Technical Protocol for the key comparison EURAMET.M.D-K5

Comparison on density determination of liquid samples using oscillation-type density meters

Pilot Laboratory: BEV- Bundesamt für Eich- und Vermessungswesen
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(Lukas Prochaska)

Supported by
PTB, Germany

1 Outline

The aim of the key comparison EURAMET.M.D-K5 "Comparison on density determination of liquid samples using oscillation-type density meters" is to compare the results of the density determinations of liquid samples by oscillation-type density meters of the participating laboratories.

Density measurements of liquids are mainly performed by laboratories to provide a means of calibrating or checking liquid density measuring instruments such as oscillation-type density meters.

The BEV is the Pilot Laboratory for the comparison supported by the PTB, (Germany). The comparison is a EURAMET key comparison according to the Mutual Recognition Arrangement [1]. For the addresses of the participants, see Appendix A.

This comparison is carried out simultaneously with CCM.D-K5 "Comparison on density determination of liquid samples using oscillation-type density meters". Accordingly, no link between this key comparison and CCM.D-K5 has to be established. Consequently this technical protocol corresponds to the CCM.D-K5 technical protocol in many sections except for the list of participants and the total amount of the liquids.

For the comparison samples of dodecane, perfluoro-compound $C_{10}HF_{22}N$ (Fluorinert FC-40), and of oil with a high viscosity will be measured. The temperature range is from 15 °C to 40 °C. The measurements should be carried out at atmospheric pressure by using a digital density meter.

The reference values for the comparison liquids will be calculated with Cox formalism [2] using density values determined by the hydrostatic method at BEV and PTB. The degree of equivalence (D_i) and the normalized error (E_n) will be used to evaluate the results of the participants.

During the May 2016 meeting of the EURAMET Working Group on Density, it was agreed that this comparison should be conducted. Draft A of the Report should be distributed until September 2022 and Draft B of the report should be available by November 2022 (for the timetable, see Appendix B).

There will be 6 participants including the pilot laboratory.

2 Purpose of this document

The purpose of this document is to provide the participating laboratories with instructions for the handling of the liquids and to report on the measurement results, the measuring procedure and the measuring device. It is important that all instructions given in this document be followed. This will ensure that the measurement data are obtained under comparable conditions and are presented in the same format. Any deviation from the instructions has to be reported to the Pilot Laboratory.

3 Liquid samples

For the comparison, a volume of at least 2 litres of dodecane, FC-40 and of an oil with a viscosity of approximately 170 mm^2/s (at 20 C) will be prepared or purchased by the pilot laboratory.

Before sending, each liquid will be homogenised and filled into 20 millilitre transport bottles, (9 for FC-40 and the viscosity oil; 21 for dodecane). Three samples of each liquid (the first, the middle, and the last according to the order of filling) will be used for monitoring purposes by measuring the density at 20°C with an oscillation-type density meter (DMA 5000). This is performed by the pilot laboratory in order to assess inhomogeneity-caused deviations among the density values determined by the participants. Additionally, the density of one sample of each of the three liquids will be measured periodically by the pilot laboratory to evaluate the stability of the liquid. Thus, a total of 30 bottles will be prepared.

4 Transportation

For transportation, the liquids will be filled into glass bottles of 20 millilitre volume. The individual bottles will be provided with the name of the liquid, the volume, and a safety warning. The bottles will be numbered and separately put into cardboard boxes and packed in a package for shipping.

Each participant will receive 3 samples of dodecane and one sample each of FC-40 and the viscosity oil. The package will contain a list of the content with the numbers of all bottles, safety data sheets, a form to inform the pilot laboratory (see Appendix C), weight and size of the whole package, number of separate boxes and handling requirements. The date of shipment will be mailed to the participants.

The liquids will be transported unaccompanied by courier service. The package will be provided with a warning: "*To be opened only by laboratory personnel*."

The participants are responsible for completing their local customs formalities.

After delivery, the participating laboratories must inform the pilot institute without any delay giving details of the state of the packages and their contents by completing the form contained in the package and sending it back to the pilot laboratory by fax or e-mail (pdf). The template will also be sent in parallel by e-mail.

5 Preparation of the measurements

After receiving the samples, each participant has to start the measurements as soon as possible, but any regulations of the participating laboratory (e.g. handling regulations of liquid samples according to the quality systems of the laboratory) have to be followed.

The bottles and the seals should be opened only for the measurements. Before opening, please check the individual bottles once more for obvious damage or contamination.

Any remarkable observations should be reported.

Each liquid sample should be handled according to the regulations of the laboratory. These handling regulations shall be reported.

Do not degas the samples.

Act with caution in order to prevent changing the density irreversibly.

6 Measurement procedure

The following target temperatures were chosen for the comparison:

Dodecane: 15 °C, 20 °C, 40 °C,
FC-40: 20 °C
Viscosity oil: 20 °C.

The participating laboratories have to make measurements at each temperature.

For each liquid and temperature, a series of measurements sequences have to be performed. Afterward, the liquids can be disposed of.

Values of the cubic expansion coefficients and isothermal compressibility of the liquids are listed in Appendix E together with their uncertainties. These values should be used as necessary.

Mean ambient conditions (pressure and temperature) during the measurements must be reported. If required for the evaluation of your measurements, the calculation of the air density must be based on the CIPM formula (CIPM - 2007) [3].

Do not send the samples or bottles back to the pilot laboratory.

Each participant must start the measurements within 14 days of delivery.
Additionally, the pilot laboratory must be informed of completion of the measurement at the participant.

7 Reports

The reports on the measurements and the results should be made using the enclosed report forms 1 and 2. The report form 1 is an MS Excel sheet and report form 2 is an MS Word document. For each liquid and temperature one Excel sheet of report form 1 has to be completed. The report form 2 should contain a summary for all measurements, and may be reported only once if they are no differences in the procedures.

7.1 Measurement results

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

a) Date of arrival of the liquid.
b) Condition of package, seals and bottles (Pre-Measurement Comments).
c) Date of opening the bottles and numbers of bottles used.
d) Preparation of liquid (Pre-Measurement-Comments).
e) Density meter type (being used for the comparison)
f) Date and time of measurement.
g) Mean density at actual temperature and pressure, actual temperature, actual pressure.
h) Densities and uncertainties at target temperature and pressure (1013.25 hPa) with complete uncertainty budget.
i) Ambient conditions during the measurements of the liquid.
j) Any post measurement comments if necessary

7.2 Detail information about the national density standard

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

a) What is your national reference in density?
b) Principle of the reference apparatus
c) To which primary standard is the density traceable? In mass:
d) To which institute is it traceable?
e) To which primary standard is the density traceable? In volume:
f) To which institute is it traceable?
g) Give a short description of the hierarchic scheme in density at your institute

7.3 Detailed information about the density meter used

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

a) Density meter type (being used for the comparison),
b) Readability,
c) Accuracy,
d) Repeatability,
e) Measuring range,
f) Calibration interval,
g) Internal adjustments of the density meter,
h) Used reference materials for the adjustment

   a. How often?
   b. With water?
   c. With air?
   d. With other reference materials (which one)?
   e. At which temperatures?

i) How do you validate the device, that means how do you check / monitor the measuring capability?
j) How do you detect e.g. contamination of the tube?
k) According to your quality system: How do you document these adjustments or checks?
l) Give a short description of these tests (especially maximum permissible errors of these tests)
m) Describe the procedures in the case of deviations from normal conditions (e.g. one of the tests is outside a limit)
n) Do you perform calibration of your density meter?
   a. in density?
   b. in temperature?
   c. in viscosity?
   d. How often?
   e. How?
o) According to your quality system: give a short description of these calibrations. How do you document these measurements?
p) How do you consider the results of these calibrations?
q) Do you consider any other calibrations factors to your final density results? Which one?

7.4 Detail information about the measurements with the density meter

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

a) Describe the storage conditions of liquid samples according to your quality system.
b) How do you prepare the liquid samples for the measurement?
c) How do you insert the liquid samples into the unit. What amount do you use?
d) Describe your measurement procedure.
e) Describe your cleaning procedure of the unit between the measurement series.
f) 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.

7.5 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 U_{95} 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 ISO "Guide to the Expression of Uncertainty in Measurement" [4].

7.6 Deadline

The reports must be sent to the pilot laboratory by e-mail as soon as possible and **six weeks** after the measurements are completed at the latest. The exact deadline (for all participants the same) will be fixed by the pilot institute after sending the liquids and receiving the reports of delivery. A result is not considered to be complete if no associated uncertainty supported by a complete uncertainty budget is given. The results are confidential until Report Draft A will be distributed. Draft A is confidential to the participants of the comparison.

8. Special problems

8.1 Failure of travelling standard

If a liquid sample is spoiled or lost during transportation, a new sample can be sent as long as enough liquid is available at the pilot laboratory.

8.2 Late entry of a participant

Due to the tight timetable, it is not possible for an additional participant to join after the samples were distributed.

9 References

[1] "Mutual recognition of national measurement standards and of calibration and measurement certificates issued by national metrology institutes," BIPM, Paris, 14 October 1999
[2] Cox, Metrologia 2002, **39**, 589-595
[3] A. Picard, R. S. Davis, M. Gläser, K. Fujii: “Revised formula for the density of moist air (CIPM-2007)”, Metrologia, 2008, **45**, 149-155.
[4] "Guide to the Expression of Uncertainty in Measurement," International Organization for Standardization (ISO), 1995.
[5] W. M. Haynes, David R. Lide, Thomas J. Bruno, “CRC Handbook of Chemistry and Physics: A Ready-Reference Book of Chemical and Physical Data (CRC Handbook of Chemistry & Physics)”, CRC Press; 95 edition (June 4, 2014).
[6] C. Buchner et al., “Final report on EURAMET key comparison EURAMET.M.D-K2: Comparison of liquid density standards”, Metrologia, 52, 07015.
[7] H. Fehlauer, H. Wolf, “Compressibility measurements using an oscillation-type density meter”, Measurement Science and Technology, 17 (2006), 2593-2596
[8] NIST Chemistry WebBook, http://webbook.nist.gov/chemistry/
[9] T. Brunet et al, “Resonant ultrasonic attenuation in emulsions”, Journal of Physics: Conference Series 457 (2013) 012006

Appendices

A. Participants

Laboratory (country)	Mailing address for the packages	Person responsible for the comparison
Austria: BEV	Bundesamt für Eich- und Vermessungswesen Arltgasse 35 1160 Vienna Austria	Lukas Prochaska Tel.: +43 1 21110 826363 E-mail: lukas.prochaska@bev.gv.at
Germany: PTB	Physikalisch- Technische Bundesanstalt Bundesallee 100 38116 Braunschweig Germany	Jürgen Rauch Tel.: +49 531 592-3141 Fax: +49 531 592-3305 e-mail: juergen.rauch@ptb.de
Switzerland: METAS	Eidgenössisches Institut für Metrologie METAS Lindenweg 50 3003 Bern-Wabern, Schweiz	Gabriel Guerry, M. Sc. FH Tel.: +41 58 387 09 39 Fax: +41 58 387 02 10 E-Mail: Gabriel.Guerry@metas.ch
Croatia: DZM	State Office for Metrology (DZM) Laboratory for Mass and Density Ibrišimovićeva 11 10000 Zagreb Croatia	Maja Zebić Avdičević Tel.: +385 (0)1 5635293 Mobile: +385 (0) 99 3907 848 E-mail: maja.zebicavdicevic@dzm.hr
Romania: INM	Institutul National de Metrologie Sos. Vitan-Bârzesti, nr. 11 042 122, Bucuresti Romania	Florin Benga Tel.: E-Mail: florin.benga@inm.ro
Denmark: FORCE Technology	FORCE Technology Park Allé 345. 2605 Broendby Denmark	Lise-Lotte Grue Tel.: +45 43267109 Fax.: +45 43267010 E-mail: LLG@forcetechnology.com; JED@forcetechnology.com

B. Timetable for the comparison

May 2016	Decision of comparison on the EURAMET Working Group on Density meeting
October 2016	Questionnaire
December 2016	Deadline for answers to questionnaire
July 2017	Decision on participants
July 2017	Decision on liquids, temperatures and pressure
September 2017	First draft of Technical Protocol
January 2022	Agreement on Technical Protocol
January 2017	Purchase of liquids and bottles Confirmation of participation
March/April 2022	Hydrostatic tests and stability test of liquids at BEV
March/April 2022	Hydrostatic tests at PTB, stability test of liquids at BEV
May 2022	Delivery of liquids to the participants
November 2022	Hydrostatic measurements second batch n-dodecane at PTB and BEV
December 2022	Delivery of second batch of n-dodecane to the participants
March 2023	Reports from all participants
May 2023	Draft A of comparison report
June 2023	Draft B of comparison report

C. E-mail: Receipt of a comparison package

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

Lukas Prochaska
Bundesamt für Eich- und Vermessungswesen BEV
Arltgasse 35
1160 Wien
Austria
lukas.prochaska@bev.gv.at

This report should contain the following information:

- Participating laboratory
- Contact person
- Telephone
- Mail address and a text like this:

  The packages of the EURAMET.M.D-K5 Project were received on (date).

The seals of the bottles were (not) broken.

The packages seem, after short inspection, (not) to be damaged.

If damaged: (not) seriously.
The contents is probably (not) suitable for use.

Remarks: (e. g. No. of bottles with broken seals)

Date of delivery

D. E-mail: Progress report

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

Lukas Prochaska
Bundesamt für Eich- und Vermessungswesen BEV
Arltgasse 35
1160 Wien
Austria
lukas.prochaska@bev.gv.at

when the measurements are completed. This report should contain the following information:

Participating laboratory
Contact person
Telephone
Fax

and a text like this:

Key Comparison EURAMET.M.D-K5 "Comparison on density determination of liquid samples using density meters”

The measurements were completed on (date).

Remarks:

E. Physical constants of the liquids

Uncertainties are standard uncertainties (k = 1).

Cubic thermal expansion

Liquid	Nominal density in kg/m^3	Cubic thermal expansion in kg/(m^3 K)	Uncertainty (k = 1) in kg/(m^3 K)
Dodecane			
at 15°C	753 [8]	0.725*	0.001*
at 20°C	749 [8]	0.725*	0.001*
at 40°C	735 [8]	0.729*	0.001*
FC-40 (20°C)	1866**	2.23**	0.06***
Viscosity oil EF170 (20°C)	846 [6]	0.61 [6]	0.05 [6]

* measured
** from Datasheet 3M
*** estimated from Datasheet 3M

Isothermal compressibility

Liquid	Isothermal compressibility in 10^{-11}/Pa	Uncertainty (k = 1) in 10^{-11}/Pa
Dodecane		
at 15°C	92 [7]	2.2 [7]
at 20°C	96 [7]	2.1 [7]
at 40°C	111 [7]	3.1 [7]
FC-40 (20 °C)	131 [9]	5*
Viscosity oil EF170 (20 °C)	62.9 [6]	1.25 [6]

* estimated

F. 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. 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 must 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 must 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.