**Technical Protocol for the**

**17RPT02 rhoLiq Project Consolidation Density Measurement Comparison**

**by Hydrostatic Weighing**

**Comparison of liquid density standards**

Pilot Laboratory: BEV – Bundesamt für Eich-u. Vermessungswesen / Austria

Supported by: PTB - Physikalisch-Technische Bundesanstalt, Bundesallee 100  
38116 Braunschweig / Germany

# Outline

According to EMPIR 17RPT02 RhoLiq project in WP2, task 2.1.2, a "Consolidation Comparison on liquid density measurement" shall be realized. The measurement results of the link laboratories (BEV, PTB) will be corrected according to the degrees of equivalence of EURAMET.M.D-K2 (BEV) and CCM.D-K2 (PTB)

For the purpose of this comparison it is proposed to determine the density of deuterated ultra-pure water (air-saturated), Tetrachloetylene and an oil with a high viscosity (VO EF168) at 2 temperatures (5°C, 20°C). The measurements should be carried out at atmospheric pressure by hydrostatic weighing of a solid density standard.

BEV is the pilot laboratory for the comparison. For the addresses of the participants, see Appendix A. The present document is largely based on the technical protocol of the EURAMET Key Comparison EURAMET.M.D-K2 (1019) [3].

# Purpose of this document

The purpose of this document is to provide the participating laboratories with instructions for the handling of the samples of liquids and to report on the measurement results, the measuring procedure and the apparatus.

It is important that all instructions given in this document are followed. This will ensure that the measurement data are obtained under comparable conditions and presented in the same format. Any deviation from the instructions has to be reported to the pilot laboratory.

# Liquid samples

Three liquids were chosen for the consolidation comparison i.e., deuterated ultra-pure water (air-saturated), Tetrachloretylene (TCE) and an oil with a high viscosity (VO EF168). The necessary amount of the liquids has been prepared by PTB. The deuterated water is a mixture of ultrapure tap water from PTB (Braunschweig/Germany) and of heavy water (D2O) with a concentration of approximately 0.2 vol%. The resulting mixture is air-saturated.

The liquids have already been sent to the laboratories as part of the diagnostic comparison.

Before sending, each liquid was homogenised and applied to pretesting by PTB.

The pretesting of the samples consists of testing the homogeneity and the stability. For this purpose, two 10 ml samples of each liquid and each individual laboratory sample was taken prior sending them to the laboratories.

The homogeneity will be checked by density measurements with a standard oscillation- type densitometer (first 10mL sample). After completion of measurements by all project partners density measurements of the second 10mL sample shall confirm the stability of the samples.

For transportation the liquids were filled into glass bottles of 1 litre volume. The individual bottles are provided with the name of the liquid, the volume, a clear sample identifier and a safety warning. The bottles are numbered. The samples with the deuterated ultra-pure water are labeled with ‘D’.

The total number of packages depends on the amount of liquid the participating laboratory needs.

The packages contain complete lists of the contents with the numbers of all bottles, safety data sheets, weight and size of the whole package, number of separate packages and handling requirements. This information has already been mailed to the participants as part of the diagnostic comparison (A2.1.1).

The packages are provided with a warning: To be opened only by laboratory personnel.

# Preparation of the measurements

The bottles and the seals should be opened only for the measurements. Before opening, check the individual bottles once more for obvious damage or contamination. Any remarkable observations should be reported to the pilot laboratory. Each laboratory should wait for the BEV e-mail announcing the measurements may now be initiated.

It is recommended to degas the water sample to avoid the formation of air bubbles. It is not recommended to degas Tetrachloetylene (TCE) and the high viscosity oil (VO EF168).

In each case, care should be taken not to irreversibly change the density of the liquid,

i.e. the liquid should only be heated up to the lowest temperature necessary and only for a short time interval. The same care is necessary when using vacuum to degas the liquid or to fill it into the apparatus.

# Measurement procedure

It is proposed to use the following sample sequence: Water, Tetrachloetylene and VO EF168. The following target temperatures were chosen for the comparison:

Water: 20°C

Tetrachloetylene (TCE): 5°C, 20°C

High viscosity oil VO EF168): 20°C

Temperatures outside the claimed temperature range are optional.

For each liquid and temperature, at least ten weighing sequences have to be performed.

Approximate values of the isothermal compressibility factors of the liquids are listed in Appendix E together with their uncertainties. These values should be used unless a participant determines the values by experiment.

The mean, minimum and maximum values of the parameters contributing to air density evaluation are to be recorded, e.g. pressure, temperature, relative humidity, and CO2 content (measured or assumed). For the calculation of the air density the CIPM formula (CIPM - 2007) is to be used [1]. Mean, minimum and maximum values of the air density are to be reported.

The measurements shall be performed in January and February 2021 and have to be finished in March 2021 by the latest.

# Reports

The reports on the measurements and the results should be made up using the enclosed Report forms both excel and word. These forms should be filled by participants. The Report Forms should contain a summary for all measurements and may be reported only once if they are same.

The reports have to be delivered to the pilot laboratory in November 2021.

* 1. Measurement results

The following information is to be given for each liquid and target temperature using the format in Report Form 1.

1. Date of arrival of the liquid at the laboratory.
2. Condition of package, seals and bottles.
3. Date of opening the bottles and numbers of bottles used.
4. Preparation of liquid (degassed?).
5. Name of density standard and its immersion depth.
6. Material and diameter of wire (if applicable).
7. Date and time of measurement.
8. Mean density at actual temperature and pressure, actual temperature, actual pressure.
9. Densities and uncertainties at target temperature and pressure (1013.25 hPa) with complete uncertainty budget.
10. Ambient conditions during the measurements of the liquid.
11. Date of taking the sample from the apparatus.
12. Date of shipment of the liquid.
    1. Volume or density standard of the participating laboratory

For the volume or density standard(s) (sinker) used in the comparison, the following information is to be given using the format in Report Form 2.

1. Identification, material, shape and dimensions of sinker.
2. Traceability of mass measurement, date of last calibration.
3. Traceability of volume or density measurement, date of last calibration, method of calibration and reference temperature (ITS-90).
4. Traceability of expansion coefficient, date of last calibration, method of calibration.
5. Traceability of (isothermal) compressibility, date of last calibration, method of calibration.

(Values and uncertainties are to be given in the uncertainty budgets of Report Form 1.)

* 1. Mass standards

For the mass standards (weights) used to calibrate the balance or to substitute the apparent weights of the density standard, the following information is to be given using the format in Report Form 2.

1. Identification and material of weights.
2. Masses of weights and their uncertainties.
3. Traceability of mass values, date of last calibration.
4. Volumes of weights at their reference temperature and uncertainties.
5. Traceability of volume values, date of last calibration, method of determination and reference temperature.
   1. Measuring instruments

For the balance used to determine the densities of the liquid samples, the following information is to be given using the format in Report Form 3.

1. Manufacturer and type of balance.
2. Maximum capacity, electronic range, resolution.
3. Standard deviation, maximum nonlinearity, out-of-centre error.
4. Adjustment: method, uncertainty, frequency and traceability.

For the instruments used for the measurement of air pressure, temperature, humidity and CO2 content, the following information is to be given using the format in Report Form 3.

1. Manufacturer, type.
2. Siting of sensor.
3. Resolution.
4. Frequency of measurement.
5. Calibration uncertainty, date and traceability.

For the instruments used for the measurement of the liquid temperature, the following information is to be given using the format in Report Form 3.

1. Manufacturer and type of sensor.
2. Siting of sensor, frequency of measurement.
3. Manufacturer and type of resistance bridge and standard resistor (if applicable).
4. Resolution of temperature measurement.
5. Calibration uncertainty, date and traceability of thermometer (whole temperature range).
6. Frequency of calibration at one temperature (e. g. triple point of water).
   1. Details of hydrostatic weighing (Report Form 4)

Give a summary of the apparatus with figures or photos and include information about:

1. Thermostat: manufacturer, type, volume, cooling system, temperature regulator.
2. Preparation of wire (if applicable).
3. Evaporation shield.
4. Support of sinker and weight exchange.

Give a summary of the following procedures:

1. Preparation of apparatus.
2. Handling of liquid including degassing.
3. Adjustment of balance.
4. Measurement procedure and weighing sequence.

Give the mathematical model equations for calculating the density of the liquid samples at the target temperature and pressure.

Describe how the standard uncertainties of the individual influence quantities of Report Form 1 in the uncertainty of the liquid density were estimated. If you have determined the cubic expansion or isothermal compressibility of the liquid by experiment, describe the procedure.

Please give references to publications about your apparatus.

* 1. Uncertainty of measurement

Appendix F gives a list of main components of the uncertainty budget. Please add any additional component occurring in your measurements. Do not include a term for a potential long-term drift of the density of the liquid sample.

The uncertainty of the densities is to be given as expanded uncertainty for a confidence level of 95%. This is obtained by combining the individual standard uncertainties obtained from Type A and Type B evaluations. The uncertainties are to be calculated and reported according to „Evaluation of measurement data - Guide to the expression of uncertainty in measurement“ [2].

# Deadline

The reports have to be delivered to the pilot laboratory in November 2021 (M43 of the rhoLiq project).

# Special problems

* 1. Unexpected delays

Due to the tight timetable, it is not possible to wait in case an unexpected delay occurs at a participating laboratory.

# 9 References

[1] A. Picard, R. S. Davis, M. Gläser, K. Fujii: “Revised formula for the density of moist air (CIPM-2007)”, Metrologia, 2008, vol. 45, pp. 149-155.

[2] „Evaluation of measurement data - Guide to the expression of uncertainty in measurement“, JCGM 100:2008.

[3] Christian Buchner: "Technical Protocol for the EURAMET Project 1019"

Appendices

# Participants

|  |  |  |
| --- | --- | --- |
| Laboratory  (country) | Mailing address for the packages | Person responsible  for the comparison |
| IPQ  (Portugal) | Instituto Português da Qualidade Rua António Gião 2  2829-513 CAPARICA  Portugal | Andreia Furtado Tel.: +35 1212948164 Fax: +35 1212948188 e-mail: afurtado@ipq.pt |
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1. **Timetable for the comparison**

|  |  |
| --- | --- |
| May 2018 | Decision on liquids, temperatures and pressure |
| December 2018 /  January 2019 | Purchase of liquids and bottles Confirmation of participation |
| January to March 2019 | Preparation, distribution of samples, homogeneity and stability tests by pilot laboratory (PTB). |
| January/February 2019 | Sending out the forms, Agreement on Technical Protocol, and preparation of the samples |
| Beginning of April 2019 | Delivery of liquids to the participants |
| Jannuary - February 2021 | Measurements by all participants |
| March 2021 | Check measurements at PTB |
| November 2021 | Reports from all participants send to pilot laboratory (BEV) |
| February 2022 | Draft A of comparison report |
| March 2022 | Draft B of comparison report |
| April 2022 | Final report |

# E-mail: Progress report

To monitor the progress of the comparison, we ask to kindly send a report by e-mail to

Lukas Prochaska

e-mail: lukas.prochaska@bev.gv.at

Bundesamt für Eich-u. Vermessungswesen (BEV) Arltgasse 35

1160 Wien

AUSTRIA

When the measurements are completed the results should be sent to pilot laboratory. This report should contain the following information:

Participating laboratory Contact person Telephone

and a text like this:

EMPIR 17RPT02RhoLiq Project

The measurements were completed on (date).

[The liquids were shipped on (date) through the forwarding agency xx.] [The results were sent to the Pilot Laboratory on (date).]

Remarks: Date

# Physical constants of the liquids

Uncertainties are standard uncertainties (*k* = 1) with degrees of freedom = 50.

Cubic thermal expansion

|  |  |  |
| --- | --- | --- |
| Liquid | Cubic thermal expansion in kg/(m3 K) | Uncertainty  (*k* = 1) in kg/(m3 K) |
| Water | 0.21 | 0.02 |
| TCE | 1.66 | 0.05 |
| VO EF168 | 0.60 | 0.05 |

Isothermal compressibility

|  |  |  |
| --- | --- | --- |
| Liquid | Isothermal compressibility in 10-11/Pa | Uncertainty (*k* = 1) in 10-11/Pa |
| Water at 20 °C | 46 | 2 |
| TCE  at 5 °C  at 20 °C | 65 73 | 10 5 |
| VO EF168 at 20 °C | 68 | 5 |

Nominal surface tension and density values

(Can be used to estimate the mass of the meniscus.)

|  |  |  |
| --- | --- | --- |
| Liquid | Nominal surface tension in mN/m | Nominal density  in kg/m3 |
| Water at 20 °C | 73 | 998 |
| TCE  at 5 °C  at 20 °C | 34 32 | 1648 1623 |
| VO EF168 at 20 °C | 31 | 846 |

# Main components of uncertainty

The uncertainties of the following components can be taken into consideration for the calculation of the uncertainty of the liquid density. These uncertainty contributions are recommended to be taken into account. If a partner has a more elegant and easier access, it can be used. In any case, the nature of the uncertainty contributions listed below should be considered.

If you have additional uncertainty components, please add them in Report Form 1.

Mass of sinker (volume or density standard)

Uncertainty contribution has to be taken into consideration. See also Report Form 2.

Volume of sinker at its reference temperature t0

Uncertainty contribution has to be taken into consideration. See also Report Form 2.

Thermal expansion of sinker volume, V(t) - V(t0)

Uncertainty contribution has to be taken into consideration. See also Report Form 2 and Report Form 4.

Contains a (negligible) contribution due to the uncertainty of the temperature. Please give the equation for the volume expansion in Report Form 4.

(Isothermal) compressibility of sinker

Only important if a hollow sinker is used for measurements.

Mass of weights (mass standards)

Uncertainty contribution has to be taken into consideration. See also Report Form 2.

Volume of weights

Uncertainty contribution is usually small. See also Report Form 2.

Meniscus mass difference

Uncertainty contribution has to be taken into consideration if the sinker is weighed via a wire.

The meniscus during weighing with sinker usually differs from the meniscus during weighing without sinker, due to elongation of the wire or a rise of the liquid surface level. There are other ways to tackle the influence of the meniscus. One of these methods is the usage of a strong correlation between weighing of the sinker and weighing of the calibration weights (reproducibility of the meniscus).

An uncertainty budget should report a reasonable value for this influence. In the subsequent comparisons (consolidation and robustness) uncertainty budgets without that quantity will not be accepted!

Temperature of liquid at sinker

Uncertainty contribution has to be taken into consideration.

This must contain the uncertainty of the temperature measurement using the thermometer and an estimate of the (uncertainty of the) temperature difference between thermometer and sinker.

Cubic thermal expansion of liquid

Uncertainty contribution has to be taken into consideration. The values of Appendix E can be used.

Isothermal compressibility of liquid

The values of Appendix E can be used.

Calibration, nonlinearity and out-of-centre error of balance Uncertainty contribution has to be taken into consideration. Particularly important if no substituted weight is used.

See also Report Form 3.

Density of air

Uncertainty contribution has to be taken into consideration.

This contains uncertainties of pressure, temperature, humidity and carbon dioxide. If the carbon dioxide content is not measured, use the value 0,04% with an uncertainty of 0,02% (rectangular probability distribution). For the CIPM equation of the air density, a relative uncertainty of 0,0001 (rectangular) should be used. Add uncertainty contributions due to gradients in temperature etc.

See also Report Form 3.

Pressure in liquid at sinker

The density of the liquid has to be given for 1013,25 hPa.

Height difference of weights and sinker

The weight (gravitational force) of an object depends on the height due to the gradient in gravitational acceleration.

Gradient of gravitational acceleration

Necessary only for highest accuracy (relative uncertainty less than 3·10-6). If unknown, use a gradient of 0,3·10-6/m with an uncertainty of 0,1·10-6/m (rectangular).

Mean density and experimental standard deviation

Type A uncertainty, please give the experimental standard deviation of the mean.