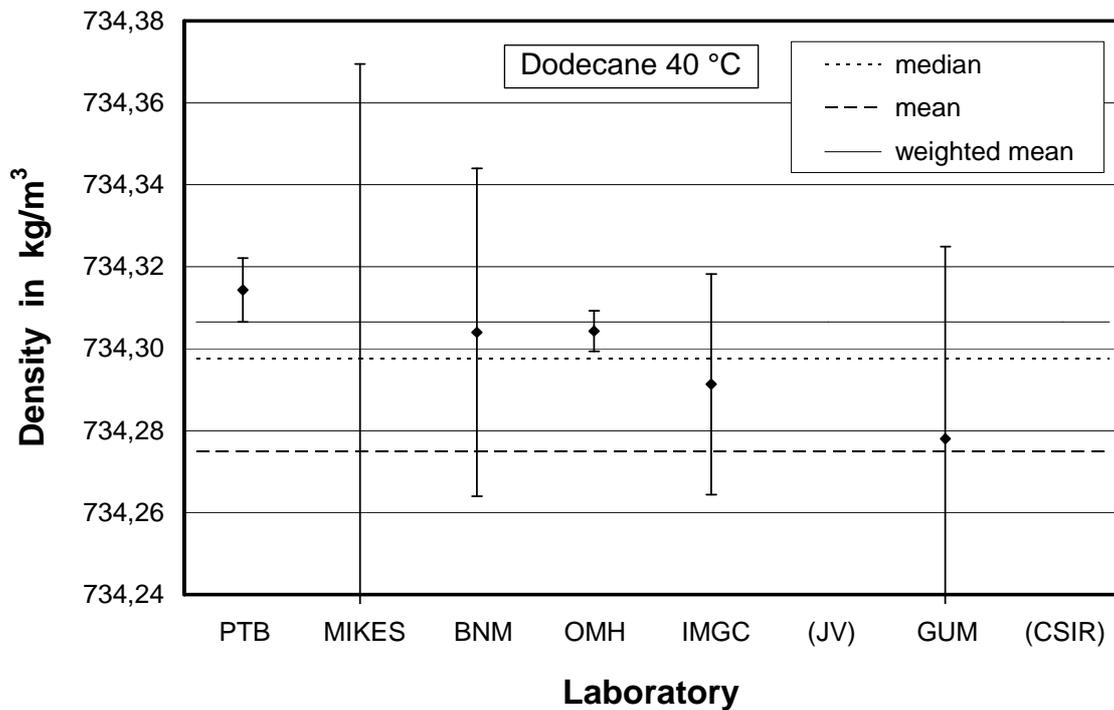


Fig. 9a: Same as Fig. 7, but with expanded scale.

5.3 Viscosity oil VO-1

This liquid posed special problems, since it has a high viscosity and is nearly opaque. The apparatus of IMGC/IT obviously failed to measure this oil, which is probably due to the high viscosity. The results were withdrawn.

The liquid sample of BNM/FR significantly decreased its density during the measurements at BNM/FR. This was confirmed by the density meter measurements at PTB, see chapter 4. The reason for the density variation could not be identified. (High temperature is no explanation since it would increase the density of VO-1 instead of reducing it.) The density change probably occurred after the 15 °C measurement and before the 40 °C measurement. BNM/FR decided to withdraw all results for VO-1. Median, mean value and weighted mean value were therefore calculated without the results of IMGC/IT and BNM/FR.

The maximal normalised deviation from most other laboratories is $E_n = 1.9$ for the measurements by JV/NO and CSIR/ZA, which indicates that the values of JV/NO and CSIR/ZA are discrepant. Inhomogeneity or drift of the liquid density cannot explain this deviation.

The normalised deviation for the first measurement by MIKES/FI at 20 °C from most other laboratories is $E_n = 1.3$.

Table 12: Reported results of the participants for viscosity oil VO-1 at 20 °C. The uncertainties are for a confidence level of 95% and do not include contributions due to drift or inhomogeneity of the liquid. The values are not corrected for the temporal drift of the liquid density. BNM/FR and IMG/IT withdrew their results.

Institute/ country	Density at 20 °C (1) in kg/m ³	Uncert. (95%) in kg/m ³	Effective degrees of freedom	Density at 20 °C (2) in kg/m ³	Uncert. (95%) in kg/m ³	Effective degrees of freedom
PTB/DE	911.4331	0.0057	100	911.4317	0.0058	102
MIKES/FI	911.068	0.2857	137	911.183	0.2836	132
BNM/FR						
OMH/HU	911.4333	0.0076	18	911.4327	0.0071	431
IMG/IT						
JV/NO	911.1728	0.1339	138			
GUM/PL	911.460	0.0411	55	911.456	0.0512	52
CSIR- NML/ZA	911.07	0.19	23			
median	911.3030	0.2442		911.4322	0.0267	
mean	911.2729	0.1547		911.3759	0.1291	
weighted	911.4329	0.0045		911.4322	0.0045	

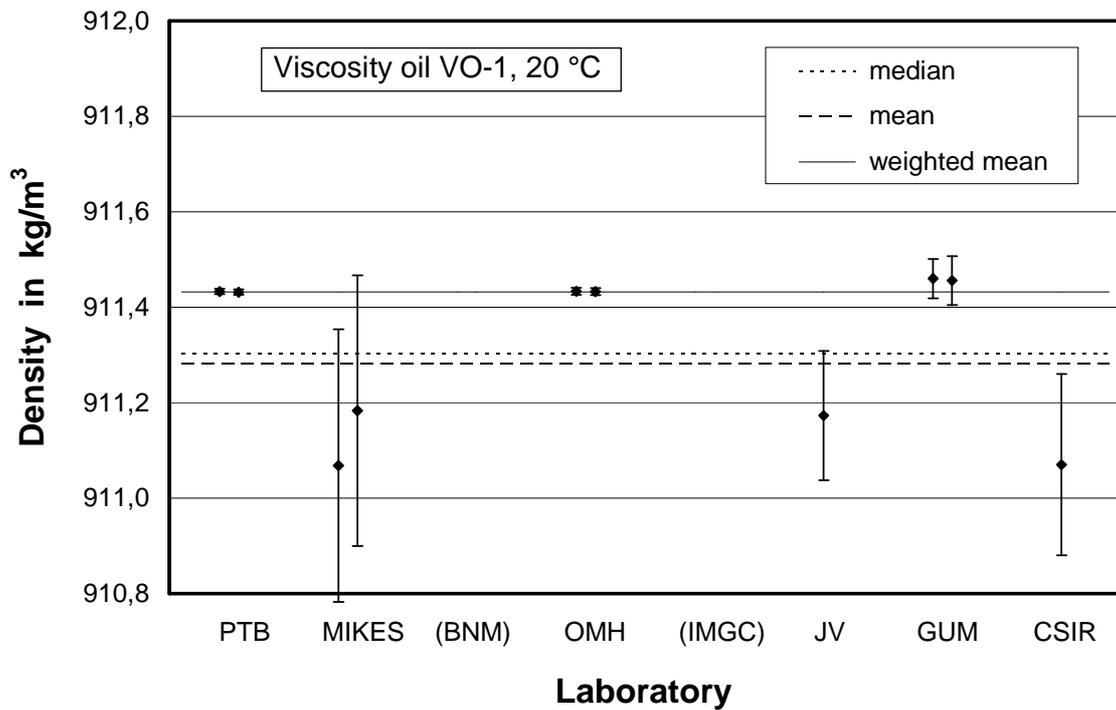


Fig. 10: Results of the participants for viscosity oil VO-1 at 20 °C. Left point of each laboratory: first measurement at 20 °C. The uncertainties (confidence level 95%) do not include contributions due to drift or inhomogeneity of the liquid. The values are not corrected for the temporal drift of the liquid density.

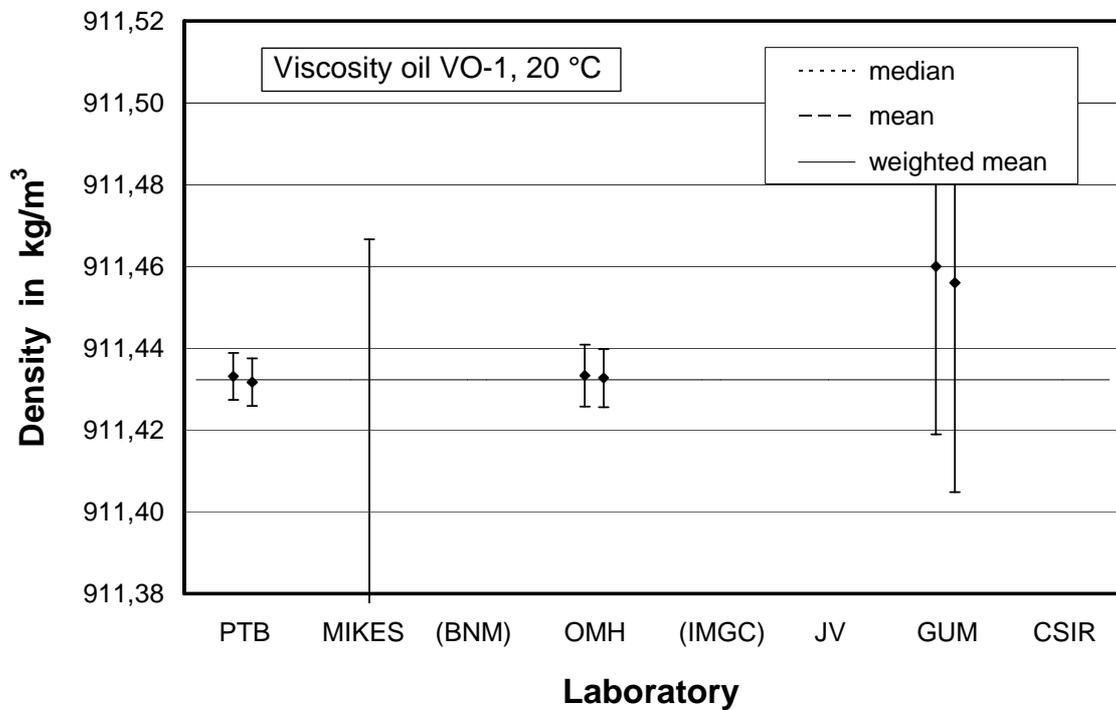


Fig. 10a: Same as Fig. 10, but with expanded scale.

Table 12a: Reported results of the participants for viscosity oil VO-1 at 15 °C and 40 °C. The uncertainties are for a confidence level of 95% and do not include contributions due to drift or inhomogeneity of the liquid. The values are not corrected for the temporal drift of the liquid density. BNM/FR and IMG/IT withdrew their results.

Institute/ country	Density at 15 °C in kg/m ³	Uncert. ($k = 2$) in kg/m ³	Effective degrees of freedom	Density at 40 °C in kg/m ³	Uncert. ($k = 2$) in kg/m ³	Effective degrees of freedom
PTB/DE	914.5011	0.0059	109	899.2304	0.0069	88
MIKES/FI	914.245	0.2873	137	899.196	0.3071	86
BNM/FR						
OMH/HU	914.4973	0.0077	19	899.2337	0.0084	113
IMG/IT						
JV/NO						
GUM/PL	914.597	0.3084	51	898.934	0.4163	53
CSIR- NML/ZA						
median	914.4992	0.1094		899.2132	0.0414	
mean	914.4601	0.1506		899.1485	0.1440	
weighted	914.4996	0.0047		899.2317	0.0053	

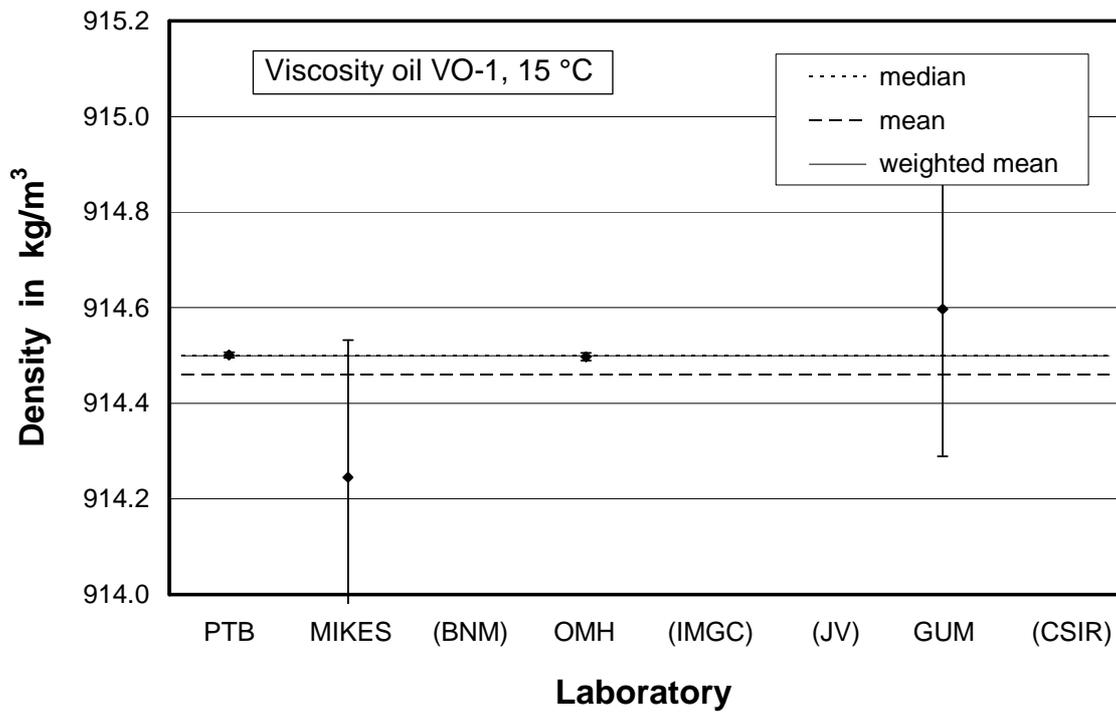


Fig. 11: Results of the participants for viscosity oil VO-1 at 15 °C. The uncertainties (confidence level 95%) do not include contributions due to drift or inhomogeneity of the liquid. The values are not corrected for the temporal drift of the liquid density.

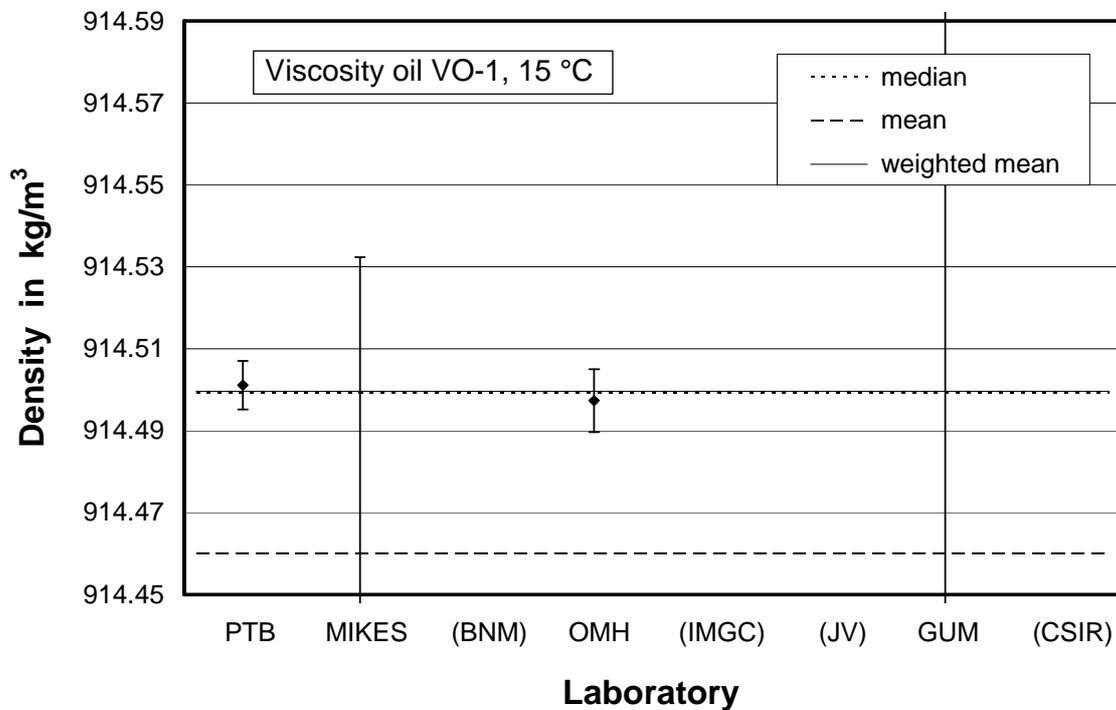


Fig. 11a: Same as Fig. 11, but with expanded scale.

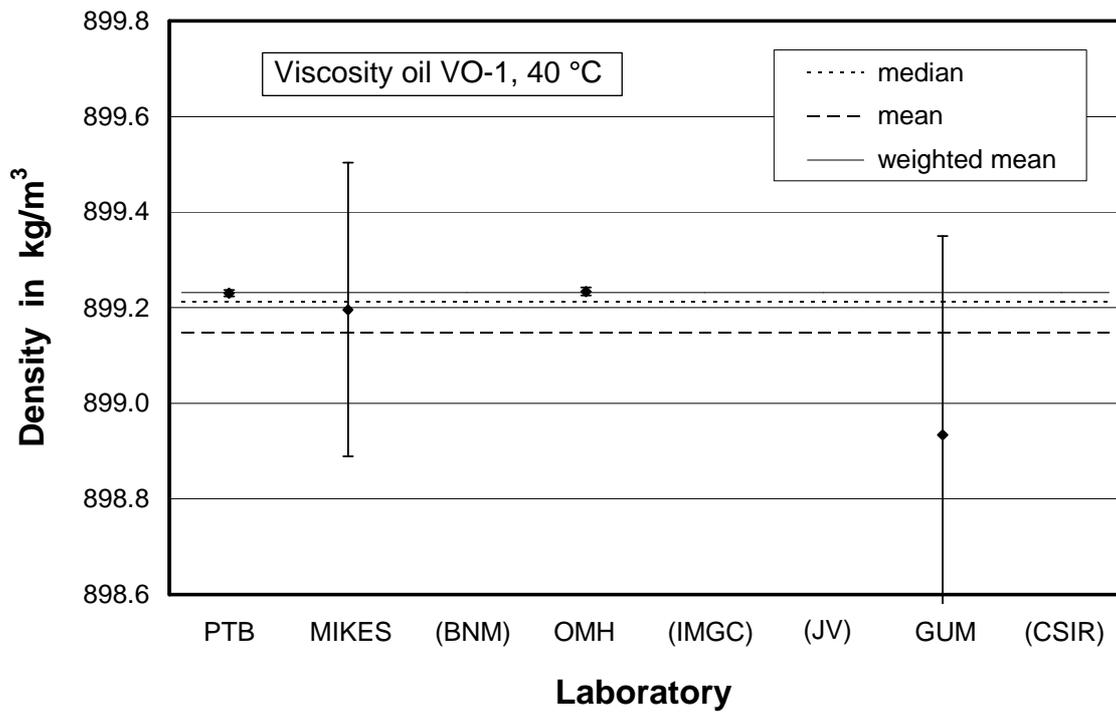


Fig. 12: Results of the participants for viscosity oil VO-1 at 40 °C. The uncertainties (confidence level 95%) do not include contributions due to drift or inhomogeneity of the liquid. The values are not corrected for the temporal drift of the liquid density.

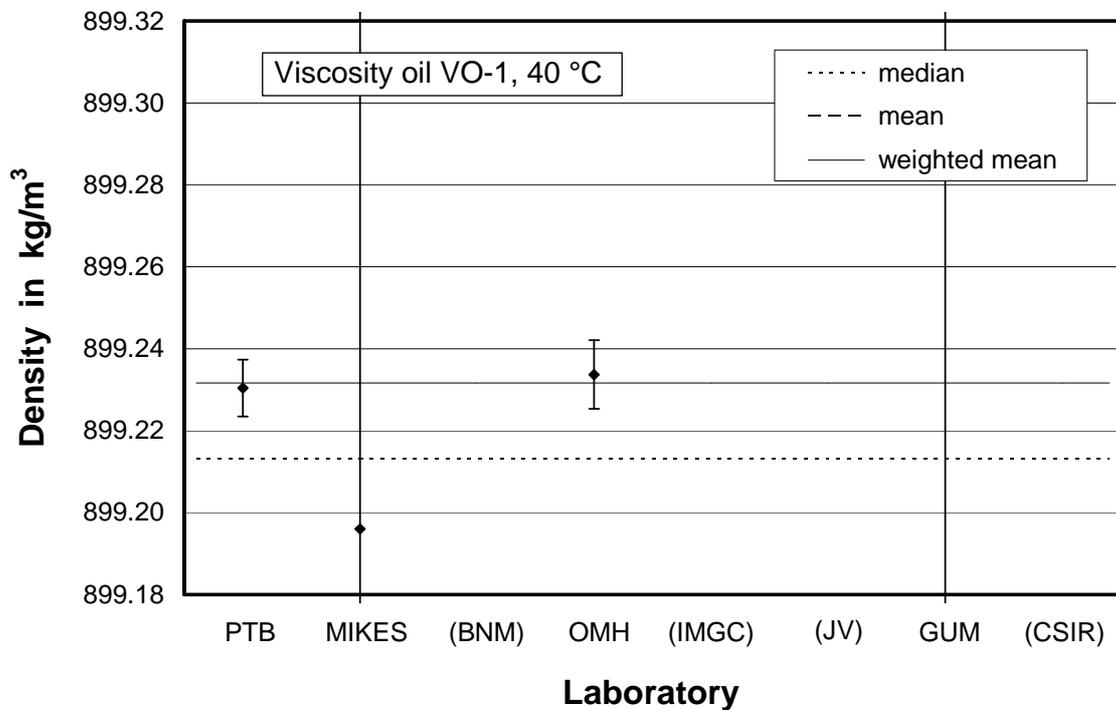


Fig. 12a: Same as Fig. 12, but with expanded scale.

6 Reference values

No link was performed to the subsequent CCM key comparison CCM.D-K2 and, thus, no reference values for this comparison were calculated, because CCM.D-K2 had a different scope and the EUROMET 627 comparison was soon superseded by the EURAMET 1019 comparison.

7 Summary

For this comparison the densities of dodecane, water and an oil of high viscosity were measured at 15 °C, 20 °C and 40 °C. The measurements were carried out at atmospheric pressure by hydrostatic weighing of a solid density standard.

The results generally show good agreement among the participants. Only for the simple Mohr-Westphal balances do the uncertainties seem to be underestimated by the laboratories. Furthermore, the measurement of high-viscosity oil is difficult for some laboratories.

Nevertheless, the five laboratories PTB/DE, BNM/FR, OMH/HU, IMGC/IT and GUM/PL agree with each other for stated uncertainties of 0.05 kg/m³ or less. This satisfies the current needs of customers who wish to calibrate or check liquid density measuring instruments such as oscillation-type density meters.

8 References

- [1] ISO 15212-1: "Oscillation-type density meters - Part 1: Laboratory instruments," Oct. 1998
- [2] "Mutual recognition of national measurement standards and of calibration and measurement certificates issued by national metrology institutes," BIPM, Paris, 14 October 1999
- [3] P. Richard: "Euromet Project no. 339 - Intercomparison of volume standards by hydrostatic weighing - Final report," OFMET, Switzerland, August 2002, 35 pages.

- [4] M. M. Menaché, M. C. Beauverger, M. G. Girard: "Étude de la variation de la masse volumique de l'eau (eau pure et eau de mer) en fonction de la composition isotopique et de la teneur en gaz atmosphériques dissous," Annales Hydrographiques, 1978, vol. 6, pp. 37-76
- [5] G. Girard, M. Menaché: "Variation de la masse volumique de l'eau en fonction de sa composition isotopique," Metrologia, 1971, vol. 7, pp. 83- 87
- [6] M. Tanaka, G. Girard, R. Davis, A. Peuto, N. Bignell, "Recommended table for the density of water between 0 °C and 40 °C based on recent experimental reports," Metrologia, 2001, vol. 38, pp. 301-309
- [7] R. S. Davis: "Report of Density Intercomparisons Undertaken by the Working Group on Density of the CCM," Metrologia, 1990, vol 27, pp. 139-144
- [8] ISO 5024: "Petroleum liquids and liquefied petroleum gases - Measurement - Standard reference conditions," May 1999
- [9] ISO 8973: "Liquefied petroleum gases - Calculation for density and vapour pressure," July 1997

9 Comments of participants

a) Istituto di Metrologia "G. Colonnetti" (IMGC-CNR)

The high viscosity and the dark colour of the VO-1 oil produced some problems during the hydrostatic weighing. The IMGC-CNR failed the density measurements of this oil and decided to withdraw the results. The reason for this negative result was due to a defect in the sphere loading and its suspension device.

The experience with this comparison has suggested improvements that have been taken into account in a new hydrostatic apparatus for liquid density measurements. Its main improvements concern the suspension device, the thermostatic system and a more accurate temperature measurements.

b) Norwegian Metrology & Accreditation Service (JV/NO)

We calculated the density of the liquids at 20 ° C from measuring the buoyancy in liquid and in air of a sinker with nominal volume 10 cm³ suspended in a wire with diameter 0.2 mm.

To calculate the volume of the sinker we measured the buoyancy in distilled water and in air, and used the densities for water given in OIML R49. The density of air was calculated using R.S. Davis' formula, accepted by CIPM.

At first we transferred the results in column 1 in the table to the co-ordinator for Euromet 627.

According to JV's normal procedure, we have here not taken into account the effect of the liquid surface tension on the wire.

Type of liquid	1 No correction for surface tension (JV's normal procedure) kg/m ³	2 Correction for surface tension based on arbitrary estimation of the angle of contact (Randwinkel) kg/m ³	3 Correction for surface tension based on drag force measurements kg/m ³
Water	998.3737 ± 0.0847	998.3737 ± 0.0847	998.3737 ± 0.0847
n-Dodecane	748.8014 ± 0.1403	748.6479 ± 0.1403	748.7635 ± 0.1403
Viscosity oil VO-1	911.3039 ± 0.1354	911.1728 ± 0.1354	911.2660 ± 0.1354

When reading the following sentences in a mail from the co-ordinator: "After checking all available reports, I found a value, that has probably a significant deviation. I ask you to check your report and calculations." we thought we had better try to make corrections for the difference in surface tension for water and the other liquids. As we did not know the angle of contact (Randwinkel) between the liquid surface and the wire, we made an arbitrary estimation of that angle, and got the density values in column 2 of the table, that in this way was corrected for the surface tensions.

After seeing the draft report, we understood that we had overestimated the corrections, and therefore we asked the co-ordinator if he would use the first density values he had received from us in his report.

When that was refused, we measured the difference in drag force from the surface tensions of water and oil, by putting the end of a 0.2 mm wire suspended under the weighing machine just under the surface of the liquids. Based on these

measurements we calculated more accurate corrections for the effect of surface tensions, and now we got the densities in column 3.

After these unambiguous calculations, in detail transferred to the co-ordinator, we hoped that the densities in column 3 could be JV's official results in the final report from Euromet 627.*

c) Central Office of Measures (GUM/PL)

Since the comparison, the reference hydrostatic weighing stand of GUM has been significantly changed. The new 1 kg silicon sphere has been calibrated in PTB, the suspension and support system has been modified and new measuring vessels have been purchased to be deeply immersed in thermostatic bath. To confirm the improvement of measurement capability, GUM has applied to the new EUROMET comparison on liquid density planned for 2005.

*) This is not possible since the meniscus investigations of JV/NO were performed after all results were distributed to the participants.