**Technical Protocol for the**

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

**by**

**Oscillating-type density Meters**

**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 WP3 task A3.1.2, a "Consolidation Comparison on liquid density measurement" shall be realized. The reference values for the comparison liquids will be determined by the hydrostatic method. 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 using an oscillation-type density meter.

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 CCM Key Comparison CCM.D-K5 [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), Tetrachloetylene (TCE) and an oil with a high viscosity (VO EF168). The necessary amount of the liquids have 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 5x10 mL glass vials.

The individual vials are provided with the name of the liquid, the volume, and a safety warning.

Each laboratory has received 5 samples of each liquid. The package contains a list of the content with the numbers of all bottles and safety data sheets.

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

# Preparation of the measurements

The vials 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.

Each liquid sample should be handled according to the regulations of the laboratory.

Do not degas the samples.

Anyway, act with caution in order to prevent changing the density irreversibly.

# Measurement procedure

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.

Each participating laboratory shall give a statistically relevant number of measurements for each temperature (at least 5).

Each participating laboratory is free to choose the temperature sequence according to the internal procedures.

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 February and March 2021 and have to be finished in April 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.

# Measurement results

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

1. Condition of package, seals and bottles (Pre-Measurement Comments).
2. Date of opening the bottles and numbers of bottles used.
3. Preparation of liquid (Pre-Measurement-Comments).
4. Density meter type (being used for the comparison)
5. Date and time of measurement.
6. Mean density at actual temperature and pressure, actual temperature, actual pressure.
7. Densities and uncertainties at target temperature and pressure (1013 hPa) with complete uncertainty budget.
8. Ambient conditions during the measurements of the liquid.
9. Any post measurement comments if necessary

# Detail information about the national density standard

Use the format in **Report Form 2.**

1. What is your national reference in density?
2. Principle of the reference apparatus
3. To which primary standard is the density traceable? In mass:
4. To which institute is it traceable?
5. To which primary standard is the density traceable? In volume:
6. To which institute is it traceable?
7. Give a short description of the hierarchic scheme in density at your institute

# Detailed information about the density meter used

Use the format in **Report Form 2**.

1. Density meter type (being used for the comparison),
2. Readability,
3. Accuracy,
4. Repeatability,
5. Measuring range,
6. Calibration interval,
7. Internal adjustments of the density meter,
8. Used reference materials for the adjustment
   1. How often?
   2. With water?
   3. With air?
   4. With other reference materials (which one)?
   5. At which temperatures?
9. How do you validate the device, that means how do you check / monitor the measuring capability?
10. How do you detect e.g. contamination of the tube?
11. According to your quality system: How do you document these adjustments or checks?
12. Give a short description of these tests (especially [maximum](file:///\\rz0-fil-04\eichwesen$\Documents%20and%20Settings\buchnerc\Local%20Settings\Temporary%20Internet%20Files\Schl・selvergleich%20Liquid%20EURAMET%201019\ende%3flp=ende&p=DOKJAA&search=maximum&trestr=0x2001) [permissible](file:///\\rz0-fil-04\eichwesen$\Documents%20and%20Settings\buchnerc\Local%20Settings\Temporary%20Internet%20Files\Schl・selvergleich%20Liquid%20EURAMET%201019\ende%3flp=ende&p=DOKJAA&search=permissible&trestr=0x2001) [errors](file:///\\rz0-fil-04\eichwesen$\Documents%20and%20Settings\buchnerc\Local%20Settings\Temporary%20Internet%20Files\Schl・selvergleich%20Liquid%20EURAMET%201019\ende%3flp=ende&p=DOKJAA&search=errors&trestr=0x2001) of these tests)
13. Describe the procedures in the case of deviations from normal conditions (e.g. one of the tests is outside a limit)
14. Do you perform calibration of your density meter?
    1. in density?
    2. in temperature?
    3. in viscosity?
    4. How often?
    5. How?
15. According to your quality system: give a short description of these calibrations. How do you document these measurements?
16. How do you consider the results of these calibrations?
17. Do you consider any other calibrations factors to your final density results? Which one?

# Detail information about the measurements with the density meter

Use the format in **Report Form 2**.

1. Describe the storage conditions of liquid samples according to your quality system.
2. How do you prepare the liquid samples for the measurement?
3. How do you insert the liquid samples into the unit. What amount do you use?
4. Describe your measurement procedure.
5. Describe your cleaning procedure of the unit between the measurement series.
6. Describe your cleaning procedure of the unit after the measurement series.

Give the mathematical equations (model) 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 by participant. Please give references to publications about your apparatus if existing.

# Uncertainty of measurement

Appendix F gives a list of main components of the uncertainty budget. Please add any additional uncertainty component (due to e.g., the measurement principle, calibration correction, viscosity correction, resolution (display accuracy) etc.) 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 density is to be given as expanded uncertainty U95 for a confidence level of 95%. This is obtained by combining the individual standard uncertainties obtained from Type A and Type B evaluations. The uncertainty evaluation should include the list of all influence quantities, the values and the standard uncertainties, together with their degrees of freedom and the combined standard uncertainty, as well as the effective degrees of freedom. 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] Markus Schiebl: "Technical Protocol for the CCM.D-K5 Project"

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 |
| BEV-PTP  (Austria) | Bundesamt für Eich- und Vermessungswesen Arltgasse 35 A-1160 Vienna Austria | Lukas Prochaska Tel.: +43 1 21110 826363 e-mail:  lukas.prochaska@bev.gv.at |
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| INM-MD | I.P. Institutul Naţional de  Metrologie  Str. Eugen Coca nr. 28, mun. Chişinău MD2064, Republic of Moldova | Ana Ciubara  Anatolii Bescupschii  e-mail: anatolii.bescupschii@inm.gov.md ana.curdov@inm.gov.md |
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| UME  (Turkey) | Ulusal Metroloji Enstitüsü  P.K. 54, 41470, Gebze – Kocaeli  Turkey | Gökce S. Sariyerli  Ümit Y. Akcadag  Tel.: + 90 (262) 679 50 00  Fax: + 90 (262) 679 50 01  e-mail:  gokce.sariyerli@tubitak.gov.tr  umit.akcadag@tubitak.gov.tr |
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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 |
| Februry - March 2021 | Measurements by all participants |
| April 2021 | Check measurements at PTB |
| May 2021 | Reports from all participants send to pilot laboratory (BEV) |
| June 2021 | Draft A of comparison report |
| July/August 2021 | Draft B of comparison report |
| August/September 2021 | Final report |

# E-mail: Progress report

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

Markus Schiebl

e-mail: markus.schiebl@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 |

# 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.

Mean density and experimental standard deviation

Type A uncertainty, Please give the experimental standard deviation of the mean, see "Guide to the Expression of Uncertainty in Measurement," chapter 4.2.3.

Temperature of liquid

Uncertainty contribution has to be taken into consideration.

This shall contain the uncertainty of the temperature.

Cubic thermal expansion of liquid

The density of the liquid has to be given for the desired temperatures.

The values of Appendix E can be used.

Pressure in liquid

Uncertainty contribution has to be taken into consideration.

This shall contain the uncertainty of the pressure measurement.

Isothermal compressibility of liquid

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

The values of Appendix E can be used.