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Comparison meaurement of

Electrolytic conductivity at pure water level

Draft B

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Summary

In this comparison the equivalence of conductivity measurement results has been investigated in the conductivity range from ultra pure water level (5.5 µS m^{-1}) up to 1500 µS m^{-1}. The measurements were performed in a closed pure water loop with primary methods and with commercial devices. To this end the conductivity measurement cells of the participating institutes were integrated in series with the primary cell of PTB, which in this way linked the results. In general the primary methods of PTB and DFM are consistent within an expanded uncertainty of 0.5%. A slight inconsistency at the ultrapure water level resulted from a small leakage during that measurement. SP, using a commercial device, measured consistent values. CMI, also using a commercial device, underestimated its measurement uncertainty.

Background

Pure water is of great importance in many industrial applications, such as the pharmaceutical or the microelectronics industry. Since electric conductivity is very sensitive to dissolved ions standards and test instructions often require to measure conductivity in order to verify water purity. The typical measurement range for such applications is from 5.5 µS m^{-1} (ultra pure or highly purified water) to 5 S m^{-1}.

Aqueous reference solutions are not stable in this range because of the influence of carbon dioxide. Therefore an alternative calibration method is used at metrology institutes and calibration laboratories to calibrate sensors for pure water applications. Such sensors are integrated into a closed system that prevents contact between pure water and atmospheric carbon dioxide. Calibration is performed with ultra pure water or with ultra pure water which conductivity is increased by adding small amounts of salt (typically KCl). The conductivity reference value is then either calculated using formula out of literature, which relate conductivity to KCl concentration, or it is measured with another conductivity cell simultaneously. The cell constants of such cells are either calibrated traceable to the conductivity value of stable aqueous reference solution at 15 mS m^{-1} or with more stable reference solutions of lower conductivity, but having a different matrix. Recently, primary conductivity cells that can be implemented into closed water flow systems have been invented.

A former comparison measurement (EURAMET study 989) that investigated the equivalence of the reference conductivity values showed relatively large differences of roughly 1%. The deviation rose mainly from instabilities of the measurement setup in use. Considering that the uncertainty demands on conductivity sensors are typically of the same order, the results were unsatisfying. The pure water calibration loop developed at PTB within the European imera+ project “TP-Health” showed promising stability. Therefore the EURAMET TC-MC subcommittee on Electro Analysis decided in its meeting held February 2013 in Braunschweig to perform a conductivity comparison measurement of primary and secondary cells integrated into the PTB loop, using the results of the primary PTB cell to link the results.

General process

Only one cell could be added in series to the PTB cell. Therefore PTB has put up a measurement schedule in agreement with the participating institutes. Each participating institute has sent a responsible to PTB, who has performed the conductivity measurement with the system of the institute. The conductivity measurement cell had been sent to PTB one week before the agreed measurement date and had been integrated immediately after its arrival into PTB’s pure water loop. Then the loop had been cleaning down to the highly purified water level until the participant has arrived. The measurements have been performed (approximately) at 5.5 µS m^{-1}, 0.1 mS m^{-1}, 0.5 mS m^{-1} and 1.5 mS m^{-1}, whereas the conductivity level has been increased stepwise by addition of small amounts of KCl. With each institute the measurements have been finished within one day.

Measurement setup

Figure 1 shows a sketch of the general measurement setup. A 5 L bottle made of bore silicate glass was filled with ultra pure water from a Millipore MilliQ A10 system. The water was pumped with a gear pump through the conductivity cell of the participating institute, then through the primary conductivity cell of PTB and back into the bottle. This was the conductivity measurement loop. Note that the gear pump was placed behind the PTB cell (in contrast to figure 1), to prevent an interference of water temperature in the cell, since the gear pump heated the water to some extent. The purification system was connected in parallel to the measurement loop such that the water could be permanently cleaned. Using a dosage unit, small amounts of KCl could be added to the bottle. After KCl had been added the purification

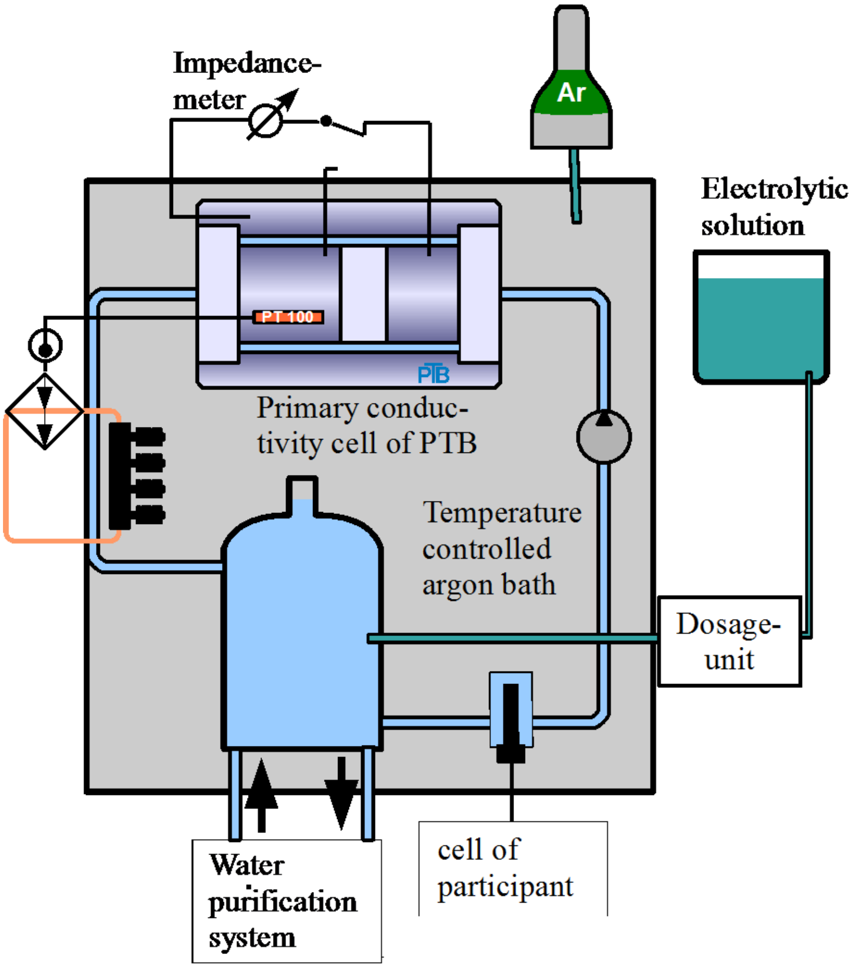

Figure 1 Sketch of the measurement setup. Note that the actual position of the pump is behind the PTB cell.

has been switched off. In this way any conductivity between 5.5 µS m^{-1} (ultra pure water) and 15 mS m^{-1} could be (roughly) adjusted. The complete setup is placed in a closed box that is flooded with argon to prevent atmospheric CO_2 from penetrating into the loop. The temperature in the box is controlled with a thermostat and a ventilated heat exchanger. The cells of the institutes have been thermally insulated with foam, such that water temperature in the cell is not directly affected by the circulated air. The water temperature in the reservoir bottle responds rather slowly to a change in set temperature of the thermostat. Hence, measurements were performed when the temperature equilibrium was achieved at a few hundred mK around 25°C rather than adjusting the temperature close to 25°C in a time consuming way.

The cell of the participating institutes had to comply with the following requirements to be implemented in the loop:

- The conductivity measurement cell had to be a flow-through cell or it must have been possible to integrate it in a flow through adapter. The cell or the adapter had to be connected to PE tubes of 8 mm outer/6 mm inner diameter.
- The cell should have had integrated a calibrated temperature measurement facility, which allows temperature measurement in the cell or close to it. If necessary, PTB could estimate the temperature within the cell from the temperature measured in the

primary cell. This estimate would have had a standard uncertainty of about 30 mK. DFM and CMI used their temperature measurement device, SP that of PTB.

- The conductivity meter had to be situated outside the box. Thus the wires connecting the cell were lead outside the box through a hole of 10 mm in diameter. The plug was dissembled in case (only CMI). The BNC wires of DFM system were too thick to be lead outside in either way and were replaced by thinner BNC cables of PTB.

Reporting

Participants were asked to submit a measurement report including the following information:

- Name and address of the laboratory performing the measurements.
- Date of measurement.
- Description of the measurement method used, in particular including the procedure to determine the conductivity values, i.e. impedance at a fixed frequency, frequency extrapolation, secondary cell constant determination, etc.
- The measurement temperature and the measured conductivity value, referred to the measurement temperature.
- Uncertainties of the reported conductivity values. The participants should report uncertainties calculated according to the “Guide to the Expression of Uncertainty in Measurement”[1] or its supplement.
- The uncertainty budget.
- The route of traceability.

Time schedule and contact

July/August 2013	Information of technical details to be sent to PTB
September 2013	Preparation of cell integration at PTB
October/November 2013	Measurement period
17. January 2014	Deadline for receipt of the report
February 2014	TC-MC SCEA meeting: discussion of results and report

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[1] http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf

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Communication with laboratories

The reported uncertainty value of DFM at the ultrapure water level was twice the value compared to the preliminary comparison performed in February 2013. DFM was asked to check the uncertainty budged. They confirmed a mixing up of the standard uncertainty with the expanded uncertainty and have sent a corrected report.

Measurement results

The results are indicated in the following tables 1a to 1c. Information about the participating institute, the date of measurement, the measurement system and traceability are given in the upper part. Light blue background indicates the results of the linking laboratory (PTB), light orange background indicates the results measured with the cell in series to the PTB cell. Uncertainties are given as standard uncertainties.

Table 1a

Linking laboratory	Physikalisch-Technische Bundesanstalt (PTB) Working Group 3.41 Bundesallee 100 38116 Braunschweig Germany Email: steffen.seitz@ptb.de
System	Primary
Traceability	Cell constant of primary cell calculated from geometric measurements, value: 0.702 m^{-1}
Institute	Czech Metrology Institute (CMI) Department of primary metrology of physical chemistry Okruzni 31, 638 00 Brno Czech Republic Email: mrozikova@cmi.cz
Date of measurement	19.11.2013
Participants/Contact	Matilda Ruziková Email: mrozikova@cmi.cz Martina Vičarova, Alena Vospělová
System	Commercial: Mettler Toldedo 7500 with InPro 7002 cell
Cell constant stored during measurement, (cm^{-1})	0.0960
Traceability	Calibration of cell constant using a n-propanol/water reference solution at 100, 500 and 1000 µS m^{-1}

temperature t_{PTB}	conductivity $\kappa_{PTB}(t_{PTB})$ with primary PTB cell,	$u(\kappa_{PTB}(t_{PTB}))$	temperature t_{inst}	conductivity $\kappa_{inst}(t_{inst})$ with institute system	$u(\kappa_{inst}(t_{inst}))$
°C	µS m^{-1}	µS m^{-1}	°C	µS m^{-1}	µS m^{-1}
25.000	5.496	0.012	25.0	5.4	0.027
25.415	131.13	0.18	25.4	127.2	0.38
25.415	530.2	0.5	25.4	513.7	1.55
25.432	1556.0	1.8	25.4	1511	4.55

Table 1b

Institute	SP Technical Research Institute of Sweden Brinellg 4 501 15 Borås Sweden
Date of measurement	03.12.2013
Participant / Contact	Rauno Pyykkö Email: rauno.pyykko@sp.se
System	Commercial: Knick Laboratory Conductivity Meter 703 with WTW LR 352/01 cell
Cell constant stored during measurement, (cm^{-1})	0.100
Traceability	Calibration of cell constant in a closed pure water flow through system, with KCl added. Reference values calculated from amount of dissolved KCl according to literature.

temperature t_{PTB}	conductivity $\kappa_{PTB}(t_{PTB})$ with primary PTB cell,	$u(\kappa_{PTB}(t_{PTB}))$	temperature t_{inst}	conductivity $\kappa_{inst}(t_{inst})$ with institute system	$u(\kappa_{inst}(t_{inst}))$
°C	µS m^{-1}	µS m^{-1}	°C	µS m^{-1}	µS m^{-1}
25.000	5.489	0.012	25.051	5.61	0.1
25.252	130.27	0.19	25.277	131.7	1.1
25.314	542.6	0.6	25.332	544.9	5.5
25.348	1592.2	1.9	25.346	1605	16

Table 1c

Institute	Danish Fundamental Metrology Ltd. (DFM) Matematiktorvet 307 DK-2800 Kgs Lyngby
Date of measurement	10.11.2013
Participants/Contact	Hans Jensen Email: hdj@dfm.dk Carsten Thirstrup
System	Primary
Traceability	Cell constant of primary cell calculated from geometric measurements, value: 1.190 56 m^{-1}

temperature t_{PTB}	conductivity $\kappa_{PTB}(t_{PTB})$ with primary PTB cell,	$u(\kappa_{PTB}(t_{PTB}))$	temperature t_{inst}	conductivity κ_{inst} (t_{inst}) with institute system	$u(\kappa_{inst}(t_{inst}))$
°C	µS m^{-1}	µS m^{-1}	°C	µS m^{-1}	µS m^{-1}
25.000	5.507	0.012	25.000	5.466	0.011
25.310	140.67	0.19	25.329	140.5	0.10
25.317	567.9	0.5	25.334	567.1	0.40
25.313	1633.5	1.4	25.336	1631.3	1.15

Degrees of equivalence

The comparison reference values (CRV) and the degrees of equivalence (DoE) have been calculated only from the primary measurement results according to reference [1], procedure A. The other values have been excluded from CRV calculation not for statistical reasons (meaning that are assumed to be outliers), but for traceability reasons. Fundamentally, results can only be included in the reference value calculation, if they are traceable to the same metrological reference. Otherwise apples and oranges are compared. The CMI results are traceable to the conductivity value of an alcohol solution. Up to now a sound metrological basis has not been established for such reference solutions. In particular, since their stability is questionable and the influence of the different matrix on the conductivity determination is not clarified. The results of SP are traceable to literature values, which correlated the concentration of an aqueous KCl solution with conductivity (Kohlrausch equation). The metrological reference of the SP results is difficult to backtrace. However, it is very likely that those values are traceable to conductivity values of KCl solutions orders in magnitude larger than investigated here. As a consequence, in the metrological sense of comparability none of the secondary results can be compared with the other results. Thus only the primary, SI traceable results of PTB and DFM have been used to calculate the CRVs, in particular considering the SI should be the metrological reference of choice. In the EURAMET TC-MC SCEA meeting held 5th of February in Teddington, UK, the participants of the meeting (including those of EURAMET 1271) agreed on this point of view.

The results are shown in table 2. The second column indicates the mean temperature t_m calculated from the PTB and the DFM temperature measurement results. The third column shows the linear temperature coefficients α_{25} referred to 25°C. The fourth and fifth column show the conductivity values of the DFM and PTB measurements, each related to t_m using

$$\kappa(t_m)=\kappa(t)/(1+\alpha_{25}(t-t_m)). \qquad (1)$$

The uncertainty of α_{25} has a negligible effect on the uncertainty of the conductivity values since $(t-t_m)$ is just around 10mK. Therefore it has not been considered. The sixth and seventh columns (green background) show the comparison reference value and its standard uncertainty, given as the weighted mean and its uncertainty. The last column on the right hand side shows the difference $d_{PTB}=\kappa_{PTB}-\kappa_{CRV}$ of the PTB conductivity values from the corresponding CRV. The last line shows the results of a preliminary comparison between PTB and DFM. It has been performed in February 2013 at the PTB under the same conditions as reported here.

Table 2 Results of the calculation of the conductivity reference values

nominal conductivity µS m^{-1}	t_m °C	α_{25} %/K	$\kappa_{PTB}(t_m)$ µS m^{-1}	$\kappa_{DFM}(t_m)$ µS m^{-1}	κ_{CRV} µS m^{-1}	u(κ_{CRV}) µS m^{-1}	d_{PTB} µS m^{-1}
5.5	25.000	5.1	5.507	5.466	5.485	0.008	0.022
130	25.320	1.9	140.70	140.45	140.51	0.09	0.19
500	25.326	1.9	568.01	567.04	567.42	0.31	0.59
1500	25.324	1.9	1633.9	1630.9	1632.1	0.9	1.7
5.5 (*)	25.000	5.1	5.495	5.474	5.485	0.008	0.011

(*) results from preliminary comparison in February

Tables 3a and 3b show the DoE (=$d_{\mathrm{institute}}$) of the primary measurement results of DFM and PTB. Note that the uncertainty of the DoE of the primary measurement results is given by

$$u^2(d_{\mathrm{institute}})=u^2(\kappa_{\mathrm{institute}})-u^2(\kappa_{\mathrm{CRV}}) \quad (2)$$

since the CRV depends on the measured conductivities [1]. The last column relates the DoE to its expanded uncertainty. If the value is larger than one the measurement result is inconsistent with the CRV.

Table 3a Degrees of equivalence of DFM results

nominal conductivity µS m^{-1}	d_{DFM} µS m^{-1}	$U(d_{\mathrm{DFM}})$ µS m^{-1}	$d_{\mathrm{DFM}}/U(d_{\mathrm{DFM}})$
5.5	-0.02	0.015	-1.26
130	-0.05	0.09	-0.55
500	-0.39	0.50	-0.77
1500	-1.2	1.5	-0.82
5.5 (*)	-0.010	0.017	-0.62

Table 3b Degrees of equivalence of PTB results

nominal conductivity µS m^{-1}	d_{PTB} µS m^{-1}	$U(d_{\mathrm{PTB}})$ µS m^{-1}	$d_{\mathrm{PTB}}/U(d_{\mathrm{PTB}})$
5.5	0.022	0.018	1.26
130	0.19	0.34	0.55
500	0.59	0.77	0.77
1500	1.7	2.1	0.82
5.5 (*)	0.011	0.017	0.62

(*) results from preliminary comparison in February

Tables 4a and 4b show the DoE of CMI and SP. The second column shows the corresponding reference value. It has been calculated from the conductivity value measured with the PTB cell minus the corresponding d_{PTB}. The results at ultrapure water level are related to 25°C. At the other conductivity levels temperature correction to a mean temperature has only been applied to the results related to SP. Temperature resolution of the commercial CMI device was poor (0.1 °C). Therefore the correction would have introduced a larger error than the expected deviation of the actual temperatures in the cells.

In contrast to eq. (2) in tables 4a and 4b the uncertainty of the DoE is given by

$$u^2(d_{\mathrm{institute}})=u^2(\kappa_{\mathrm{institute}})+u^2(\kappa_{\mathrm{ref}}) \quad (3)$$

since here κ_{ref} does not depend on the results of these institutes [1].

Table 4a Degrees of equivalence of CMI results

nominal conductivity µS m^{-1}	$\kappa_{ref}(t_{PTB})$ µS m^{-1}	d_{CMI} µS m^{-1}	$U(d_{CMI})$ µS m^{-1}	$d_{CMI}/U(d_{CMI})$
5.5	5.474	-0.074	0.056	-1.3
130	130.94	-3.74	0.78	-4.8
500	529.57	-15.87	3.16	-5.0
1500	1554.3	-43.3	9.3	-4.7

Table 4b Degrees of equivalence of SP results

nominal conductivity µS m^{-1}	$\kappa_{ref}(t_m)$ µS m^{-1}	d_{SP} µS m^{-1}	$U(d_{SP})$ µS m^{-1}	$d_{SP}/U(d_{SP})$
5.5	5.467	0.129	0.201	0.6
130	130.11	1.56	2.21	0.7
500	542.06	2.75	11.02	0.2
1500	1590.5	14.6	32.0	0.5

Observations and remarks

Typical measurement time was 10 min (10 conductivity measurements with the PTB cell). CMI did the measurement during this period. The SP device deteriorated the signal to noise ratio of the LCR meter used by PTB significantly. Therefore it was turned off during the PTB measurement and the conductivity value the SP device was measured immediately after the measurement of PTB had been finished. DFM did computer controlled measurements in the same time window as PTB.

Temperature variation during the measurement was typically in the order of less than 0.01%. An offset of about 20mK was measured between the PTB and the DFM cell, which is larger than the measurement uncertainty. However, temperature distribution in the box volume is not homogenous. Despite the thermal isolation a difference in that order can be expected.

Measurement temperature during measurements at the ultra pure water level was within tens of mK above 25°C. At higher conductivity levels temperature had increased about two to three hundred mK because the water in the reservoir bottle was heated by the gear pump to a new temperature equilibrium after the fresh and cooler water from the purification loop had been turned off. Typically, this took about 2 hours.

The main observation is the untypical conductivity value measured with the PTB cell at the ultrapure water level while the DFM cell was being integrated. The value was about 0.3% larger compared to the measurements with the other cells and compared to the preliminary comparison performed between PTB and DFM 5th of February 2013 at the PTB under equal conditions. There are several reliable indications that the water in the PTB cell had in fact a larger conductivity than in the DFM cell. First of all, back at DFM, a small leakage has been observed at the outlet connector of the cell. Since the pump pulled the water from the reservoir bottle ambient gas could have sucked into the loop. As a consequence residual CO_2 could have entered into the loop, thereby increasing the water conductivity only in the PTB cell. It might also be possible that subsequent air bubble formation caused a distortion of the PTB value. Moreover, the permanently monitored value measured with the PTB cell showed the expected value of 5.490 µS m^{-1} in the morning of the measurement. However, by the time of the measurement it had increased to the value measured later on. Finally, the deviation of PTB value from the values usually measured is larger than the spread of those values (0.003 µS m^{-1} around a mean of 5.490 µS m^{-1}) The results measured with the CMI and SP cells integrated fit well to this distribution just like that of the preliminary comparison with DFM. These indications and the fact that DFM has measured an even lower value than in spring make it obvious that the conductivity value measured within the PTB cell has been slightly contaminated between the DFM cell and the PTB cell. There was no time to repeat the measurements.

Consistency of results

Following CCQM guidelines for key comparisons reference values results which normalized DoEs (last column in tables 3 and 4) are smaller or equal to one are considered consistent with the CRV. Institutes whose results are consistent with the CRV can claim the measurement uncertainty stated here with respect to possible CMC claims. In order that inconsistent results can be used as evidence for CMCs the minimal standard uncertainty u_{inst}(CMC) an institute is allowed to state must be increased according to [2]:

$$u_{inst}(\mathrm{CMC}) = \sqrt{u^2(\kappa_{inst}) + \frac{DoE_{inst}^2}{4} - u^2(DoE_{inst})} \qquad (4)$$

This also applies to the assessment of the measurements of PTB and DFM at ultra pure water level. In fact the corresponding CRV is deemed less reliable than that of the preliminary comparison for the mentioned reasons. From a technical point of few it would be reasonable to use the CRV of the preliminary comparison to calculate the DoEs. However, it might be difficult to justify this in front of other instances, which are less familiar with the technical details. Therefore, the worse CRV and the resulting inconsistency of the PTB and DFM ultrapure water conductivity results should be accepted and u_{inst}(CMC) should be increased according to eq. to (4).

“How far does the light shine” statement

Electrolytic conductivity measurements within a few degrees around 25°C in closed loop or closed flow through systems of purified water in the conductivity range 5 µS m^{-1} to 5000 µS m^{-1}.

References

[1] M. G. Cox, The evaluation of key comparison data, Metrologia 39 (2002), pp. 589-595.

[2] Maurice Cox, Peter Harris and Martin Milton, Method for determination acceptable CMCs to ensure consistency with KC results, NPL, 2009-03-04, available: http://www.bipm.org/cc/CCQM/Restricted/15/CCQM09_03.pdf