EURAMET TC Project
Final Report

Project Title

Bilateral comparison: Calibration of conductivity probe in low conductivity range (20 µS/cm and 100 µS/cm)

Coordinator, Institute, Country

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EURAMET Registration No.

1450

Subject Field

Metrology in Chemistry

KCDB Identifier

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Date

2023-08-23

EURAMET Study 1564

Bilateral comparison LNE-PTB
Calibration of conductivity probe in low conductivity range
(20 µS/cm and 100 µS/cm)

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23.08.2023

Summary

The results obtained by LNE in the framework of the EURAMET study 1462 (supplementary CCQM comparison EURAMET.QM-S12) did not support its requirements to calibrate customer conductivity probes in the low conductivity range. The unsatisfactory results obtained in the EURAMET comparison might be explained by inadequate temperature control. It was considered to be unrepresentative with respect to the ones LNE typically sets up for the calibration of its customer devices. Therefore, a bilateral comparison has been conducted between LNE and PTB aiming to confirm the quality of measurement results produced by LNE for the calibration of customers conductivity probes in low conductivity ranges. PTB served as linking laboratory to link the results to EURAMET study 1462 and CCQM-EURAMET.QM-S12 respectively.

A commercial conductivity measurement device (henceforth called unit under test, UUT) was provided by LNE to be used in a Round Robin comparison scheme. LNE and PTB used the UUT to measure the conductivities of two reference solutions at 20 µS/cm and 100 µS/cm (nominal values).

Equivalences of the results were estimated by comparing adjusted cell constants of the UUT at both nominal conductivities. They are calculated from the conductivity reference values and the corresponding conductivity values indicated by the UUT. Equivalences are then evaluated by calculating EN scores from the adjusted cell constants and their uncertainties at both nominal values, considering PTB values as reference. The result of LNE at 20µS/cm is consistent with the comparison reference value, EN(20µS/cm)=0.05. The result of LNE is slightly inconsistent at 100 µS/cm, EN(100µS/cm)=1.42.

Participants

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Timeline

Event	Date
Assessment of the temporal stability of conductivity probe	August 2022
Measurements at LNE	12.10.2022
UUT sent to PTB	September 2022
Measurement at PTB	30.09.2022
Data treatment	November/December 2022
Report draft A	End of 2022

LNE has sent a revised report 14.11.2022. The missing information was added. The reported measurement results have not been changed. The results of PTB and the first evaluation have been disclosed to LNE 15.11.2023.

Measurements

LNE and PTB have measured conductivity reference values $\kappa_{ref/part}(\kappa_i)$ at the nominal values κ_i according to their standard operation procedure. Additionally, conductivities $\kappa_{UUT/part}(\kappa_i)$ have been measured with the unit under test (UUT) provided by LNE. Measurements with the UUT have been conducted without temperature compensation.

The corresponding $\kappa_{ref/part}$ and $\kappa_{UUT/part}$ values had to be referred to the same temperature $t_{ref/part}$ if the actual reference temperatures of $\kappa_{ref/part}$ and $\kappa_{UUT/part}$ deviated from $t_{ref/part}$, $\kappa_{ref/part}$ and $\kappa_{UUT/part}$ had to be compensated to $t_{ref/part}$. To this end, a linear dependence of conductivity from temperature was assumed in the range of interest. A temperature coefficient of 1.95 %/°C has to been used for the correction. The reference temperature had to be in the range of 25°C ± 0.5°C.

A temperature value Δt_{me} had to be estimated. It represents the maximal difference between the temperature at the location where the temperature has actually been measured and the location of the conductivity measurement using the UUT. The uncertainty of the temperature measurement associated with the UUT measurement had to consider this deviation by calculating $u(\Delta t_{me}) = \left(\frac{\Delta t_{me}}{2\sqrt{6}}\right)$, assuming a triangular probability distribution function for Δt_{me}.

Reported results

The participant had to provide the following information:

- Name and address of the participant
- Date of measurements
- Measured conductivity values using the UUT.
- Reference conductivity values and their route of traceability.
- Standard measurement uncertainties (k = 1) of the conductivity values.
- The corresponding reference temperature.
- Δt_{me} and $u(\Delta t_{me})$

- Brief description of the measurement procedure or, alternatively, reference to a standard operation procedure of the laboratory.

The calibration procedure applied by LNE for a customer device provides the difference of a UUT compared to the reference value provided by LNE. Therefore, LNE has reported the difference $\mathrm{correction}_{part}(\kappa_i) = \kappa_{ref/part}(\kappa_i) - \kappa_{UUT/part}(\kappa_i)$ and its uncertainty as additional information. However, this value has not been used to calculate degrees of equivalence. In fact, it is not possible to compare such a value with a respective difference calculated from PTB's results, since both institutes have measured different reference solutions at (slightly) different conductivities.

Communication with LNE

LNE has sent it measurement report 28 October 2022. After a first evaluation of the results, it was realized that the report lacked information on

- full name of institute and address,
- date(s) of measurement(s),
- cell constant stored in the UUT during the measurements, and
- route (source) of traceability of both measurements

as requested by the measurement protocol. LNE was asked November 11th to send a revised report.

Furthermore, LNE was asked to check the results for any typing or transcription errors, since one of the results showed a deviation from the reference value. No numerical information was given to LNE about the deviation.

Data evaluation

Data have been evaluated by PTB.

Using the cell constant (K_{UUT}) saved in the settings of the UUT, the adjusted cell constant $K_{adj/inst}(\kappa_i)$ of the UUT can be calculated for each institute ($inst$) and for each nominal conductivity κ_i.

$$K_{adj/inst}(\kappa_i) = \frac{\kappa_{ref/inst}(\kappa_i)}{\kappa_{UUT/inst}(\kappa_i)} K_{UUT} \quad , \tag{1}$$

The uncertainties of the reference temperatures of $\kappa_{ref/inst}$ and $\kappa_{UUT/inst}$ must be considered in the uncertainty of $K_{adj/inst}$.

Consistency of the $K_{adj/LNE}(\kappa_i)$ results reported by LNE have been evaluated with respect to the reference $K_{adj/PTB}(\kappa_i)$ calculated from the results provided by PTB.

It should be noted that the dependence of the cell constant on temperature and water conductivity is negligible within the ranges relevant in this comparison, since κ_{ref} and κ_{UUT} are affected by both quantities in the same manner (also see eq. 1) Thus, actual measurement temperatures and conductivities may deviate between the LNE and PTB.

It should also be noted that the comparison results can likewise be expressed in terms of conductivity using:

$$R(\kappa_i) = \frac{K_{UUT}}{\kappa_i} \tag{2}$$

$R(\kappa_i)$ corresponds to the resistance of a solution measured with the UUT and having a conductivity of κ_i. Then, linking conductivities can be calculated for LNE and for PTB that both refer to the same solution of nominal conductivity κ_i.

$$\kappa_{link/LNE}(\kappa_i) = \frac{K_{adj/LNE}(\kappa_i)}{R(\kappa_i)} \quad (3a)$$

$$\kappa_{link/PTB}(\kappa_i) = \frac{K_{adj/PTB}(\kappa_i)}{R(\kappa_i)} \quad (3b)$$

Eqs. 3a and 3b have the same scaling factor $R(\kappa_i)^{-1}$. Thus, it makes actually no difference if adjusted cell constants or conductivities calculated thereof are compared. In this report, comparison results are nevertheless stated in both terms. It must however be emphasized that the uncertainties assigned to the linking conductivities do not include the (stability) uncertainty contributions u(κ_{UUT}) and u(Δt_{me}). Like this, the DoEs of the linking conductivities can rather be used to evaluate the equivalence of the reference conductivity values $\kappa_{ref/inst}$ reported by the institutes (see the final report of CCQM QM-S12 for a more detailed discussion).

The results of PTB serve as refence values. Since PTB has successfully participated in the EURAMET study 1462, the results of this comparison can also serve to link them to the final reports of EURAMET and CCQM-EURAMET.QM-S12, respectively. Therefore, the adjusted cell constants and linking conductivities calculated from the reported results have been corrected for the DoEs of PTB in those studies. To this the relative deviations DoE_{rel}(PTB)=DoE(PTB)/$KCRV_{EURAMET1462}$, have been calculated from the values given in the final report of EURAMET 1462. Then, the adjusted cell constants and the linking conductivity values of PTB have been corrected according to

$K_{adj/PTB}$(corrected)=$K_{adj/PTB}$-DoE_{rel}(PTB)*$K_{adj/PTB}$, and (4a)

$\kappa_{link/PTB}$(corrected)= $\kappa_{link/PTB}$ -DoE_{rel}(PTB)* $\kappa_{link/PTB}$. (4b)

Degrees of Equivalence

Degrees of equivalence of LNE have only been calculated for the adjusted cell constants. Note that the EN values are the same for adjusted cell constants and linking conductivities. DoE have been referred to the corrected PTB values calculated according to eqs. 4a. The expanded uncertainties of the DoEs have been calculated according to

$$U(DoE_{LNE}) = 2\sqrt{u^2(K_{adj,PTB}) + u^2(K_{adj,LNE}) + (u(KCRV)_{rel}K_{adj,PTB})^2} \quad (5)$$

with $u(KCRV)_{rel}$ being the relative uncertainty of the KCRV at 50 µS/cm.

Reported Results and derived Quantities

Table 1 shows the reported temperature results.

Inst.	nominal conductivities µS/cm µS cm^{-1}	t_{ref} °C	Δt_{me} °C	u(Δt_{me}) * °C	temperature indicated by UUT ** °C
PTB	20	25.037	0.03	0.006	25.1
PTB	100	25.036	0.03	0.006	25.1
LNE	20	25.001	-0.006	0.029	25.0
LNE	100	25.003	-0.006	0.029	25.0

* LNE has additionally included the uncertainty of the temperature measurement in u(Δt_{me}); at PTB this value must only be included in u(κ_{ref}), which explains why u(Δt_{me}) is significantly smaller for PTB, even though Δt_{me} is larger at PTB.

** just for information, values are not used for data evaluation

Table 2 shows the reported conductivity results.

Inst.	nominal conductivities µS cm^{-1}	κ_{ref} µS cm^{-1}	u(κ_{ref}) µS cm^{-1}	κ_{UUT} µS cm^{-1}	stability u(κ_{UUT}) µS cm^{-1}	κ_{UUT}-κ_{ref} µS cm^{-1}	u(κ_{UUT}-κ_{ref}) µS cm^{-1}
PTB	20	19.505	0.049	19.72	0.01	n/a	n/a
PTB	100	99.73	0.25	100.5	0.0	n/a	n/a
LNE	20	20.24	0.1	20.46	0.0057	0.22	0.10
LNE	100	100.05	0.26	99.81	0.0029	-0.24	0.26

Table 3 shows the derived adjusted cell constants and linking conductivities and their standard uncertainties

Inst.	nominal conductivities µS cm^{-1}	K_{adj} cm^{-1}	K_{adj} * cm^{-1}	standard uncertainty u(K_{adj}) cm^{-1}	linking conductivity κ_{link}* µS cm^{-1}	u(κ_{link}) w/o u(Δt_{me}) and w/o u(κ_{UUT}) µS cm^{-1}
PTB	20	0.10781	0.10777	0.00028	19.77	0.05
LNE	20	0.10783	0.10783	0.00054	19.78	0.10
PTB	100	0.10816	0.10812	0.00027	99.19	0.25
LNE	100	0.10926	0.10926	0.00029	100.24	0.26

*PTB value corrected for its DoE in EURAMET 1462

Table 4 Degrees of Equivalence for adjusted cell constants

Inst.	nominal conductivities	DoE	U(DoE)*	EN= DoE/U(DoE)
	µS cm^{-1}	cm^{-1}	cm^{-1}	
LNE	20	0.000059	0.0012	0.05
LNE	100	0.0011	0.00080	1.42

Expanded uncertainties using a coverage factor k=2

Minimal uncertainties consistent with the reference value

20µS/cm

The LNE results at 20 µS/cm are consistent with the reference value, since EN(at 20µS/cm)<1. Thus, the minimal relative standard uncertainty for the calibration of the cell constant of a customer device that can be stated by LNE according to table 3 is 0.00054/0.10783=0.50 %.

100µS/cm

At 100 µS/cm, the inconsistency with the reference value has to be considered, since EN(at 100µS/cm)>1. There, the minimal relative standard uncertainty of the adjusted cell constant that can be stated by LNE in consistency with the reference value is

$$u_{\min\_rel}\left(100\ \mu\frac{S}{cm}\right) = \frac{\sqrt{DoE^2 - 4u^2(K_{adj,PTB}) - 4u^2(u(KCRV)_{rel}K_{adj,PTB})}}{K_{adj,PTB}} = 0.46\ \%\ , \quad (6)$$

which derives from the consistency criterium U(DoE)≥DoE, with U(DoE) expressed by eq. 5. Values in eq. (6) are taken from tables 3 and 4. The relative standard uncertainty $u(KCRV)_{rel}$ of EURAMET 1462 is 0.11% at 50 µS/cm.

The same minimal relative standard uncertainties must be applied to the conductivity reference values, if differences are stated in respective calibration certificates of LNE.

How far the light shines

The HFLS statement of the final report of EURAMET 1462 (CCQM-EURAMET.QM-S12, respectively) has to be applied. This means in particular that this report can provide evidence for the calibration capability of LNE only up to 150 µS/cm, since this is the upper CMC limit of PTB. 5 µS/cm can be seen as a reasonable lower limit that is in accordance with the CMC guidelines of the EAWG of CCQM.