EURAMET TC-MC / Subcommittee on Electrochemical Analysis
CCQM WG on Electrochemical Analysis and Classical Chemical Methods

EURAMET Reg. No. 1619

KCDB-ID EURAMET.QM-K19.2018

Subsequent Key Comparison of the pH of a Borate Buffer

Final report

Joanna Dumańska and Monika Pawlina (GUM); Zuzana Hanková and Michal Máriássy (SMU)

Nagy Dániel and Nagyné Szilágyi Zsófia (BFKH); Ivan Georgiev and Boryana Koleva (BIM); José Luis Ortiz Aparicio and Jazmin Montero Ruiz (CENAM); Matilda Roziková and Martina Vičarová (CMI), Alan Snedden and Kim Segelcke (DFM), Jose Luis Gonzales Quino and Jimena Patricia Torrez (IBMETRO); Javier Vásquez Arellán and Christian Uribe Rosas (INACAL); Henrry Torres Quezada, Gina Torres Lopéz and Olga Brigette Suaza Diaz (INM-CO); Anastasia Popov, Olga Neamtu and Ana Curdov (INM-MD); Raquel Quendera and Olivier Pellegrino (IPQ); Eric Ortiz Apuy, Jimmy Venegas Padilla and Bryan Calderón Jiménez (LACOMET); Simone Fajardo and Victoria Gelabert (LATU); Béatrice Lalere and Paola Fisicaro (LNE); Nongluck Tangpaisarnkul and Patumporn Rodruangthum (NIMT); Chikako Cheong and Toshiaki Asakai (NMIJ); Frank Bastkowski and Beatrice Sander (PTB); Abdulrahman Alaskar and Rashed Aldosari (NMCC/SASO); Ayu Hindayani and Dyah Styarini (SNSU-BSN); Anton Petrenko and Oleksandr Melnykov (UMTS)

14 July 2025

Summary

The regional key comparison registered under the EURAMET No. 1619 and the KCDB ID EURAMET.QM-K19.2018 is a subsequent comparison of CCQM-K19.2018. It is organized mainly for European institutes that either could not participate in the CCQM-K19.2018 or could not provide results due to the ramifications of the corona pandemics in 2021.

The comparison was performed to demonstrate the capability of the participating institutes to measure pH of borate buffer (pH ~ 9.2) at 15 °C, 25 °C and 37 °C, optionally at 5 °C and 50 °C. The institutes could use a method of their choice, but the use of a method of the highest available level was expected. The results of PTB and NMIJ were used as a link to the KCRV of the original CCQM-K19.2018. Good agreement of the results is demonstrated by most of the participants.

Table of Contents

1 Coordinating institute and contact person

Main contact

Joanna Dumańska
Central Office of Measures (GUM)
Elektoralna 2
00-139 Warszawa, Poland
email: joanna.dumanska@gum.gov.pl
phone: +48 22 581 9395

Co-piloting institute

Zuzana Hankova
Slovak Institute of Metrology (SMU)
Karloveská 63
842 55 Bratislava, Slovakia
email: hankova@smu.gov.sk
phone: +421 2 602 94 708

2 List of participants

Table 1 List of participants

Institute	Acronym	Country	contact person	email
Government Office of the Capital City Budapest	BFKH	Hungary	Nagy Dániel Nagyné Szilágyi Zsófia	nagy.daniel2@bfkh.gov.hu nagyne.szilagyi.zsofia@bfkh.gov.hu
Bulgarian Institute of Metrology	BIM	Bulgaria	Ivan Georgiev Boryana Koleva	i.georgiev@bim.government.bg b.koleva@bim.government.bg
Centro Nacional de Metrología	CENAM	Mexico	José Luis Ortiz Aparicio Jazmin Montero Riuz	jortiz@cenam.mx jmontero@cenam.mx
Czech Metrology Institute	CMI	Czech Republic	Matilda Roziková Martina Vičarová	mrozikova@cmi.cz mvicarova@cmi.cz
Dansk Fundamental Metrologi A/S	DFM	Denmark	Alan Snedden Kim Segelcke	asn@dfm.dk kse@dfm.dk
Central Office of Measures	GUM	Poland	Joanna Dumańska Monika Pawlina	joanna.dumanska@gum.gov.pl monika.pawlina@gum.gov.pl
IBMETRO	IBMETRO	Bolivia	Jose Luis Gonzales Quino Jimena Patricia Torrez	jgonzales@ibmetro.gob.bo jtorrez@ibmetro.gob.bo
National Quality Institute	INACAL	Peru	Javier Vásquez Arellán Christian Uribe Rosas	jvasquez@inacal.gob.pe curibe@inacal.gob.pe
Instituto Nacional de Metrología	INM (CO)	Colombia	Henrry Torres Quezada Gina Torres Lopéz Olga Brigette Suaza Diaz	htquezada@inm.gov.co, gatorres@inm.gov.co obsuaza@inm.gov.co

Institute	Acronym	Country	contact person	email
Institutul Național de Metrologie / National Institute of Metrology	INM-MD	Moldova	Anastasia Popov Olga Neamtu Ana Curdov	anastasia.popov@inm.gov.md olga.neamtu@inm.gov.md ana.curdov@inm.gov.md
Instituto Português da Qualidade	IPQ	Portugal	Raquel Quendera Olivier Pellegrino	rquendera@ipq.pt opellegrino@ipq.pt
Laboratorio Costarricense de Metrologia	LACOMET	Costa Rica	Eric Ortiz Apuy Jimmy Venegas Padilla Bryan Calderón Jiménez	eortiz@lcm.go.cr jvenegas@lcm.go.cr bcalderon@lcm.go.cr
Laboratorio Tecnológico del Uruguay	LATU	Uruguay	Simone Fajardo Victoria Gelabert	sfajardo@latu.org.uy mgelabert@latu.org.uy
Laboratoire National de metrologie et d'essais	LNE	France	Béatrice Lalere Paola Fisicaro	beatrice.lalere@lne.fr paola.fisicaro@lne.fr
National Institute of Metrology (Thailand)	NIMT	Thailand	Nongluck Tangpaisarnkul Patumporn Rodruangthum	nongluck@nimt.or.th patumporn@nimt.or.th
National Metrology Institute of Japan	NMIJ	Japan	Chikako Cheong Toshiaki Asakai	c-kato@aist.go.jp t-asakai@aist.go.jp
Physikalisch-Technische Bundesanstalt	PTB	Germany	Frank Bastkowski Beatrice Sander	frank.bastkowski@ptb.de beatrice.sander@ptb.de
Saudi Standards, Metrology and Quality Org.	SASO/NMCC	Saudi Arabia	Abdulrahman Alaskar Rashed Aldosari	ar.askar@saso.gov.pl r.dosari@saso.gov.sa
National Measurement Standards - National Standardization Agency of Indonesia	SNSU-BSN	Indonesia	Ayu Hindayani Dyah Styarini	ayu.hindayani@bsn.go.id duah.stya@bsn.go.id
SE Ukrmetrteststandart	UMTS	Ukraine	Anton Petrenko Oleksandr Melnykov	pavpostbox@gmail.com amelnykov@ukrcsm.kiev.ua

3 Time Schedule

Invitation	February 2024
Registration deadline	31 March 2024
Sample preparation and shipment	July/August 2024
Reporting deadline	30 November 2024
Draft A	Spring 2025

4 Description of Samples

The solutions used for the comparison have been produced by the coordinating institute. A borate buffer with a nominal pH value of approximately 9.2 at 25 °C has been prepared from deionized water and disodium tetraborate decahydrate, $Na_2B_4O_7 \cdot 10H_2O$. The material had a purity of ≥99.5 % and was stored in a desiccator over a saturated aqueous solution of NaCl and saccharose at the room temperature. The batch of the solution was prepared by mixing portions of the solution of about 7 kg each. The portions were shaken on a laboratory shaker for about 24 hours. Then, after mixing all the portions of the solution, a batch of about 90 kg was obtained. It was shaken for about several hours a day for the next few days. The solution was filled in 1 L type bottles and closed in aluminized plastic bags.

Bottle labels indicated the comparison number - EURAMET.QM-K19.2018, the nominal pH value, the bottle number and the mass fraction of water. Shipment to all participants started at the same time. The bottles were shipped by a courier. The tracking number was reported by email to the contact person of the participating laboratory. The contents was stated as “Non-hazardous aqueous solution” with a value of 1 € per bottle.

4.1 Homogeneity

The homogeneity of the samples was assessed by SMU. Ten bottles have been chosen for homogeneity measurement. The bottles were measured against one of them, bottle No 53, using a differential cell. The results of the homogeneity test are shown in Figure 1. The pH range for the bottles was 0.000 52 and the standard deviation was 0.000 15 in terms of pH, the standard uncertainty was 0.000 58. This is significantly smaller than the typical measurement uncertainties of the reported pH measurement results. Verification of the between-bottle homogeneity is sufficient for this comparison. The results of the individual measurements are shown in Table 1. Since aqueous electrolyte solution can be assumed sufficiently homogenous within a bottle, the within bottle homogeneity has not been measured.

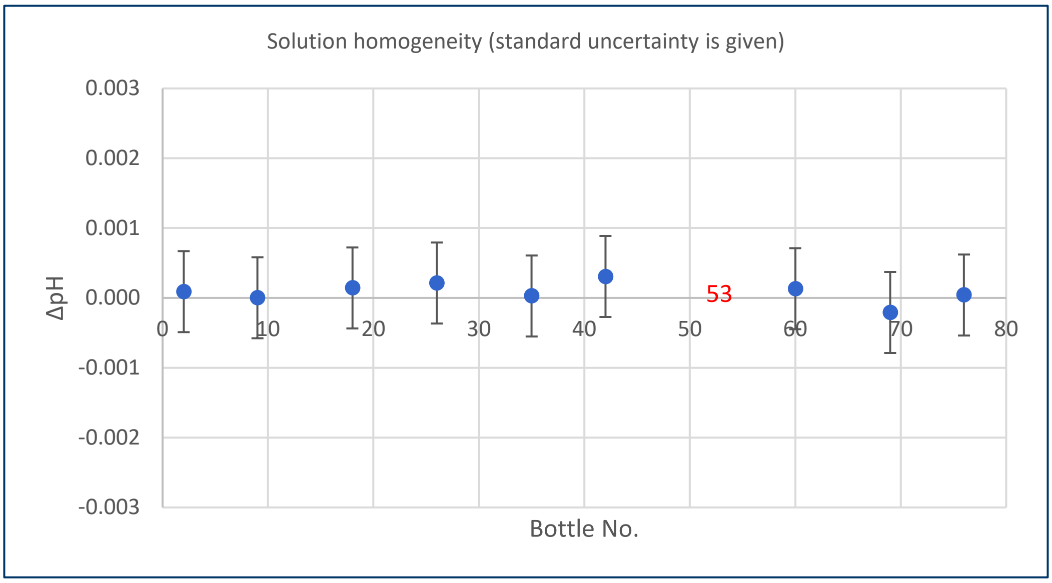


Figure 1 Results of the homogeneity test.

Table 2 Results of homogeneity test

bottle #	E / µV	pH_i - pH_{avg}
2	-58	0.000 09
9	-53	0.000 00
18	-59	0.000 14
26	-62	0.000 21
35	-53	0.000 03
42	-72	0.000 31
60	-59	0.000 13
69	-37	-0.000 21
76	-56	0.000 04

4.2 Stability

The stability of the solution was confirmed by Harned cell measurement. Six bottles have been arbitrary chosen and measured to verify stability of the samples in intervals of approximately 4 weeks since sample preparation throughout the whole measurement period. The results are given in Table 3.

Table 3 Results of the stability test

bottle #	date measured	temperature / °C	acidity function	pH
81, 82, 83	25 July 2024	25.0	9.2387	9.179
7, 10, 73	26 August 2024	25.0	9.2395	9.180
13, 62, 74	18 September 2024	25.0	9.2365	9.177
3, 67, 79	28 October 2024	25.0	9.2375	9.178
8, 70, 63	27 November 2024	25.0	9.2383	9.179
5, 16, 72	30 December 2024	25.0	9.2400	9.181
Mean			9.2384	9.179
Standard deviation			0.0013	0.0014

A linear regression line has been fitted through the results according to ISO Guide 35. The slope is b_1=-0.000 004, its standard deviation $s(b_1)$=0.000 011 (formulas are given in the annex).
Since

$$|b_1| < t_{0.95,n\text{-}2}\, s(b_1) \qquad (1)$$

the samples can be assumed sufficiently stable over the measurement period. n is the number of measurements and $t_{0.95,n\text{-}2}$ =2.78 is the corresponding student-t factor at a 95 % level of confidence and n-2 degrees of freedom.

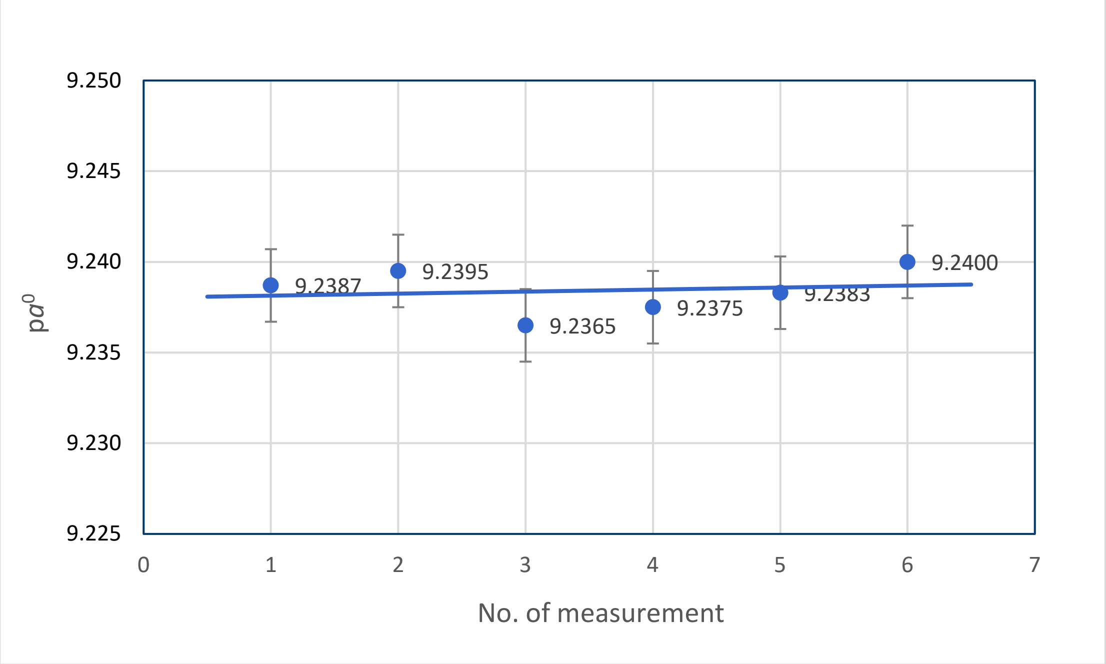


Figure 2 Results of the stability test. The error bars indicate the expanded uncertainty of the Harned cell method measurement (k = 2).

4.3 Bottle integrity

The integrity of each bottle was verified upon arrival by weighing the bottle and comparing the weighing results with those obtained in the coordinating laboratory. Once the participant had received the package with the samples, the packaging had to be removed and the bottles had to be checked for any visible damage or leakage. Prior to weighing, the bottles had to be equilibrated in the weighing room overnight. Neither the parafilm nor the label should have been removed from the bottles before weighing. Each bottle should have been weighed with a balance having 0.01 g resolution. Weighing results, pressure, temperature and relative humidity at the time of weighing were filled in the reporting Excel sheet that was sent together with the final version of the Technical protocol. Bottle masses were automatically corrected for air-buoyancy (assuming 1 000 kg m^{-3} density).

The participants were asked to confirm the receipt of the samples and report bottle masses (corrected for air buoyancy) to the coordinating laboratory by email within two weeks after arrival. If leakage was observed or the deviation of bottle masses was larger than 0.2 g, the coordinating institute was ready to send a replacement bottle as soon as possible. No visible signs of any damage to the samples were reported to the coordinating laboratory. INM-MD reported a deviation of almost 0.5 g due to an incorrect way of weighing. Since the weighing could not be repeated the pilot institute has sent an additional bottle. Figure 3 shows the differences between masses measured by the participants from those measured at the coordinating institute.

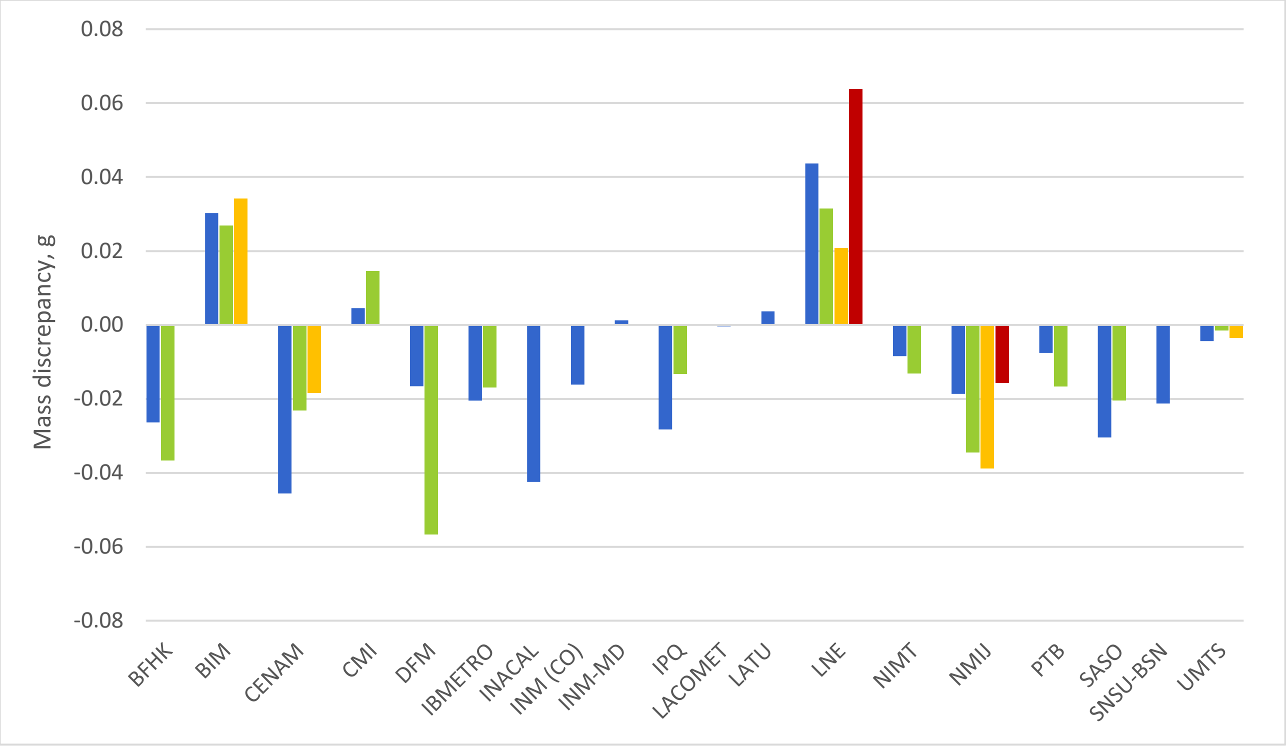


Figure 3 Measured mass differences with respect to the initial weighing at the coordinating institute. 🟦 - bottle 1, 🟩 - bottle 2, 🟨 - bottle 3, 🟥 - bottle 4.

5 Correspondence with institutes

13 June 2024	Delay of the shipment due to too small number of homogeneous bottles announced.
8 Aug 2024	The homogeneity tests completed and samples ready for shipment.
22 Aug 2024	Reporting deadline shifted to 30 Nov 2024 announced.
23 Aug 2024	LACOMET asked for the supplementary invoice. The required document was sent.
27 Aug 2024	CENAM informed about the customs problem with parcel clearing and asked for the supplementary invoice. The required document was sent.
29 Aug 2024	LNE asked for additional sample solutions (2 L).
30 Aug 2024	Additional bottles shipped to LNE.
11-30 Sept 2024	The coordinating laboratory reminded the participants who had received the parcels but had not yet confirmed receipt or reported bottle masses.
18 Sept 2024	CENAM informed about successful delivery of the parcel.
25 Sept 2024	CMI declared withdrawal from the comparison due to the lack of staff.
25 Sept 2024	LACOMET informed about successful delivery of the parcel.
1 Oct 2024	The coordinating laboratory asked INM-MD for checking integrity report for copy-paste error or/and weighing the bottle once again.
3 Oct 2024	INM-MD informed about the problem during the mass measurement and that the bottle was no longer available.
17 Oct 2024	An additional bottle was sent to INM-MD.
30 Nov 2024	The coordinating laboratory reminded the participants of the deadline for submitting the report.
30 Nov 2024	UMTS informed about the three-weeks delay with the report.
9 Dec 2024	DFM declared withdrawal from the comparison due to a problem during measurement.

17 Dec 2024	INM-MD informed that the measurement had been completed and asked for support in completing the report due to the different nomenclature relating to pH meter calibration and adjustment used in the report and in the laboratory.
5 Mar 2025	BFKH, BIM, CENAM, INACAL, INM (CO), IPQ, NIMT, NMIJ, SASO, SNSU-BSN, UMTS have been invited to check the results for numerical errors but without being informed of the magnitude or sign of the apparent anomaly.
11 Mar 2025	IPQ submitted a revised report, a correction due to molalities used.
12 Mar 2025	SASO submitted a revised report, a correction due to a typing error leading to incorrect calculations.
12 Mar 2025	INM (CO) submitted a revised report, a correction due to the pH value of the CRM used.
14 Mar 2025	INACAL submitted a revised report, a correction due to a typing error leading to incorrect calculations.
11-18 Mar 2025	BFKH, BIM, CENAM, NIMT, NMIJ, SNSU-BSN, UMTS have confirmed the original results.

6 Measurement instructions

The measurement instructions were as follows:

- Participants were requested to measure the buffer solution within four weeks of receiving the samples.
- The caps of the bottles were only to be opened immediately before the measurements. If possible, the caps should be resealed with Parafilm following each opening.
- Measurements should be performed at the following temperatures: 15 °C, 25 °C and 37 °C, and optionally at 5 °C and 50 °C.
- Recommended values of constants were:
  - Molar gas constant, R = 8.314 462 618 J mol^{-1} K^{-1}
  - Faraday constant, F = 96 485.332 12 C mol^{-1}
- The following conditions were used for primary measurements:
  - The measurements had to be evaluated using the standard pressure of 101 325 Pa.
  - The standard potential of the Ag/AgCl electrodes should be determined using hydrochloric acid (aqueous HCl solution) having a molality value close to 0.01 mol kg^{-1}. The actual molality value had to be traceable to the SI.
  - Alkali chloride (sodium chloride or potassium chloride) should be added to prepare at least three different buffer solutions with molalities in the range of 0.005 mol kg^{-1} to 0.02 mol kg^{-1}.

The bottles were recommended to be stored at temperatures between 20°C and 25°C, however, they were not to be stored above 25°C. The caps of the bottles were only to be opened immediately before the measurements. If possible, the caps should be re-sealed with Parafilm following each opening.
Each participant had to measure pH of the samples with respect to 15 °C, 25 °C and 37 °C, and optionally at 5 °C and 50 °C. It was expected that the highest-level method available at the institute was used. However, lower-level methods could additionally be used, and the results could be reported as additional information.

7 Results

7.1 Reported Results

Table 4 lists the reported results. The pH values reported by participants who used secondary methods were converted to $\text{p}a^0$ by the activity coefficient of chloride ions to the pH, $\log\gamma_{Cl}^{0}$, equal to -0.058639 for 15 °C, -0.059596 for 25 °C and -0.060844 for 37 °C. The last column lists the stated source of traceability. Figure shows the results graphically.

Table 4 Acidity functions at 15 °C, 25 °C, 37 °C, 5 °C and 50 °C and their uncertainties.

Institute *i* acronym	**15 °C** pa^0 $u(pa^0)$ $U(pa^0)$ $pH_{rep}(sec)$	**25 °C** pa^0 $u(pa^0)$ $U(pa^0)$ $pH_{rep}(sec)$	**37 °C** pa^0 $u(pa^0)$ $U(pa^0)$ $pH_{rep}(sec)$	**5 °C** pa^0 $u(pa^0)$ $U(pa^0)$	**50 °C** pa^0 $u(pa^0)$ $U(pa^0)$	Method	Source of traceability
BFKH	9.3327 0.0013 0.0025	9.2386 0.0014 0.0028	9.1469 0.0015 0.0030	--	--	Primary	--
BIM	9.3228 0.0019 0.0038	9.2314 0.0019 0.0039	9.1443 0.0019 0.0039	--	--	Primary	--
CENAM	9.3474 0.0038 0.0075	9.2612 0.0025 0.0049	9.1713 0.0039 0.0078	--	--	Primary	--
GUM	9.3344 0.0010 0.0020	9.2387 0.0010 0.0020	9.1478 0.0010 0.0020	9.4418 0.0010 0.0020	9.0726 0.0010 0.0020	Primary	--
IBMETRO	--	9.229 0.015 0.030 9.169	--	--	--	Differential cell	CENAM CMR-6200359c
INACAL	9.3483 0.0035 0.0070 9.2898	9.2509 0.0030 0.0060 9.1914	9.1578 0.0035 0.0070 9.0969	--	--	Differential cell	SMU CRM E1313322 E1305424
INM (CO)	9.296 0.021 0.041 9.237	9.206 0.016 0.032 9.146	9.073 0.020 0.039 9.012	--	--	Differential cell	CENAM CMR-6200358c
INM-MD	9.345 0.048 0.096 9.286	9.238 0.047 0.094 9.178	9.221 0.049 0.098 9.160	--	--	Glass	CRM SMU
IPQ	9.3268 0.0022 0.0044	9.2305 0.0018 0.0035	9.1439 0.0019 0.0038	--	--	Primary	--
LACOMET	9.3296 0.0016 0.0032 9.2711	9.2381 0.0016 0.0032 9.1786	9.1512 0.0017 0.0034 9.0903	--	--	Differential cell	NIST SRM 187e
LATU	--	9.2335 0.0048 0.0096 9.1740	--	--	--	Differential cell	CRM GUM 3.7 1/22
LNE	9.3267 0.0012 0.0024	9.2370 0.0019 0.0037	9.1479 0.0023 0.0045	--	--	Primary	--

Institute *i* acronym	**15 °C** pa^0 $u(pa^0)$ $U(pa^0)$ $\mathrm{pH_{rep}}$(sec)	**25 °C** pa^0 $u(pa^0)$ $U(pa^0)$ $\mathrm{pH_{rep}}$(sec)	**37 °C** pa^0 $u(pa^0)$ $U(pa^0)$ $\mathrm{pH_{rep}}$(sec)	**5 °C** pa^0 $u(pa^0)$ $U(pa^0)$	**50 °C** pa^0 $u(pa^0)$ $U(pa^0)$	Method	Source of traceability
NIMT	9.3163 0.0041 0.0082	9.2218 0.0041 0.0082	9.1272 0.0037 0.0074	--	--	Primary	--
NMIJ	9.3263 0.0019 0.0038	9.2371 0.0013 0.0026	9.1498 0.0013 0.0026	9.4351 0.0011 0.0022	9.0729 0.0018 0.0036	Primary	--
PTB	9.3294 0.0008 0.0016	9.2383 0.0008 0.0016	9.1510 0.0008 0.0015	9.4424 0.0008 0.0017	9.0773 0.0009 0.0017	Primary	--
SASO	9.2344 0.0026 0.0052 9.1759	9.2365 0.0026 0.0052 9.1770	9.2374 0.0026 0.0052 9.1765	--	--	Differential cell	CRM SMU
SNSU-BSN	9.3455 0.0020 0.0040 9.287	9.2505 0.0020 0.0040 9.191	--	--	--	Differential cell	CRM NIM China GBW13106d
UMTS	9.3511 0.0018 0.0036	9.2554 0.0024 0.0048	9.1585 0.0027 0.0054	--	--	Primary	--

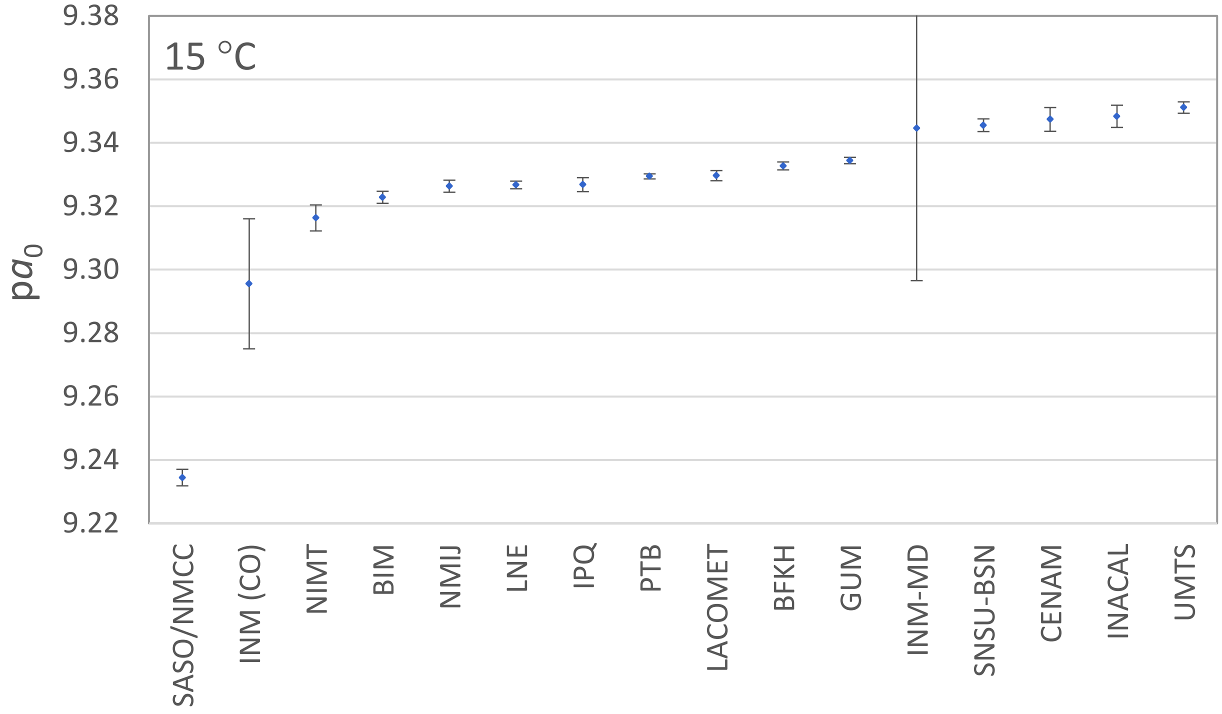


Figure 4-1 Reported pa^0 results of a buffer solution at 15 °C. The uncertainty bars indicate standard uncertainties.

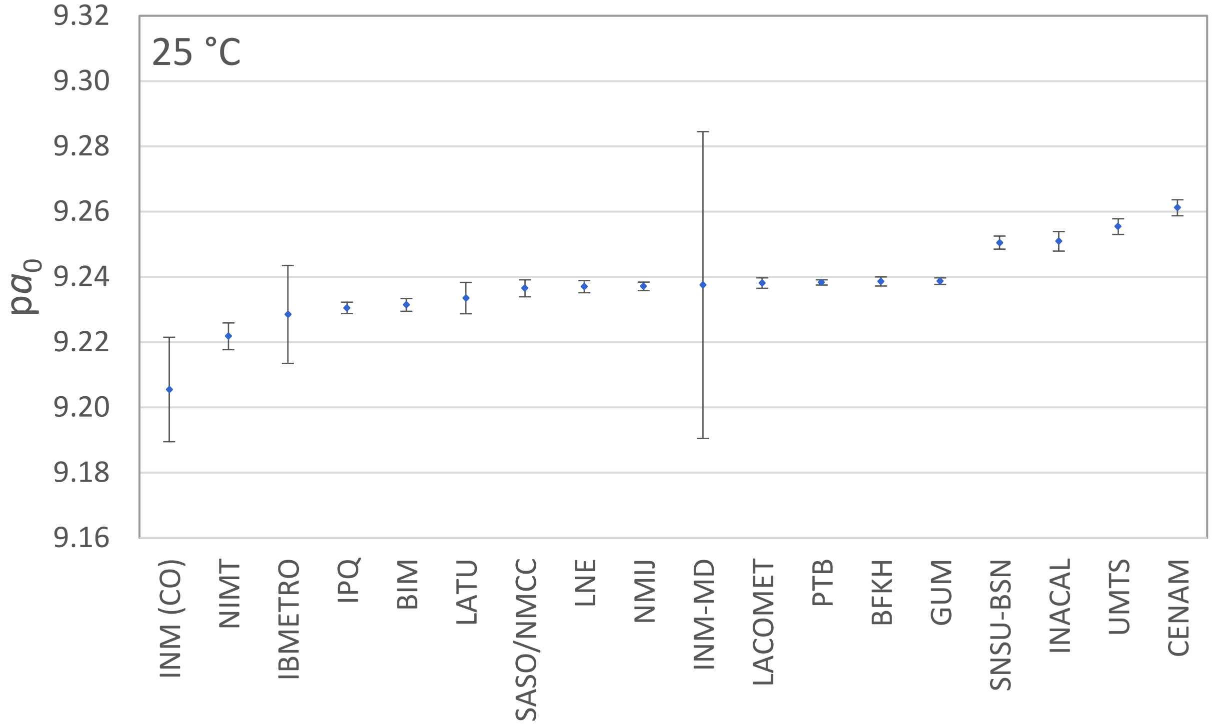


Figure 4-2 Reported pa^0 results of a buffer solution at 25 °C. The uncertainty bars indicate standard uncertainties.

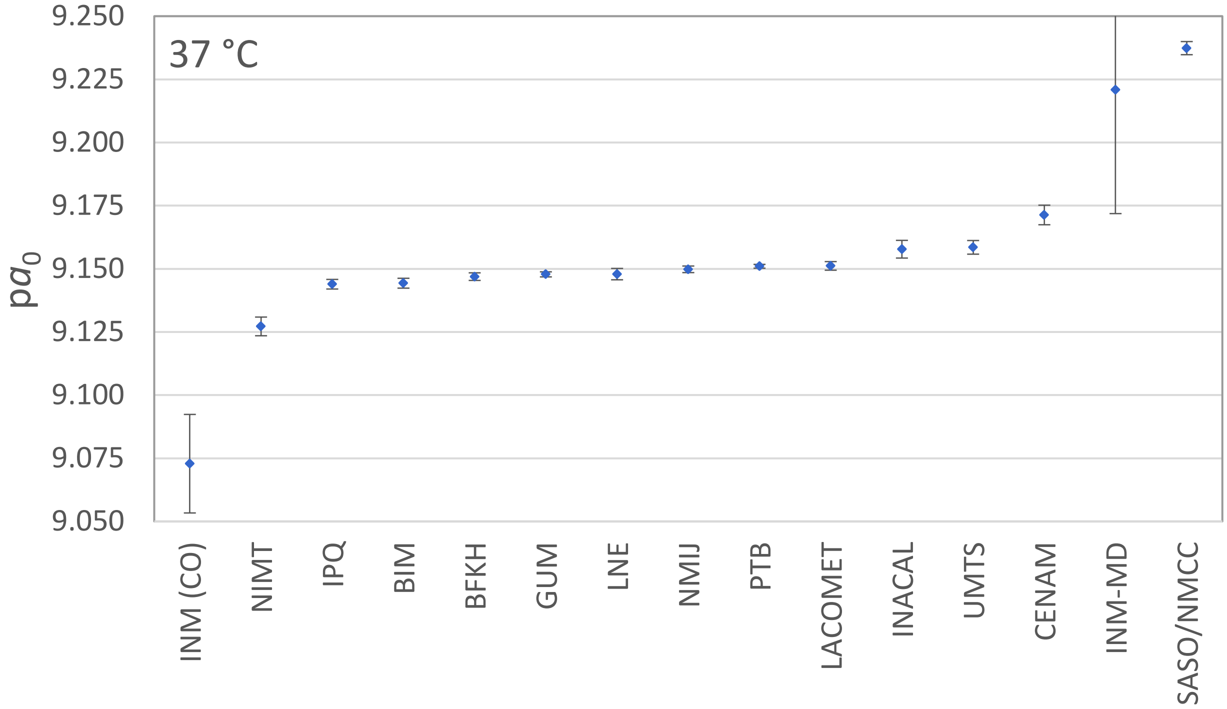


Figure 4-3 Reported pa^0 results of a buffer solution at 37 °C. The uncertainty bars indicate standard uncertainties.

Compared to the other participants, the results reported by SASO/NMCC are significantly lower at 15 °C and significantly higher at 37 °C. The pH results reported by INM(CO) at 15 °C, 25 °C and 37 °C are significantly lower.

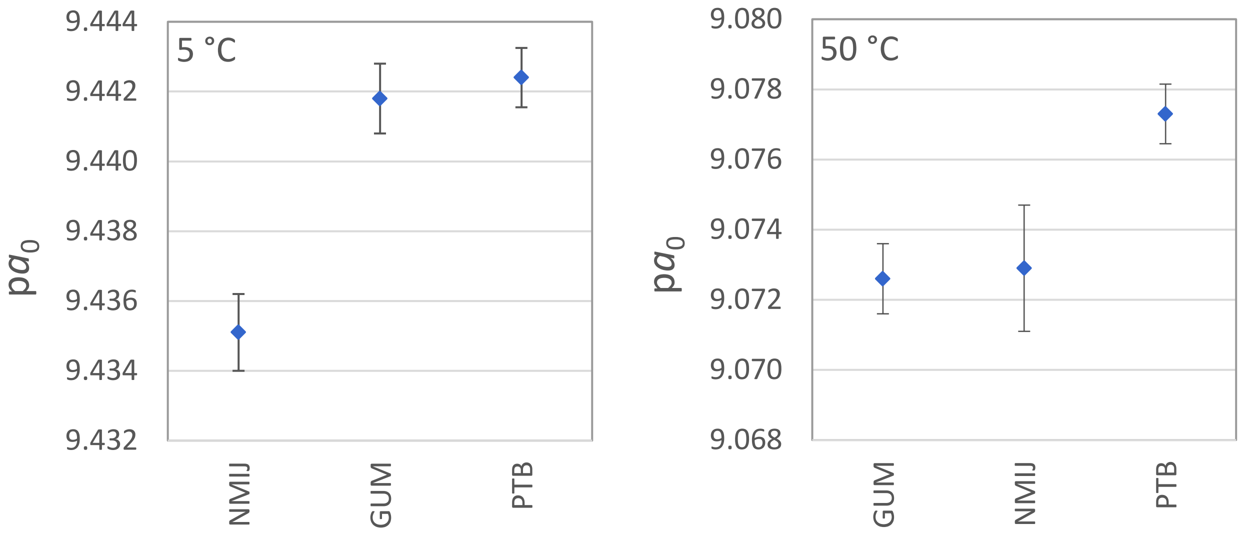


Figure 4-4 Reported pa^0 results of a buffer solution at 5 °C and 50 °C. The uncertainty bars indicate standard uncertainties.

Other information reported by the participants using the primary Harned cell method are given in the tables below.

Table 5 HCl assay reported by participants using the primary Harned cell method.

Institute *i* acronym	Method	Molality, mol kg^{-1}	*u*, mol kg^{-1}
BFKH	Coulometric titration	0.010 074	0.000 008
BIM	Potentiometric titration CRM (potassium hydrogen phthalate)	0.010 060	0.000 021
CENAM	Coulometric titration	0.009 998	0.000 004
GUM	Coulometric titration	0.009 982	0.000 005
IPQ	Acidimetric Titration NIST CRM 723e (TRIS)	0.009 994	0.000 010
LNE	Gravimetrical dilution SMU LM04 1 M HCl	0.010 000	0.000 004
NIMT	NMIJ CRM 3201 (0.1 mol/kg HCl)	0.010 038	0.000 040
NMIJ	Coulometric titration	0.010 000	0.000 005
PTB	Coulometric titration	0.010 0191	0.000 0039
UMTS	Coulometric titration	0.010 000	0.000 008

Table 6 Ag/AgCl standard potential, E^0, reported by participants using the primary Harned cell method.

Institute *i* acronym	**15 °C** E^0, V $u(E^0)$, V p*a* slope	**25 °C** E^0, V $u(E^0)$, V p*a* slope	**37 °C** E^0, V $u(E^0)$, V p*a* slope	**5 °C** E^0, V $u(E^0)$, V p*a* slope	**50 °C** E^0, V $u(E^0)$, V p*a* slope
BFKH	0.228 314 0.000 043 0.2414	0.222 090 0.000 044 -0.6220	0.213 216 0.000 045 -0.9258	--	--
BIM	0.228 588 0.000 109 -0.1732	0.222 495 0.000 112 -0.2876	0.214 233 0.000 117 -0.3416	--	--
CENAM	0.228 366 0.000 084 -2.737	0.222 337 0.000 071 -0.9699	0.214 364 0.000 119 -2.057	--	--
GUM	0.228 212 0.000 029 0.2409	0.222 511 0.000 034 -0.1004	0.214 443 0.000 034 -0.1084	0.234 371 0.000 029 -0.2908	0.204 831 0.000 034 -0.2874
IPQ	0.22823 0.00011 -1.306	0.22215 0.00008 -0.6147	0.21407 0.00010 -1.693	--	--
LNE	0.228 756 0.000 058 -0.3553	0.222 586 0.000 060 -0.4649	0.214 284 0.000 064 -0.4288	--	--
NIMT	0.229 073 0.000 204 -0.2868	0.222 975 0.000 205 -0.2553	0.214 861 0.000 205 -0.2892	--	--
NMIJ	0.228 522 0.000 085 -0.0655	0.222 396 0.000 043 -0.1315	0.214 339 0.000 052 -0.1684	0.234 117 0.000 029 0.0343	0.204 721 0.000 104 -0.1093
PTB	0.228 822 0.000 012 -0.1817	0.222 640 0.000 021 -0.1807	0.214 374 0.000 013 -0.1461	0.234 312 0.000 007 -0.1724	0.204 544 0.000 033 -0.1083
UMTS	0.228 156 0.000 050 -1.988	0.222 056 0.000 051 -2.002	0.214 045 0.000 053 -2.138	--	--

7.2 Results of further analysis or investigations

The reported results are consistent for the most part. The observed distribution coincides with former comparisons. No further investigations have been conducted.

8 Estimators for the Key Comparison Reference Value (KCRV)

The results were linked to the comparison reference value of CCQM-K19.2018 through the results of PTB and NMIJ as the linking laboratories.

9 Degrees of equivalence (DoE) based on the proposed KCRV

9.1 Degrees of equivalence for temperatures of 15 °C, 25 °C and 37 °C

For temperatures of 15 °C, 25 °C and 37 °C, the degree of equivalence of the participants of the EURAMET1619/EURAMET.QM-K19.2018 comparison was calculated relative to the original CCQM-K19.2018 using the results of linking laboratories PTB and NMIJ according to the equation (2).

$$DoE_i = \mathrm{pa}_i^0 - \mathrm{pa}^0_{\mathrm{PTB,NMIJ}} + DoE_{\mathrm{orgPTB,NMIJ}} \tag{2}$$

DoE_i	Degree of equivalence of participant *i* in the of EURAMET16/19/EURAMET.QM-K19.2018 comparison
pa_i^0	Result of participant *i* in EURAMET1619/EURAMET.QM-K19.2018
$\mathrm{pa}^0_{\mathrm{PTB,NMIJ}}$	Mean of the results of PTB and NMIJ in EURAMET1619/EURAMET.QM-K19.2018
$DoE_{\mathrm{orgPTB,NMIJ}}$	Degree of equivalence of PTB and NMIJ in CCQM-K19.2018 $DoE_{\mathrm{orgPTB,NMIJ}} = \mathrm{pa}^0_{\mathrm{orgPTB,NMIJ}} - \mathrm{pa}^0_{\mathrm{orgKCRV}}$ (3)

For the calculation of uncertainty of the degrees of equivalence equation (4) was used, assuming no significant correlation between both PTB and NMIJ results.

$$u^2(DoE_i) = u^2(\mathrm{pa}_i^0) + u^2(\mathrm{pa}^0_{\mathrm{PTB,NMIJ}}) + u^2\left(DoE_{\mathrm{orgPTB,NMIJ}}\right) \tag{4}$$

where

$$u\left(\mathrm{pa}^0_{\mathrm{PTB,NMIJ}}\right) = \frac{1}{2}\sqrt{u^2(\mathrm{pa}^0_{\mathrm{PTB}}) + u^2(\mathrm{pa}^0_{\mathrm{NMIJ}})} \tag{5}$$

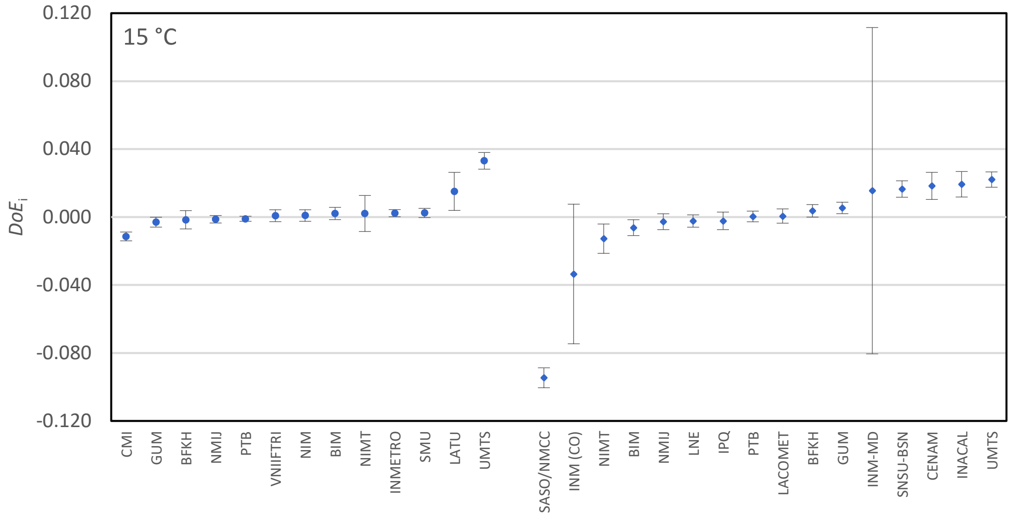
and

$$u\left(DoE_{\mathrm{orgPTB,NMIJ}}\right) = \sqrt{u^2(\mathrm{pa}^0_{\mathrm{orgPTB,NMIJ}}) + u^2\left(\mathrm{pa}^0_{\mathrm{orgKCRV}}\right)} \tag{6}$$

Table 7 Values linking EURAMET1619/EURAMET.QM-K19.2018 to original CCQM-K19.2018 for temperatures of 15 °C, 25 °C and 37 °C.

Temperature	$\mathrm{pa}^0_{\mathrm{PTB,NMIJ}}$ $u(\mathrm{pa}^0_{\mathrm{PTB,NMIJ}})$	$\mathrm{pa}^0_{\mathrm{orgPTB,NMIJ}}$ $u(\mathrm{pa}^0_{\mathrm{orgPTB,NMIJ}})$	$\mathrm{pa}^0_{\mathrm{orgKCRV}}$ $u(\mathrm{pa}^0_{\mathrm{orgKCRV}})$	$DoE_{\mathrm{orgPTB,NMIJ}}$ $u(DoE_{\mathrm{orgPTB,NMIJ}})$
15 °C	9.3279 0.0010	9.3115 0.0007	9.312 63 0.000 59	-0.001 18 0.000 88
25 °C	9.2377 0.0008	9.2200 0.0007	9.22050 0.00073	-0.000 50 0.000 98
37 °C	9.1504 0.0008	9.1322 0.0006	9.13210 0.00072	0.000 10 0.000 95

The degrees of equivalence are listed in Table 8. Figure shows the DoEs and their uncertainties in rising order. The table also states the uncertainty weighted DoE (E_n value).



$$E_n\left(\mathrm{pa}_i^0\right) = \frac{DoE_i}{U(DoE_i)} \qquad (7)$$

The result pa_i^0 of participant i is considered consistent with the KCRV if $E_n\left(\mathrm{pa}_i^0\right) \le 1$. Table 8 also shows minimal expanded uncertainties U_{minCMC} consistent with the proposed KCRV, which makes the submission and review of claims of calibration and measurement capabilities (CMC) easier. If a result is consistent with the KCRV, U_{minCMC} is equivalent with the expanded uncertainty reported by the institute. Regarding inconsistent results, it is assumed that they are the result of underestimated or unknown uncertainty contributions (dark uncertainty), provided that failure of the measurement setup or the sample can be excluded. Therefore, this comparison also supports CMC claims of institutes the results of which are inconsistent if the expanded (95 %) uncertainty of the CMC claim is equal or larger than U_{minCMC}. The calculation of U_{minCMC} is based on eq. (7):

$$\frac{DoE_i}{U(DoE_i)} \le 1 \text{ , thus } \mathrm{DoE}_i^2 \le (k \cdot u(DoE_i))^2 \qquad (8)$$

with $k = 2$ being the coverage factor at a 95 % level of confidence. $U_{\mathrm{minCMC}}(i) = k \cdot u_{\mathrm{minCMC}}$ of institute i can be calculated from eq. (8) and eq. (4), whereas $u(\mathrm{pa}_i^0)$ is replaced by u_{minCMC} in eq. (4). Finally, the equations have been solved for u_{minCMC}.

Table 8-1 Degrees of equivalence, their expanded uncertainties, E_n values and minimal expanded uncertainties admissible for CMC submission at 15 °C.

Institute i	DoE_i	$U(DoE_i)$	$E_n(\mathrm{pa}_i^0)$	$U_{\mathrm{minCMC}}(i)$
BFKH	0.0037	0.0037	1.00	0.0025
BIM	-0.0062	0.0047	-1.33	0.0062*
CENAM	0.0183	0.0080	2.30	0.0183*
GUM	0.0054	0.0034	1.59	0.0054*
INACAL	0.0193	0.0075	2.57	0.0193*
INM (CO)	-0.0335	0.0411	-0.82	0.0410
INM-MD	0.0155	0.0960	0.16	0.0960
IPQ	-0.0022	0.0052	-0.43	0.0044

Institute i	DoE_i	$U(DoE_i)$	$E_n(\mathrm{pa}_i^0)$	$U_{\mathrm{minCMC}}(i)$
LACOMET	0.0006	0.0042	0.14	0.0032
LNE	-0.0023	0.0036	-0.64	0.0024
NIMT	-0.0127	0.0086	-1.47	0.0127*
NMIJ	-0.0027	0.0047	-0.58	0.0038
PTB	0.0004	0.0029	0.13	0.0016
SASO/NMCC	-0.0946	0.0059	-16.13	0.0946*
SNSU-BSN	0.0165	0.0048	3.42	0.0165*
UMTS	0.0221	0.0043	4.90	0.0221

*The reported values are inconsistent with KCRV.

Table 8-2 Degrees of equivalence, their expanded uncertainties, E_n values and minimal expanded uncertainties admissible for CMC submission at 25 °C.

Institute i	DoE_i	$U(DoE_i)$	$E_n(\mathrm{pa}_i^0)$	$U_{\mathrm{minCMC}}(i)$
BFKH	0.0004	0.0037	0.11	0.0028
BIM	-0.0068	0.0046	-1.47	0.0068*
CENAM	0.0230	0.0055	4.18	0.0230*
GUM	0.0005	0.0028	0.16	0.0020
IBMETRO	-0.0097	0.0301	-0.32	0.0300
INACAL	0.0127	0.0065	1.96	0.0127*
INM (CO)	-0.0327	0.0321	-1.02	0.0327*
INM-MD	-0.0007	0.0940	-0.01	0.0940
IPQ	-0.0077	0.0043	-1.79	0.0077*
LACOMET	-0.0001	0.0040	-0.02	0.0032
LATU	-0.0047	0.0099	-0.47	0.0096
LNE	-0.0012	0.0045	-0.27	0.0037
NIMT	-0.0164	0.0084	-1.91	0.0164*
NMIJ	-0.0011	0.0036	-0.31	0.0026
PTB	0.0001	0.0030	0.03	0.0016
SASO/NMCC	-0.0017	0.0058	-0.29	0.0052
SNSU-BSN	0.0123	0.0047	2.61	0.0123*
UMTS	0.0172	0.0054	3.18	0.0172*

*The reported values are inconsistent with KCRV.

Table 8-3 Degrees of equivalence, their expanded uncertainties, E_n values and minimal expanded uncertainties admissible for CMC submission at 37 °C.

Institute i	DoE_i	$U(DoE_i)$	$E_n(\mathrm{pa}_i^0)$	$U_{\mathrm{minCMC}}(i)$
BFKH	-0.0034	0.0039	-0.88	0.0030
BIM	-0.0060	0.0046	-1.31	0.0060*
CENAM	0.0210	0.0081	2.59	0.0210*
GUM	-0.0025	0.0031	-0.79	0.0020
INACAL	0.0075	0.0074	1.01	0.0075
INM (CO)	-0.0774	0.0391	-1.98	0.0774*
INM-MD	0.0706	0.0980	0.72	0.098
IPQ	-0.0064	0.0045	-1.42	0.0064*
LACOMET	0.0009	0.0042	0.20	0.0034
LNE	-0.0024	0.0051	-0.47	0.0045
NIMT	-0.0231	0.0078	-2.97	0.0231*
NMIJ	-0.0005	0.0036	-0.14	0.0026
PTB	0.0007	0.0029	0.25	0.0015
SASO/NMCC	0.0871	0.0057	15.17	0.0871*
UMTS	0.0082	0.0059	1.38	0.0082*

*The reported values are inconsistent with KCRV.

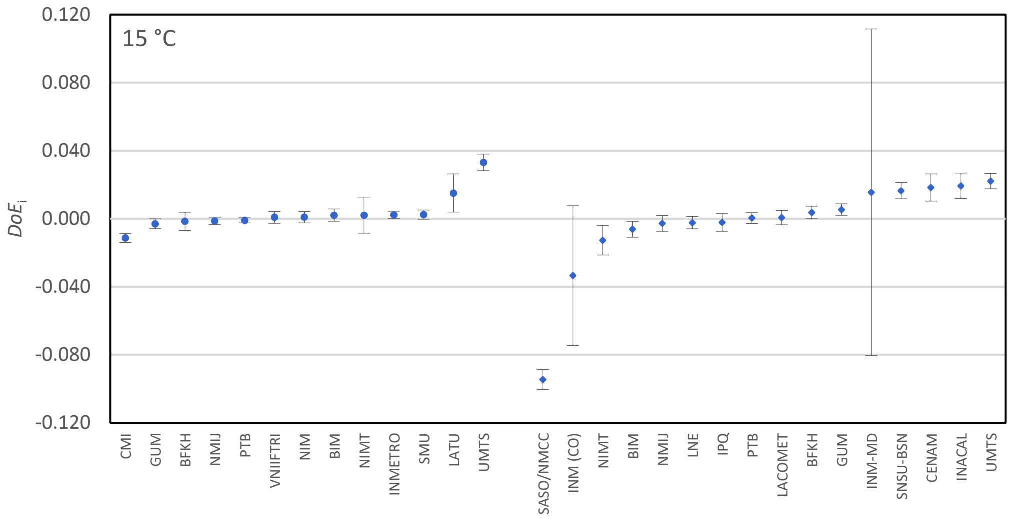


Figure 5-1 DoEs for CCQM-K19.2018 (●) and EURAMET 1619/EURAMET.QM-K19.2018 (♦) and their expanded uncertainties at 15 °C.

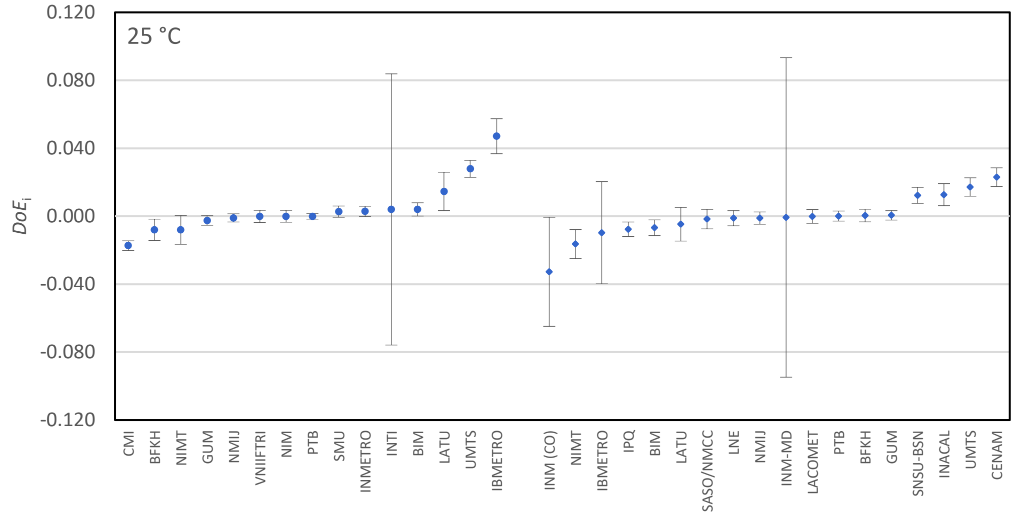


Figure 5-2 DoEs for CCQM-K19.2018 (●) and EURAMET 1619/EURAMET.QM-K19.2018 (◆) and their expanded uncertainties at 25 °C.

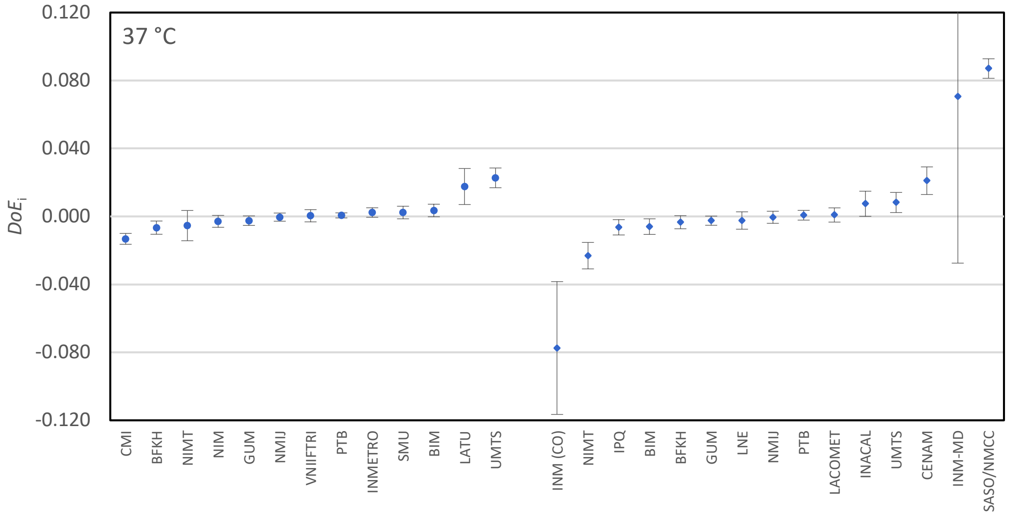


Figure 5-3 DoEs for CCQM-K19.2018 (●) and EURAMET 1619/EURAMET.QM-K19.2018 (◆) and their expanded uncertainties at 37 °C.

9.2 Degrees of equivalence for temperatures of 5 °C and 50 °C

For temperatures of 5 °C and 50 °C, the degree of equivalence of the EURAMET1619/EURAMET.QM-K19.2018 comparison participants and its uncertainty were calculated relative to the original CCQM-K19.2018 according to the equation (2) and (4), respectively. The equations were adjusted for a single PTB linking value, as NMIJ did not measure at 5 °C and 50 °C in the original comparison CCQM-K19.2018. No significant correlation was assumed between the two PTB results.

Table 8 Values linking EURAMET1619/EURAMET.QM-K19.2018 to original CCQM-K19.2018 for temperatures of 5 °C and 50 °C.

Temperature	$\mathrm{pa}^0_{\mathrm{PTB}}$ $u(\mathrm{pa}^0_{\mathrm{PTB}})$	$\mathrm{pa}^0_{\mathrm{orgPTB}}$ $u(\mathrm{pa}^0_{\mathrm{orgPTB}})$	$\mathrm{pa}^0_{\mathrm{orgKCRV}}$ $u(\mathrm{pa}^0_{\mathrm{orgKCRV}})$	DoE_{orgPTB} $u(DoE_{\mathrm{orgPTB}})$
5 °C	9.4424 0.0008	9.4247 0.0007	9.424 62 0.000 60	0.0001 0.0004

Temperature	pa^0_{PTB} $u(pa^0_{\mathrm{PTB}})$	pa^0_{orgPTB} $u(pa^0_{\mathrm{orgPTB}})$	pa^0_{orgKCRV} $u(pa^0_{\mathrm{orgKCRV}})$	DoE_{orgPTB} $u(DoE_{\mathrm{orgPTB}})$
50 °C	9.0773 0.0009	9.0586 0.0006	9.058 01 0.000 97	0.0006 0.0009

The degrees of equivalence are listed in Table 9. The table also states the uncertainty weighed DoE (E_n value).

$$E_n(x_i) = \frac{DoE_i}{U(DoE_i)} \tag{12}$$

A result is considered consistent with the KCRV if $E_n(x_i) \leq 1$. Table also shows minimal expanded uncertainties U_{minCMC} consistent with the proposed KCRV.

Table 9-1 Degrees of equivalence, their expanded uncertainties, E_n values and minimal expanded uncertainties admissible for CMC submission at 5 °C.

Institute *i*	DoE_i	$U(DoE_i)$	$E_n(x_i)$	$U_{\mathrm{minCMC}}(i)$
GUM	-0.0005	0.0027	-0.18	0.0020
NMIJ	-0.0072	0.0029	-2.49	0.0072*

*The reported values are inconsistent with KCRV.

Table 9-2 Degrees of equivalence, their expanded uncertainties, E_n values and minimal expanded uncertainties admissible for CMC submission at 50 °C.

Institute *i*	DoE_i	$U(DoE_i)$	$E_n(x_i)$	$U_{\mathrm{minCMC}}(i)$
GUM	-0.0041	0.0032	-1.29	0.0041*
NMIJ	-0.0038	0.0044	-0.87	0.0036

*The reported values are inconsistent with KCRV.

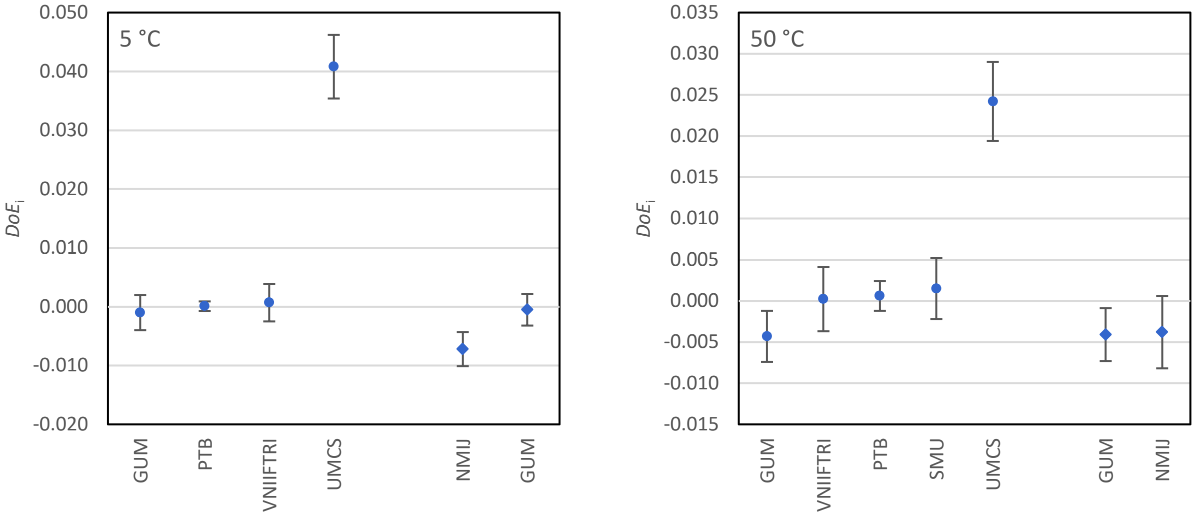


Figure 6 DoEs for CCQM-K19.2018 (●) and EURAMET1619/EURAMET.QM-K19.2018 (◆) and their expanded uncertainties at 5 °C and 50 °C.

10 How Far Does The Light Shines statement

The HFDTLS statement of CCQM-K19.2018 applies. Participants that successfully took part in EURAMET1619/EURAMET.QM-K19.2018 demonstrated their capability to measure the pH of buffers in the alkali range of pH from 8.5 to 9.5 by the primary Harned cell method, the secondary differential potentiometric cell method or the secondary glass electrode method in the temperature range from 5 °C to 50 °C. Measuring borate buffer solutions is a 'core capability' in primary Harned cell measurements.

The corresponding measurement uncertainties for each temperature must be assessed in reviewing CMC claims. Uncertainties claimed in CMC submission must not be smaller than U_{minCMC} values stated in Table , unless exceptions stated in the EAWG-CMC guidelines can be applied.

11 Acknowledgements

The coordinating laboratory is grateful to SMU for conducting the homogeneity measurements. The support of the CCQM-EAWG chair during this comparison is also gratefully acknowledge.

12 References

Toshiaki Asakai *et al*: CCQM-K19.2018 Key Comparison on pH of an unknown Borate Buffer. 2021 *Metrologia* **58** 08020. DOI 10.1088/0026-1394/58/1A/05020

CCQM/2013-22 CCQM Guidance note: Estimation of a consensus KCRV and associated Degrees of Equivalence, available at https://www.bipm.org/documents/20126/28430045/working-document-ID-5794/49d366bc-295f-18ca-c4d3-d68aa54077b5

GUM: Guide to the Expression of Uncertainty in Measurement, available at https://www.bipm.org/en/committees/jc/jcgm/publications

ISO Guide 35:2017, Reference materials — Guidance for characterization and assessment of homogeneity and stability

EAWG guidelines for CMC submission, available at https://www.bipm.org/en/committees/cc/ccqm/wg/ccqm-eawg

Annex

Formula

Verification of stability

$$b_1 = \frac{\sum_{i=1}^{n}\left(X_i - \bar{X}\right)\left(Y_i - \bar{Y}\right)}{\sum_{i=1}^{n}\left(X_i - \bar{X}\right)^2}$$

$$s\left(b_1\right) = \frac{s}{\sqrt{\sum_{i=1}^{n}\left(X_i - \bar{X}\right)^2}}$$ with $$s^2 = \frac{\sum_{i=1}^{n}\left(Y_i - b_0 - b_1 X_i\right)^2}{n-2}$$ and $$b_0 = \bar{Y} - b_1\bar{X}$$

b_0 (intercept) and b_1(slope) are the parameters of a linear regression through the stability measurement results X_i (date of measurement) and Y_i (measurement parameter, e.g. pH or pa^0). $\bar{X}$ and $\bar{Y}$ are the means of n stability measurements i=1..n. The sample can be considered stable if $|b_1| < t_{0.95,n-2}\, s(b_1)$, with $t_{0.95,n-2}$ being the 95% student-*t* factor at n-2 degrees of freedom.

Version 2. of 21 August 2024

EURAMET.QM-K19.2018 Key comparison on Borate Buffer

Technical Protocol

1. Introduction

The regional key comparison EURAMET.QM-K19.2018 is a subsequent comparison of the CCQM-K19.2018. It is organized mainly for European institutes that either could not participate in the CCQM-K19.2018 or could not provide the results due to complications related to the corona pandemics in 2021.

The comparison will be performed to demonstrate the capability of the participating institutes to measure pH of borate buffer (pH ~ 9.2) at 15 °C, 25 °C and 37 °C, optionally at 5 °C and 50 °C. The institutes can use a method of their choice, but it is expected that a method of the highest available level will be used. Only independent results, obtained by the primary method, will be used to calculate the Key Comparison Reference Value (KCRV). The results will be linked to the KCRV of CCQM-K19.2018. PTB and NMIJ will be the linking laboratories.

2. Coordinating laboratory and contact person

Coordinating laboratory:
Central Office of Measures (GUM)
Electrochemical and Inorganic Analysis Laboratory
Department of Physical Chemistry and Environment
Elektoralna 2
00-139 Warszawa
Poland

Contact person:
Joanna Dumańska
email: joanna.dumanska@gum.gov.pl, phone: +48 22 581 9395

Supporting laboratory:
Slovak Institute of Metrology (SMU)
Karloveská 63
842 55 Bratislava
Slovakia

Contact person:
Zuzana Hankova
email: hankova@smu.gov.sk, phone: +421 2 602 94 708

3. Time schedule

Invitation	February 2024
Registration deadline	31 March 2024
Sample preparation and shipment	August 2024
Reporting deadline	30 November 2024
Draft A	Spring 2025

4. Description of the sample

The solution used for the comparison will be produced by the coordinating laboratory. A borate buffer with a nominal pH value of approximately 9.2 at 25 °C will be prepared from deionized water and disodium tetraborate decahydrate, $Na_2B_4O_7{\cdot}10H_2O$, (material with a purity of 99.5 % to 103.0 % stored in a desiccator over the saturated aqueous solution of NaCl and saccharose at the room temperature). The solution will be homogenized, poured into 1 L type bottles and then closed in aluminized plastic bags.

Bottles labels will indicate: the comparison number, the nominal pH value, the bottle number and the mass fraction of water. Shipment to all participants will start at the same time. The bottles will be shipped by courier. Participants may be asked to arrange transport/delivery of the bottles themselves and pay for it, if necessary. If the shipment is handled by the coordinating laboratory, the tracking number will be reported by email to the contact person of the participating laboratory. The contents will be stated as “Non-hazardous aqueous solution” with a value of 1 € per bottle. Specific customs requirements stated by the laboratories will be considered.

Homogeneity of each solution will be measured from 10 bottles before shipment. Stability will be measured by the primary Harned cell method in intervals of approximately 4 weeks throughout the whole measurement period.

Hydrochloric acid and chloride ion sources will not be provided. It is recommended to dry the alkali chloride at not less than 400 °C for at least 2 hours and then store it over a desiccant prior to use. The mass fraction of water will be stated on the label of the sample bottles.

5. Actions after receipt of samples

- Verification of the delivered sample for possible damages

  Once you receive package with the samples, please remove the packaging and check the bottles for any visible damage or leakage. Please do not remove the Parafilm from the bottles.

- Verification of the sample integrity

  The integrity of each bottle shall be verified upon arrival at a participating laboratory by weighing the bottle and comparing the weighing results with those obtained in the coordinating laboratory. Prior to weighing, equilibrate the bottles in the weighing room overnight. Do not remove the label nor the Parafilm from the bottle before weighing. Each bottle shall be weighed with a balance having 0.01 g resolution. Weighing results, pressure, temperature and relative humidity at the time of weighing shall be filled in the reporting Excel sheet that will be sent together with the final version of this Technical protocol to each participant. Bottle masses will be automatically corrected for air-buoyancy (assuming 1 000 kg m^{-3} density).

- Confirmation to the coordinating laboratory

  Confirm receipt of samples and report bottle masses (corrected for air buoyancy) by sending filled Excel sheet “EURAMET-K19.2018 sample integrity” to the coordinating laboratory by email within two weeks after arrival. If a bottle leak is observed a replacement bottle will be sent as soon as possible.

- Sample storage

  Reseal the bottles into aluminumized bags if you start measurements later. The bottles should be stored at a temperature of 20 °C to 25 °C.

6. Instruction for measurement

- Participants are requested to measure the buffer solution within four weeks of receiving the samples.
- The caps of the bottles may only be opened immediately before the measurements. If possible, the caps should be resealed with Parafilm following each opening.
- Measurements should be performed at the following temperatures: 15 °C, 25 °C and 37 °C, and optionally at 5 °C and 50 °C.
- Recommended values of constants are:
  - Molar gas constant, R = 8.314 462 618 J mol^{-1} K^{-1}
  - Faraday constant, F = 96 485.332 12 C mol^{-1}
- The following conditions are used for primary measurements:
  - The measurements must be evaluated using the standard pressure of 101 325 Pa.
  - The standard potential of the Ag/AgCl electrodes should be determined using hydrochloric acid (aqueous HCl solution) having a molality value close to 0.01 mol kg^{-1}. The actual molality value must be traceable to the SI.
  - Alkali chloride (sodium chloride or potassium chloride) should be added to prepare at least three different buffer solutions with molalities in the range of 0.005 mol kg^{-1} to 0.02 mol kg^{-1}.

7. Reporting

A measurement report must be provided, containing the following information:

- Name and address of the laboratory performing the measurements
- Name(s) of the operator(s)
- Date of receipt of samples
- Identification of the samples (bottle numbers) measured.
- Date(s) of measurement.
- Mass of each bottle (without buoyancy correction), pressure, temperature, and relative humidity at time of weighing.
- Description of the method used, including a photo of the experimental setup, if available.
- Complete uncertainty budget according to the Guide to the Uncertainty in Measurement.

The uncertainty budget of primary measurements must include the following contributions:

- uncertainty of temperature measurement
- uncertainty of standard potential of Ag/AgCl electrodes
- uncertainty of cell potential measurement
- uncertainty of HCl molality
- uncertainty of partial pressure of H_2
- uncertainty of chloride molality
- uncertainty of calculation of acidity function at zero chloride molality.

The uncertainty budget of secondary measurements must include the following contributions:

- uncertainty of the pH measurement standard used
- measurement repeatability
- uncertainty of calibration curve, or uncertainty due to the potential difference between the sample and the standard when measured
- uncertainty of potential measurement as a function of time
- statement that the uncertainty of Bates-Guggenheim Convention is not included
- other contributions resulting from the specific set-up and measurement procedure of the participant.

- The measurement results with the associated standard uncertainties, expanded uncertainties and the corresponding coverage factors *k*, referring to a 95 % probability interval. Note that *k* is 2 if an infinitive number of degrees of freedom can be reasonably assumed.
- The route of traceability.

An Excel template will be provided for reporting. It is recommended to use the template. Please be aware that only a single result may be provided for each kind of solution at each temperature. Other results may be added (e.g. those of additional secondary measurements). However, such results must clearly be identified as additional information. If relevant information cannot reasonably be included in the Excel-file it can be provided in a Word document. The report(s) must be sent to the coordinating laboratory by email before 30 November 2024. The coordinating laboratory will confirm the receipt of the report. If the confirmation does not arrive within one week, please contact the coordinating laboratory to identify the problem.

8. Key comparison reference value

The results will be linked to the KCRV of CCQM-K19.2018. PTB and NMIJ will be the linking laboratories.

9. How Far Does The Light Shines Statement

The HFDTLS statement of CCQM-K19.2018 applies. Participants taking successfully part in EURAMET.QM-K19.2018 will demonstrate their capability to measure the pH of buffer in the alkali range of pH from 8.5 to 9.5 at the temperature range from 5 °C to 50 °C. Borate buffer solution is furthermore a ‘core capability’ buffer in primary Harned cell measurements.