CCQM WG on Electrochemical Analysis and Classical Chemical Methods
CCQM-K91.2022 Key Comparison on pH of an Unknown Phthalate Buffer

Final Report (August 2024)

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Abstract

Key comparison CCQM-K91.2022, a repetition of the previous comparison CCQM-K91 from 2011, was performed to evaluate the degree of equivalence between pH measurement results of an unknown phthalate buffer reported by participating National Metrology Institutes (NMIs) and Designated Institutes (DIs). The participants used the highest-level metrological method existing at their institution. The nominal pH value of the buffer was 4.0 at 25 °C and the suggested measurement temperatures were 5 °C, 15 °C, 25 °C, 37 °C, and 50 °C. There was a good agreement among the results from most participants at 15 °C, 25 °C, and 37 °C. Due to the lack of results, no evaluation was possible of results at 5 °C and 50 °C.

Metrology Area

Amount of substance

Branch

Electrochemistry

Subject

Determinations of the acidity function at zero chloride molality by the primary Harned cell method or of the related pH value by secondary methods with a differential potentiometric cell or glass electrode for an unknown phthalate buffer (pH ≈ 4.0 at 25 °C) at 5 °C, 15 °C, 25 °C, 37 °C, and 50 °C.

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Purpose

This key comparison has been performed to evaluate the degree of equivalence of national standard measurement procedures for the measurement of pH of phthalate buffer solutions under the umbrella of the CIPM-MRA.

The comparison was a repetition of the key comparison CCQM-K91 from 2011 [1].

The comparison was opened to NMIs or DIs of member or associate states of the Meter Convention. Only one result per temperature was accepted from each participant. No measurement method was prescribed for the comparison, but it was expected to be the metrological method at the highest level available at each institution. Only independent results, obtained by the primary method, were used to calculate the Key Comparison Reference Value (KCRV).

In this comparison, measurements of pH were performed at 15 °C, 25 °C, 37 °C and optionally at 5 °C and 50 °C.

Time Schedule

Oral invitation: April 2022 at EAWG spring meeting
Written invitation: June 2022
Registration deadline: 15 July 2022
Dispatch of samples: March 2023
Reporting deadline: 31 July 2023
Presentation of results: EAWG autumn meeting 2023
Draft A report: March 2024
Discussion of Draft A report: March and April 2024
Draft B report: May 2024
Approval of Draft B report: August 2024
Final report: August 2024

Coordinating Laboratory

Instituto Nacional de Metrologia, Qualidade e Tecnologia – INMETRO

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Participants

Table 1. List of participants in CCQM-K91.2022.

Acronym	Country	Institute	Contact Person	Measurement Technique
BFKH	Hungary (HU)	Government Office of the Capital City Budapest	Dániel Nagy Zsófia Nagyné Szilágyi	Primary
BIM	Bulgaria (BG)	Bulgarian Institute of Metrology	Boryana Koleva Lyudmila Dimitrova	Primary
SNSU-BSN	Indonesia (ID)	National Standardization Agency of Indonesia	Ayu Hindayani Dyah Styarini	Secondary (differential)
CENAM	Mexico (MX)	Centro Nacional de Metrología	José Luis Ortiz Aparicio Jazmin Montero Ruiz	Primary
CMI	Czech Republic (CZ)	Czech Metrology Institute	Matilda Roziková Martina Vičarová	Primary
IBMETRO	Bolivia (BO)	Instituto Boliviano de Metrología	Jose Luis Gonzales Quino	Secondary (differential)
INMETRO	Brazil (BR)	Instituto Nacional de Metrologia, Qualidade e Tecnologia	Fabiano Barbieri Gonzaga Leonardo da Silva Pardellas	Primary
INTI	Argentina (AR)	Instituto Nacional de Tecnología Industrial	Ariel Galli Hernán Lozano Mabel Puelles	Secondary (glass)
LATU	Uruguay (UY)	Laboratorio Tecnológico del Uruguay	Simone Fajardo Elizabeth Ferreira Victoria Gelabert	Secondary (differential)
NIM	P.R.China (CN)	National Institute of Metrology, China	Xiu Hongyu Wu Bing	Primary
NMIJ	Japan (JP)	National Metrology Institute of Japan	Masaki Ohata Igor Maksimov	Primary
UME	Turkey (TR)	Tübitak National Metrology Institute	Lokman Liv Emrah Uysal	Primary
VNIIFTRI	Russia (RU)	Russian Metrological Institute of Technical Physics and Radio Engineering	Sergey Prokunin Vladimir Dobrovolskiy	Primary

Sample Preparation and Distribution

The phatalte buffer solution was prepared by the dissolution of 451.695 g of potassium hydrogen phthalate (previously dried at 110 °C for 2 h) in 44156.4 g of deionized water, giving a calculated water mass fraction of 0.989874. The solution was bottled in 1 L high-density polyethylene bottles, properly labeled and sealed with paraffin film, resulting in a batch of 43 bottles.

The solution homogeneity was evaluated before the shipment to the participants and the solution stability was evaluated during the whole measurement period of the comparison, using primary pH measurements for both.

Each participant received one to three bottles of solution, according to the information given at the registration form. Each bottle was previously weighed and closed into an aluminum bag before the shipment. The samples were shipped to all participants 15 March. The dates of the sample receipts are given in Table 5.

No visible damage or leakage was reported by the participants to the coordinating laboratory. The relative variation of the bottle masses (differences between the masses measured by the coordinating laboratory and by the participants) are shown in Figure 1. All relative changes are lower than 0.007%, which are acceptable for key comparisons on pH measurements.

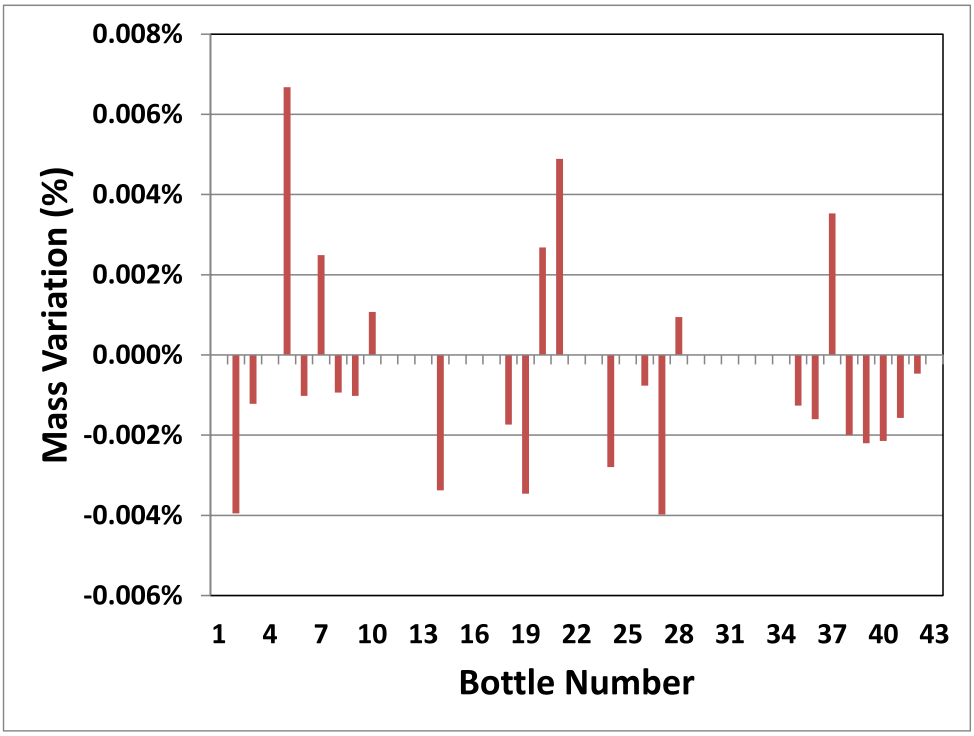

Figure 1. Relative variation of the bottle masses.

Sample Homogeneity

The sample homogeneity was evaluated by three primary pH measurements taken at 25 °C from three bottles: one from the beginning (bottle #1), one from the middle (bottle #22), and one from the end of the batch (bottle #43), considering the order of bottling. The results obtained for the acidity function at zero chloride molality ($\mathrm{p}a^0$) are shown in Table 2 and Figure 2.

Table 2. Results of $\mathrm{p}a^0$ from the homogeneity evaluation.

Bottle Number	Date of Measurement	$\mathrm{p}a^0$	*U* (*k*=2)
1	18 Jan 2023	4.0973	0.0027
43	20 Jan 2023	4.0991	0.0024
22	25 Jan 2023	4.0983	0.0024

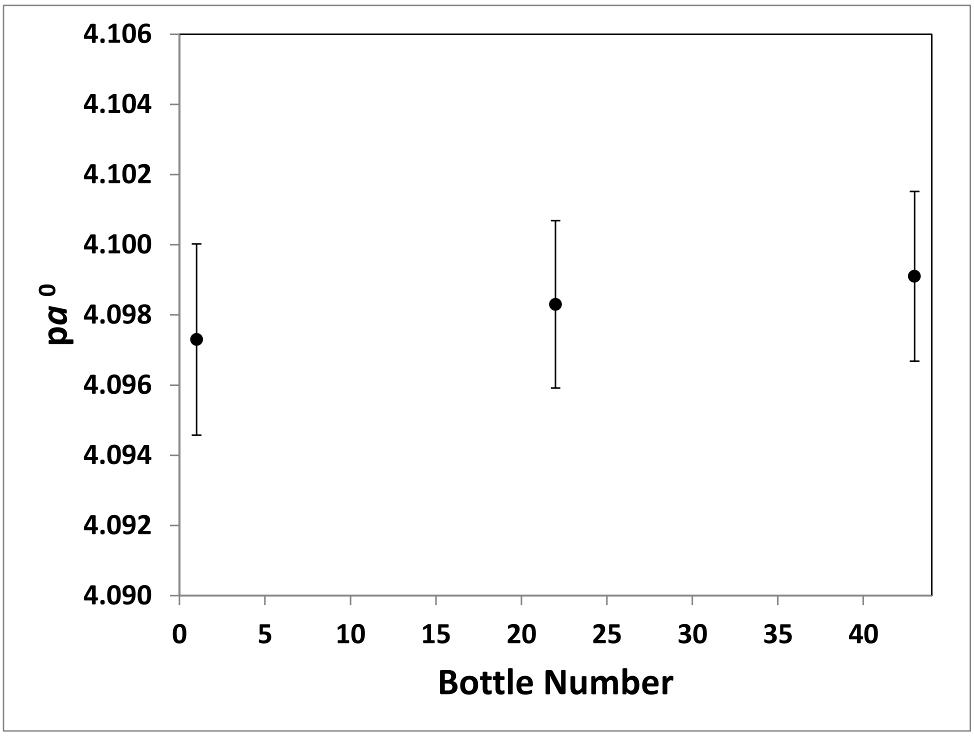

Figure 2. Results of $\mathrm{p}a^0$ from the homogeneity evaluation with expanded uncertainties (*k*=2).

The results obtained can be considered statistically similar to each other according to normalized error tests (all normalized errors were lower than 1, ranging from 0.24 to 0.49). The standard deviation is 0.00090.

Sample Stability

The sample stability was evaluated by seven primary pH measurements taken at 25 °C from seven bottles along the whole measurement period of the comparison (including the results from the homogeneity study). The $\mathrm{p}a^0$ results are shown in Table 3 and Figure 3.

Table 3. Results of $\mathrm{p}a^0$ from the stability evaluation.

Date of Measurement	$\mathrm{p}a^0$	*U* (*k*=2)
18 Jan 2023	4.0973	0.0027
20 Jan 2023	4.0991	0.0024
25 Jan 2023	4.0983	0.0024
15 Mar 2023	4.0986	0.0026
10 May 2023	4.0989	0.0026
21 Jul 2023	4.0985	0.0028
09 Aug 2023	4.0973	0.0027

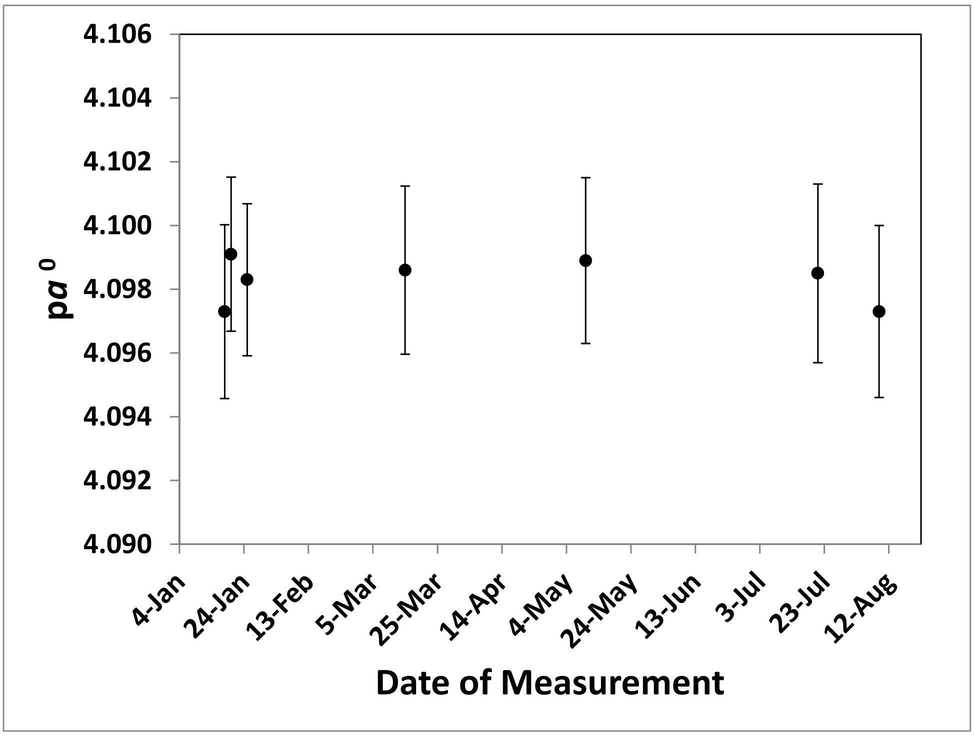

Figure 3. Results of $\mathrm{p}a^0$ from the stability evaluation with expanded uncertainties (*k*=2).

According to the linear regression statistical test (calculated *t* = 0.429 < tabled *t* = 2.571), the sample can be considered stable during the measurement period. The standard deviation is 0.00072.

Communication with Participants

Table 4. Communication between the coordinating laboratory and the participants.

Date	Description
20 Oct 2022	INMETRO asked the participants to confirm their participation in the comparison (after the coordination had been transferred from PTB to INMETRO) and sent them updated versions of the technical protocol and the measurement report template.
21 Oct 2022	LATU asked INMETRO for two extra bottles of the sample. Only one extra bottle could be provided. One extra bottle was also provided to BIM, IBMETRO, NMIJ, and UME, as requested in the registration forms.
08 Dec 2022	INMETRO informed the participants that a new comparison schedule would be proposed due to a delay in receiving bottles and aluminized plastic bags.
04 Jan 2023	INMETRO provided the new comparison schedule to the participants after receiving bottles and bags.
09 Feb 2023	Due to the impossibility of shipping the samples directly to Russia, VNIIFTRI asked INMETRO about the possibility of sending the samples to the Republic of Armenia. INMETRO replied to VNIIFTRI that the shipping to the Republic of Armenia would be possible.

15 Mar 2023	INMETRO announced the shipment of the samples to all participants. In the case of VNIIFTRI, the samples were shipped to a person in the Republic of Armenia and collected there by someone from VNIIFTRI.
29 Mar 2023	BFKH informed INMETRO about a customs problem with the parcel clearing and asked for a supplementary invoice. INMETRO provided the requested documentation.
03 Apr 2023	INMETRO asked INTI for additional information on the weighing data, according to the technical protocol. The requested information was provided by INTI.
27 Apr 2023	NMIJ informed INMETRO about a typing error on the cell D25 (worksheet “Summary”) of the measurement report model. An updated version of the measurement report model was provided by INMETRO to all participants.
22 Jun 2023	VNIIFTRI asked INMETRO for additional time to send the measurement report due to a preventive maintenance in the laboratory.
25 Jun 2023	SNSU-BSN asked INMETRO for additional time to send the measurement report due to a delay for receiving a primary pH standard and a national holiday.
30 Jun 2023	CMI informed INMETRO that the measurement report could be sent only one month later than the original deadline due to staff shortage.
03 Jul 2023	INMETRO announced to all participants the postponement of the reporting deadline from 30 June to 31 July.
14 Aug 2023	INMETRO asked BIM, CENAM, IBMETRO, INTI, and NIM for the dates of pH/acidity function measurements. These institutes reported the dates of mass measurements instead of the dates of pH/acidity function measurements in their measurement reports. All institutes provided the requested information.
01 Nov 2023	INMETRO asked all participants to reply to a survey to choose the best date for an online meeting to discuss the results of the comparison.
13 Nov 2023	INMETRO informed all participants about the date of the online meeting, (05 December, 12:00 UTC+1).
05 Dec 2023	As a result of the online meeting on 05 December (there was no CENAM representative at the meeting), INMETRO informed CENAM the decision to exclude its results from the KCRV calculation (see section “Calculation of the KCRV and its Uncertainty”), provided CENAM agreed. CENAM agreed on the decision.

Timetable of Measurements and Submission of Reports

Table 5. Timetable of shipments, measurements and reports.

Acronym	Bottle Number	Received*	Measured	Report
BFKH	19, 14	31 Mar	15 Jun	30 Jun
BIM	21, 37, 5	29 Mar	06 – 08 Jun	29 Jun
SNSU-BSN	36	27 Mar	20 – 22 Jun	25 Jul
CENAM	28, 10	30 Mar	25 – 28 Jul	31 Jul
CMI	8, 26	23 Mar	19 – 27 Jul	28 Jul
IBMETRO	20, 7	24 Mar	25 – 26 Apr	30 Jun
INMETRO	31, 12	—	10 May – 02 Jun	21 Jun
INTI	3	31 Mar	17 Apr – 18 May	28 Jun
LATU	40, 35	30 Mar	28 – 29 Jun	30 Jun
NIM	42, 9	26 Mar	04 – 10 Apr	29 May
NMIJ	39, 41, 6	23 Mar	03 – 13 Apr	18 Jun
UME	2, 24, 27	20 Mar	24 Mar – 05 Apr	14 Jun
VNIIFTRI	38, 18	04 Apr	07 Jul	31 Jul

* The samples were shipped to all participants 15 Mar.

Measurement Techniques

The participants used the highest-level metrological method existing at their institution. The Harned cell method is the primary measurement method for pH and only results obtained by this method were used for the calculation of the KCRV. The use of secondary methods by the participants, with a differential potentiometric cell or with a glass electrode, was only allowed if these were the highest-level metrological methods existing at their institute. Table 1 provides the measurement technique used by each participant.

The primary measurement method for pH [2] is based on the measurement of the potential difference of "Cell1" without liquid junction:

$$\mathrm{Pt} \mid \mathrm{H_2(g}, p^\circ) \mid \mathrm{buffer}, m_{Cl} \mid \mathrm{AgCl} \mid \mathrm{Ag} \qquad \text{Cell 1}$$

where m_{Cl} is the chloride ion molality added to the chloride free buffer at several chloride molalities in order to stabilize the potential of the Ag/AgCl electrode. The potential difference E_1 of "Cell 1" corrected to the standard pressure, p°, depends on the hydrogen ion activity, a_H, according to Equation 1:

$$E_1 = E^\circ - \frac{RT \ln 10}{F} \cdot \log\left[\left(\frac{a_H}{m^\circ}\right) \cdot \left(\frac{m_{Cl}\gamma_{Cl}}{m^\circ}\right)\right] \qquad \text{Equation 1}$$

where E° is the standard potential of the Ag/AgCl electrode, R is the ideal gas constant, T is the thermodynamic temperature, F is the Faraday constant, m° is equal to 1 mol kg^{-1}, and γ_{Cl} is the activity coefficient of the chloride ion.

The standard potential of the Ag/AgCl electrodes is determined in "Cell 2" and obtained according to Equation 2:

$$\mathrm{Pt} \mid \mathrm{H_2(g}, p^\circ) \mid m_{HCl} \mid \mathrm{AgCl} \mid \mathrm{Ag} \qquad \text{Cell 2}$$

$$E^\circ = E_2 - \frac{2RT \ln 10}{F} \cdot \log\left(\frac{m_{HCl}\gamma_{\pm HCl}}{m^\circ}\right) \qquad \text{Equation 2}$$

where E_2 is the potential difference of “Cell 2” corrected to p°, m_{HCl} is the molality of the HCl solution, whose nominal value is usually equal to 0.01 mol $\mathrm{kg^{-1}}$, and $\gamma_{\pm HCl}$ is the mean activity coefficient of HCl. $\gamma_{\pm HCl}$ values at different measurement temperatures at this nominal molality are given in literature [3].

Values for the acidity function, $\mathrm{p}a$, are then calculated for each measured E_1 value, as a function of m_{Cl}, according to Equation 3:

$$\mathrm{p}a = \frac{(E_1 - E^\circ)F}{RT \ln 10} + \log\left(\frac{m_{Cl}}{m^\circ}\right) \qquad \text{Equation 3}$$

Finally, the acidity function at zero chloride molality, $\mathrm{p}a^0$, is obtained from a linear extrapolation of the $\mathrm{p}a$ values to $m_{Cl} = 0$. The reported results for the key comparison CCQM-K91.2022 are $\mathrm{p}a^0$ values at different measurement temperatures.

Both secondary potentiometric methods, either using a differential potentiometric cell or a glass electrode, are based on measuring the pH value of the key comparison buffer with respect to primary standard solutions. The differential electrochemical cell, “Cell 3”, is used in the differential potentiometric cell method:

$$\mathrm{Pt} \mid \mathrm{H_2(g}, p^\circ) \mid \mathrm{buffer\ S_1} \parallel \mathrm{buffer\ S_2} \mid \mathrm{H_2(g}, p^\circ) \mid \mathrm{Pt} \qquad \text{Cell 3}$$

where $\mathrm{S_1}$ and $\mathrm{S_2}$ represent two quasi-identical buffers (the key comparison buffer and a primary standard solution), and || is a physical barrier constructed of a porous diaphragm that separates the two buffers. The pH of an unknown buffer (the key comparison buffer), $\mathrm{pH(S_2)}$, is given by Equation 4:

$$\mathrm{pH(S_2)} = \mathrm{pH(S_1)} - \left(E_3 - E_j\right) \cdot \frac{F}{RT \ln 10} \qquad \text{Equation 4}$$

where E_3 is the potential difference determined in “Cell 3”, and E_j is the liquid junction potential that forms between the physically separated $\mathrm{S_1}$ and $\mathrm{S_2}$ buffer solutions. Provided that $\mathrm{S_1}$ and $\mathrm{S_2}$ are quasi-identical in composition, $|\mathrm{pH(S_2)} - \mathrm{pH(S_1)}| \leq 0.02$ and $3 < \mathrm{pH} < 11$, then the relationship $\left|E_j\right| \leq 0.1E_3$ is assumed.

Many commercial pH meters have a combined glass electrode with the following cell type, “Cell 4”:

$$\mathrm{Ag} \mid \mathrm{AgCl} \mid \mathrm{conc.\ KCl} \parallel \mathrm{buffer} \mid \mathrm{glass} \mid \mathrm{dil.\ HCl} \mid \mathrm{AgCl} \mid \mathrm{Ag} \qquad \text{Cell 4}$$

The outer surface of the glass membrane at this electrode is directly affected by the hydrogen ion activity of the buffer solution under measurement. Then, the potential difference between the two Ag/AgCl electrodes at both ends is changed in a similar way as described in Equation 4. Usually, a pH meter is calibrated with two to five different primary standard solutions, and then an unknown buffer solution can be measured.

As the results reported by the participants that used secondary methods are pH values, the Bates-Guggenheim Convention was used to convert these results to $\mathrm{p}a^0$ values, allowing a direct comparison among all reported results (from the primary and secondary methods), according to Equation 5 and Equation 6:

$$\log \gamma°_{Cl} = \frac{-A\sqrt{I}}{1 + 1.5\sqrt{I}} \qquad \text{Equation 5}$$

$$\mathrm{p}a^0 = \mathrm{pH} - \log \gamma°_{Cl} \qquad \text{Equation 6}$$

where A is the Debye-Hückel temperature-dependent constant, I is the ionic strength of the buffer solution, and $\gamma°_{Cl}$ is the trace activity coefficient of the chloride ion.

Results and Discussion

The measurements of CCQM-K91.2022 were performed at 15 °C, 25 °C, and 37 °C, with a supplementary option of measurements at 5 °C and 50 °C. Results of $\mathrm{p}a^0$ from all participants are given in Table 6 and shown in Figure 4 to Figure 6. Where necessary, the results were rounded to four decimal places. Due to the low number of reported results at 5 °C and 50 °C, only one and two, respectively, these results and the related data are not shown graphically and will not be evaluated in this report (no KCRV and degrees of equivalence will be calculated).

Table 6. Results of $\mathrm{p}a^0$ with standard uncertainties (*k*=1).

Acronym	$\mathrm{p}a^0$ at 15 °C $u(\mathrm{p}a^0)$	$\mathrm{p}a^0$ at 25 °C $u(\mathrm{p}a^0)$	$\mathrm{p}a^0$ at 37 °C $u(\mathrm{p}a^0)$	$\mathrm{p}a^0$ at 5 °C $u(\mathrm{p}a^0)$	$\mathrm{p}a^0$ at 50 °C $u(\mathrm{p}a^0)$
BFKH	4.0853 0.0028	4.0957 0.0024	4.1156 0.0027	---	---
BIM	4.0834 0.0022	4.0951 0.0022	4.1182 0.0022	---	4.1543 0.0023
SNSU-BSN*	---	4.0915 0.0023	---	---	---
CENAM	4.0830 0.0173	4.1032 0.0133	4.1577 0.0171	---	---
CMI	4.0876 0.0011	4.0954 0.0010	4.1158 0.0009	---	---
IBMETRO*	---	4.0907 0.0051	---	---	---
INMETRO	4.0907 0.0013	4.0989 0.0013	4.1176 0.0015	---	---
INTI*	---	4.1146 0.0180	---	---	---
LATU*	---	4.0966 0.0016	---	---	---
NIM	4.0845 0.0018	4.0931 0.0018	4.1132 0.0018	---	---
NMIJ	4.0867 0.0014	4.0948 0.0013	4.1155 0.0013	4.0890 0.0016	4.1516 0.0016
UME	---	4.0924 0.0029	---	---	---
VNIIFTRI	4.0869 0.0018	4.0952 0.0017	4.1158 0.0018	---	---

* The pH values from secondary methods were converted to $\mathrm{p}a^0$ values.

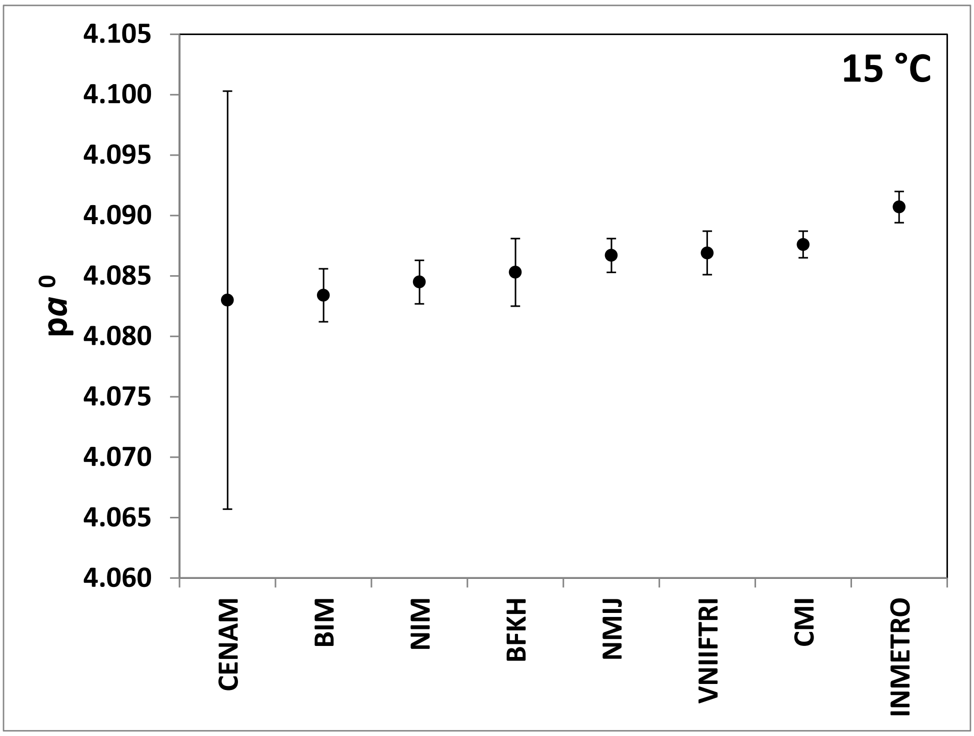

Figure 4. Results of pa^0 at 15 °C with standard uncertainties (*k*=1).

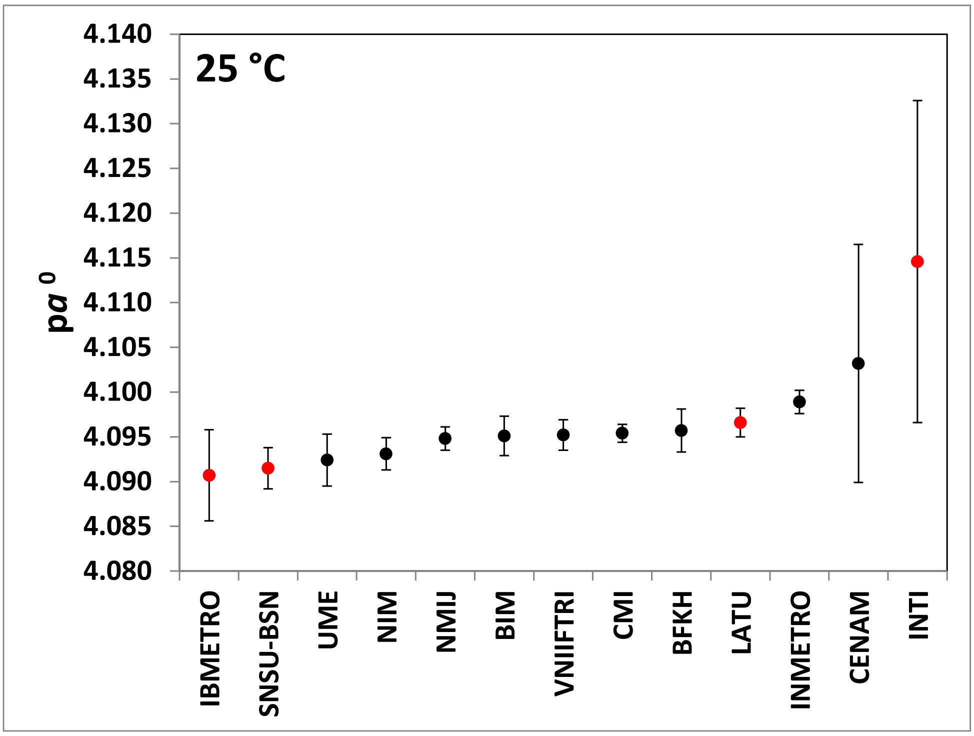

Figure 5. Results of pa^0 at 25 °C with standard uncertainties (*k*=1); black dots: primary method, red dots: secondary methods.

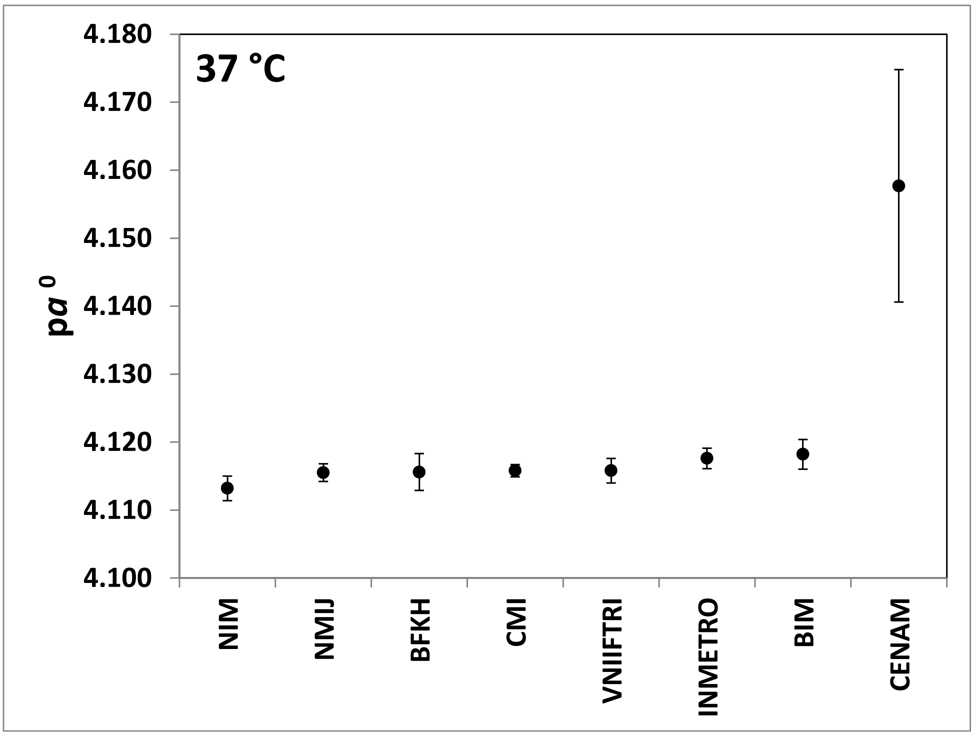

Figure 6. Results of $\mathrm{p}a^0$ at 37 °C with standard uncertainties (*k*=1).

In general, there is a good agreement among the $\mathrm{p}a^0$ results (for each measurement temperature), when taking into account the standard uncertainties, except for the CENAM’s result at 37 °C, which is significantly higher than the other ones. A Grubbs test indicated that the CENAM’s result at 37 °C is possibly an anomalous value (calculated Z = 2.462 > tabled Z = 2.127).

Additionally, the participants using the primary method also reported the HCl molalities and standardization methods, given in Table 7, the Ag/AgCl standard potentials, given in Table 8 and Figure 7 to Figure 9, and the $\mathrm{p}a$ slopes (from the linear regression against zero chloride molality), also given in Table 8. Where necessary, the HCl molalities were rounded so that their uncertainties have two significant digits, the Ag/AgCl standard potentials were rounded to six decimal places, and the $\mathrm{p}a$ slopes were rounded to four decimal places.

Table 7. Information on the HCl molality and standardization method.

Acronym	Method	Molality (mol kg^{-1})	*u* (mol kg^{-1})
BFKH	Coulometric titration	0.0100494	0.0000053
BIM	Potentiometric titration	0.010080	0.000024
CENAM	Coulometric titration	0.009998	0.000013
CMI	Coulometric titration	0.0100053	0.0000020
INMETRO	Coulometric titration	0.0099994	0.0000025
NIM	Coulometric titration	0.010007	0.000010
NMIJ	Coulometric titration	0.0099998	0.0000050
UME	Coulometric titration	0.0105939	0.0000070
VNIIFTRI	Coulometric titration	0.009959	0.000010

Table 8. Information on the Ag/AgCl standard potential, with standard uncertainties (k=1), and the $\mathrm{p}a$ extrapolation slope to zero chloride molality.

Acronym	E° at 15 °C (V) $u(E^\circ)$ (V) $\mathrm{p}a$ slope	E° at 25 °C (V) $u(E^\circ)$ (V) $\mathrm{p}a$ slope	E° at 37 °C (V) $u(E^\circ)$ (V) $\mathrm{p}a$ slope	E° at 5 °C (V) $u(E^\circ)$ (V) $\mathrm{p}a$ slope	E° at 50 °C (V) $u(E^\circ)$ (V) $\mathrm{p}a$ slope
BFKH	0.228899	0.222549	0.213789	---	---
	0.000039	0.000039	0.000040		
	−24.4681	−24.7708	−26.3324		
BIM	0.228604	0.222260	0.214254	---	0.204483
	0.000123	0.000130	0.000132		0.000136
	−0.4665	−0.3318	−0.7245		−0.7727
CENAM	0.229135	0.222336	0.214575	---	---
	0.000022	0.000029	0.000024		
	−8.8451	−9.3997	−7.7855		
CMI	0.228787	0.222625	0.214476	---	---
	0.000029	0.000030	0.000031		
	−0.6327	−0.5913	−0.5911		
INMETRO	0.228634	0.222497	0.214385	---	---
	0.000026	0.000022	0.000025		
	−0.6833	−0.6899	−0.6380		
NIM	0.228680	0.222570	0.214450	---	---
	0.000063	0.000064	0.000063		
	−0.5593	−0.5917	−0.6441		
NMIJ	0.228702	0.222561	0.214429	0.234140	0.204626
	0.000051	0.000044	0.000045	0.000052	0.000054
	−0.6594	−0.6613	−0.6741	−0.6475	−0.7550
UME	---	0.221992	---	---	---
		0.000070			
		−0.4013			
VNIIFTRI	0.227701	0.222161	0.214130	---	---
	0.000074	0.000074	0.000074		
	−0.1888	−0.9266	−0.9802		

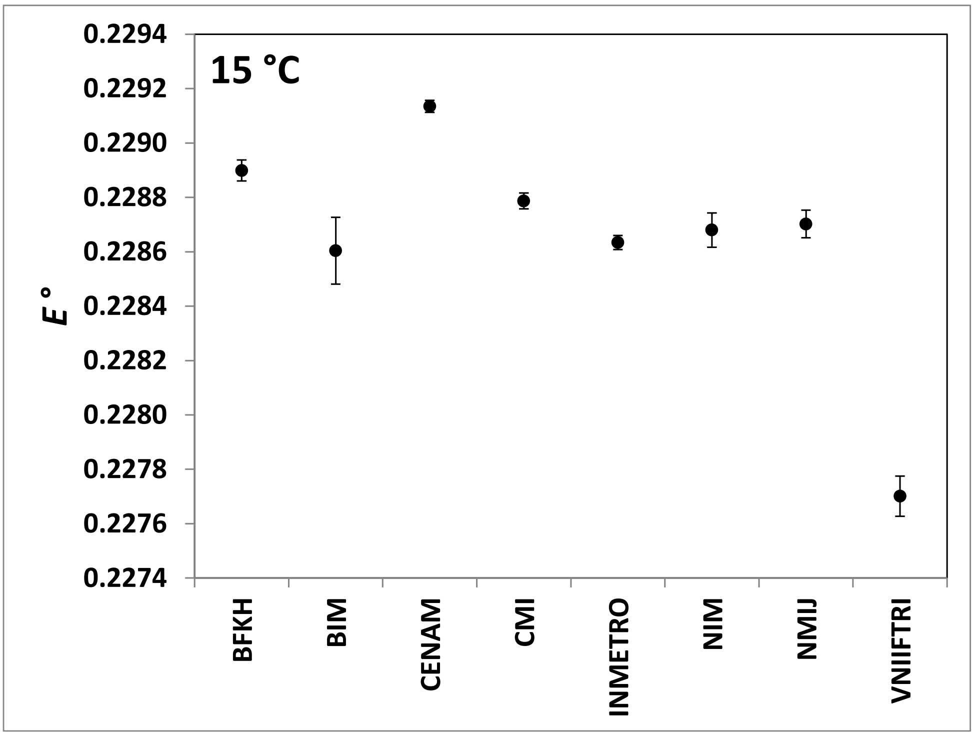

Figure 7. Results of Ag/AgCl standard potential at 15 °C with standard uncertainties (*k*=1).

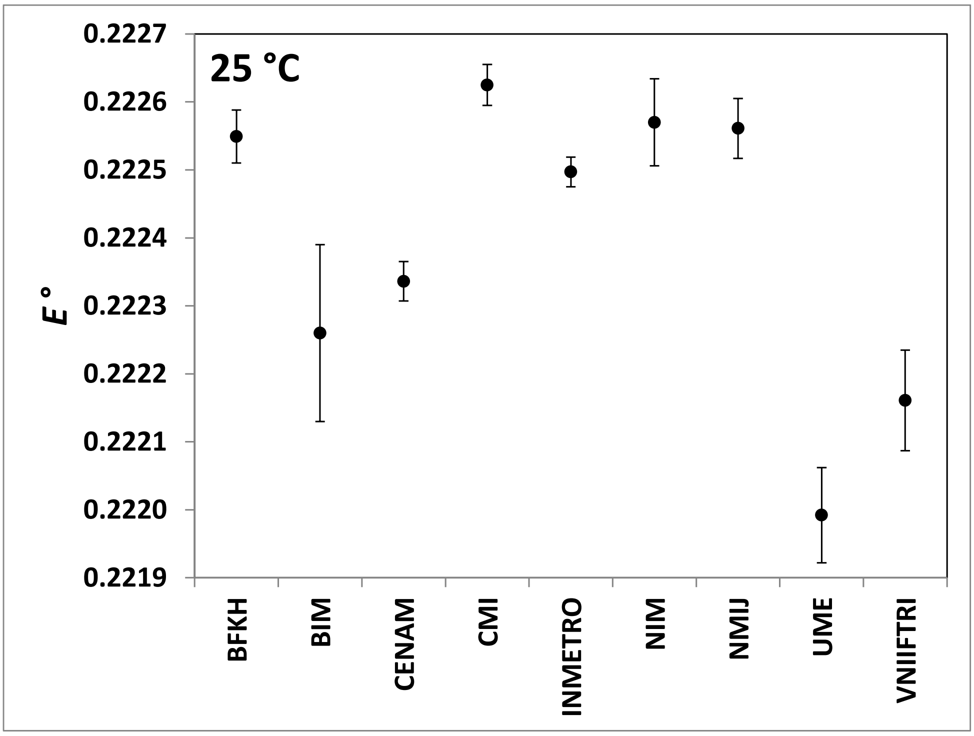

Figure 8. Results of Ag/AgCl standard potential at 25 °C with standard uncertainties (*k*=1).

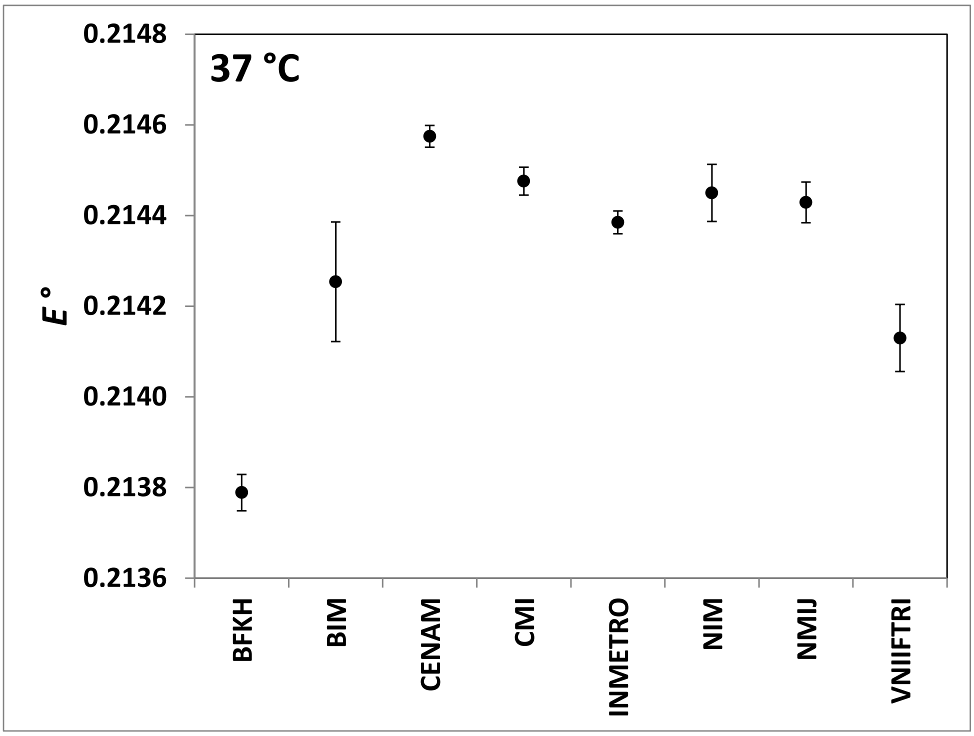

Figure 9. Results of Ag/AgCl standard potential at 37 °C with standard uncertainties (*k*=1).

For the Ag/AgCl standard potentials, the reported values agree quite well to the literature reference value [4], and to each other, except for the VNIIFTRI's value at 15 °C, the UME's value at 25 °C, and the BFKH's value at 37 °C, which are significantly lower than the other values. However, these deviations from the other values did not affect the $\mathrm{p}a^0$ results of these participants at the cited temperatures.

Before the KCRV calculation, the $\mathrm{p}a^0$ results were inspected for anomalous values, as shown in Figure 10 to Figure 12, using the function $[\mathrm{p}a^0 - \mathrm{median}(\mathrm{p}a^0)]/u(\mathrm{p}a^0)$ as a parameter of relative consistency. In this case, results from secondary methods were not evaluated since they are not taken into account for KCRV calculation. The $\mathrm{p}a^0$ results were also evaluated in correlation to their $\mathrm{p}a$ slopes, as shown in Figure 13 to Figure 15.

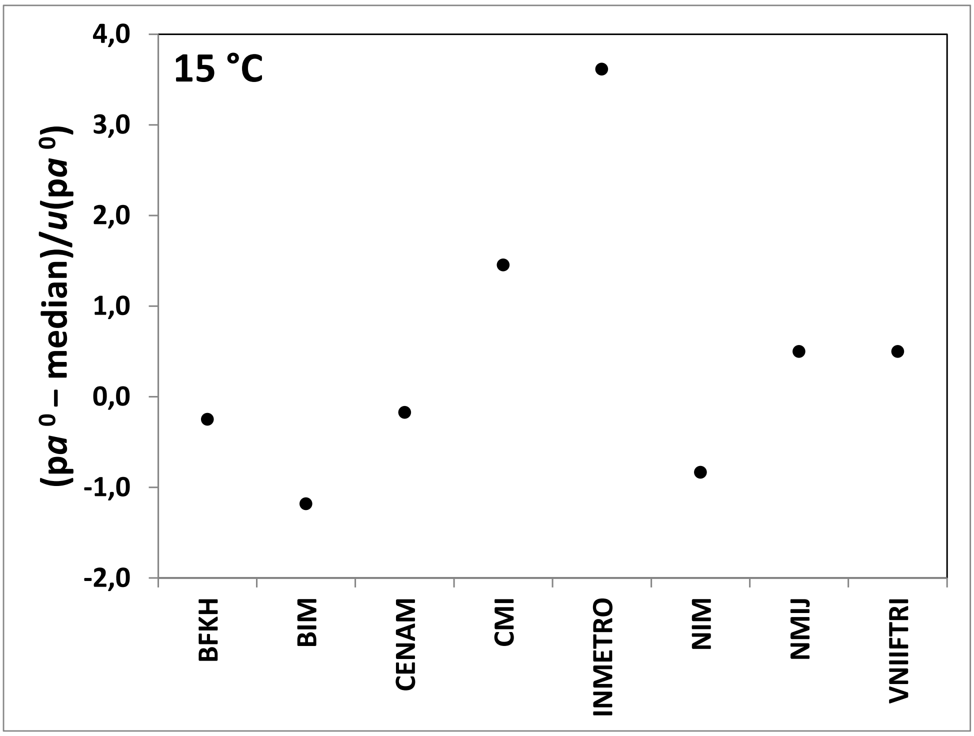

Figure 10. Inspection for anomalous pa^0 results at 15 °C.

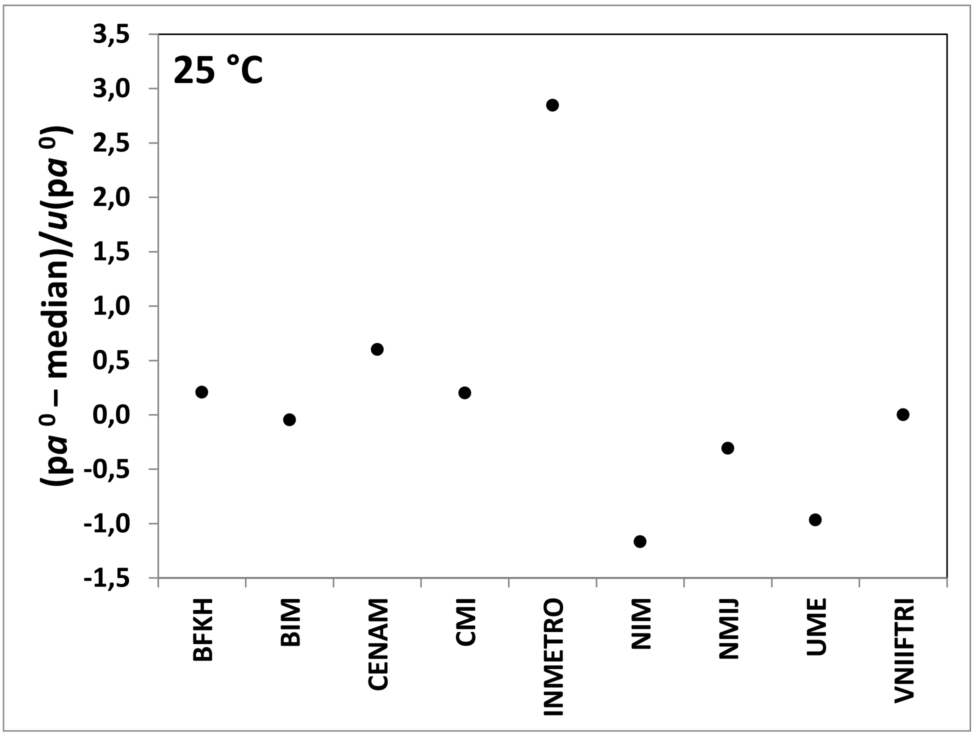

Figure 11. Inspection for anomalous pa^0 results at 25 °C.

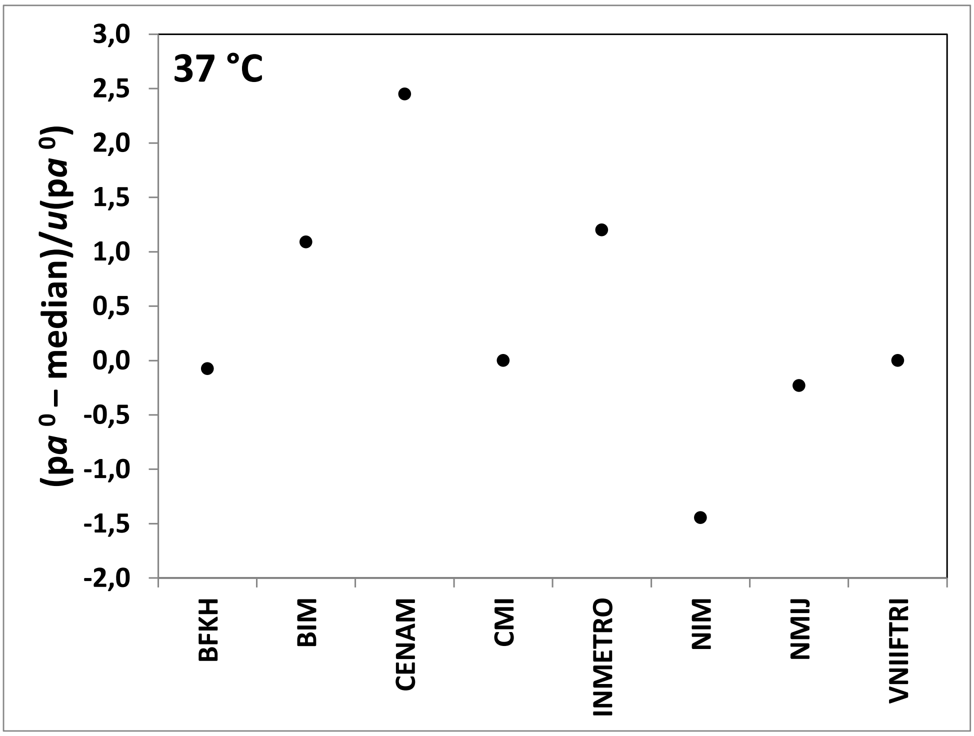

Figure 12. Inspection for anomalous pa^0 results at 37 °C.

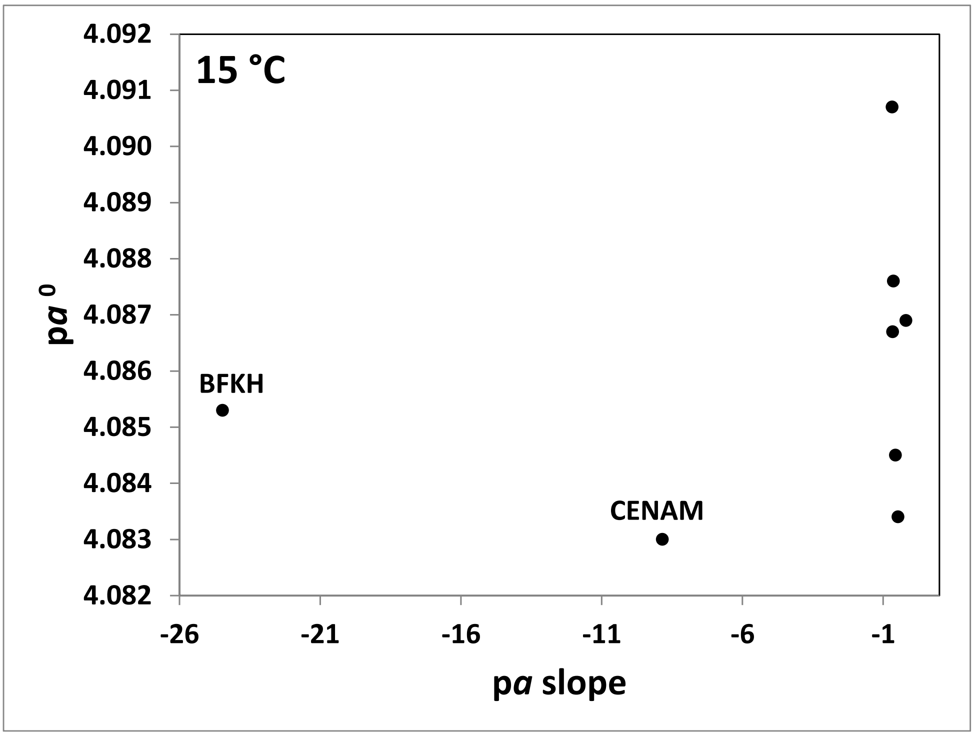

Figure 13. Comparison between the pa^0 results and pa slopes at 15 °C.

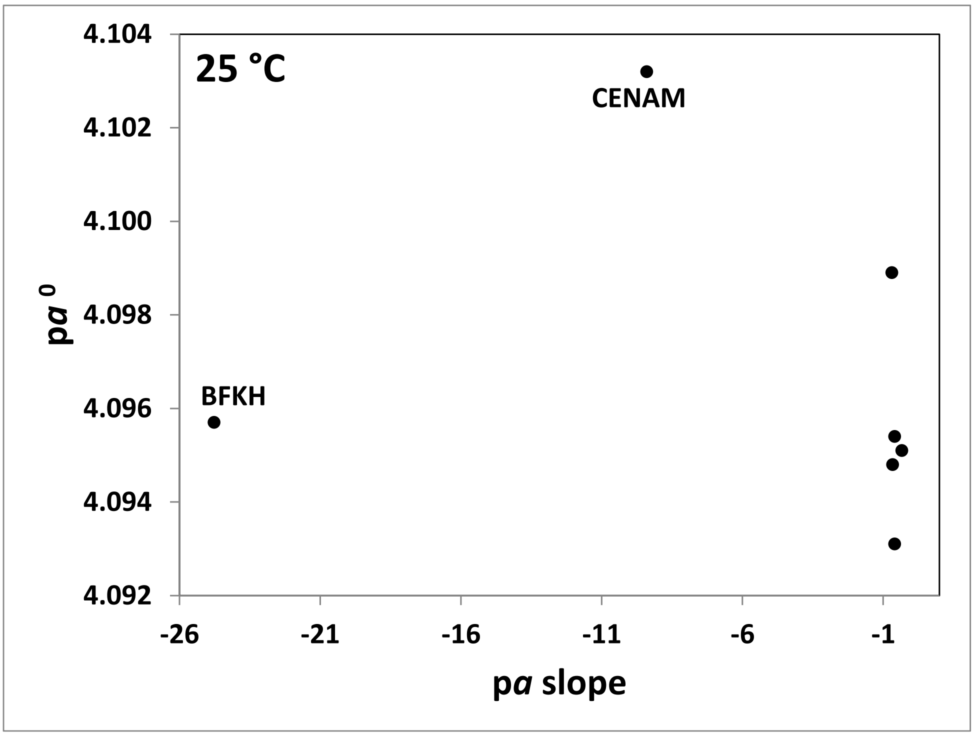

Figure 14. Comparison between the $\mathrm{p}a^0$ results and $\mathrm{p}a$ slopes at 25 °C.

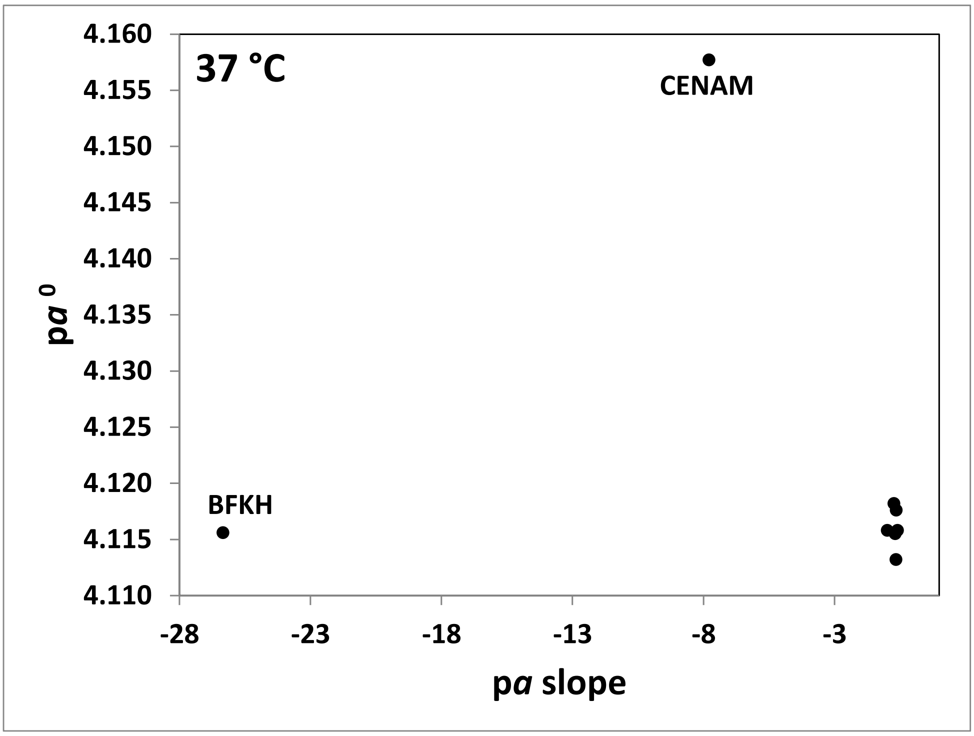

Figure 15. Comparison between the $\mathrm{p}a^0$ results and $\mathrm{p}a$ slopes at 37 °C.

Although INMETROS's results for the expression $[\mathrm{p}a^0 - \mathrm{median}(\mathrm{p}a^0)]/u(\mathrm{p}a^0)$ deviate the furthest from zero at 15 and 25 °C, they are not as high as to consider the corresponding $\mathrm{p}a^0$ results anomalous at these temperatures, as can be seen in Figure 4 and Figure 5. In addition, although CENAM's $\mathrm{p}a^0$ result is significantly higher compared to the other results at 37 °C (as discussed before), the expression $[\mathrm{p}a^0 - \mathrm{median}(\mathrm{p}a^0)]/u(\mathrm{p}a^0)$ does not defer significantly due to the large uncertainty of the $\mathrm{p}a^0$ result.

In relation to the $\mathrm{p}a$ slopes, most values are between 0 and −1, except for the CENAM's and BFKH's values, which are lower than −7 and −24, respectively. Usually, more negative values show a tendency to result in higher $\mathrm{p}a^0$ results (and vice versa). This tendency can be seen in the CENAM's $\mathrm{p}a^0$ results at 25 and 37 °C. It was not possible to explain why the BFKH's values were so low. However, no effect was observed in the BFKH's $\mathrm{p}a^0$ results.

Calculation of the KCRV and its Uncertainty

EAWG (online meeting of December 5th, 2023) decided to exclude the CENAM's results from the calculation of the KCRV for all measurement temperatures, with CENAM kindly accepting the decision. The main reason, in addition to the points raised in the previous section, was that CENAM's results varied in an unexplained way with measurement temperature (the result at 15 °C was the lowest one whereas the results at 25 °C and 37 °C were the highest ones compared to the other primary results – and with a significantly higher deviation at 37 °C). Also considering the large uncertainty stated by CENAM it seems that there is a problem with repeatability.

Five possibilities for determination of the KCRV are listed in Table 9 [5,6]. For each estimator, only results obtained using the primary method were used in the calculation, excluding the CENAM's results.

Table 9. Values of candidate estimators for the KCRV.

Estimator	15 °C		25 °C		37 °C	
	Value	u (*k*=1)	Value	u (*k*=1)	Value	u (*k*=1)
Arithmetic Mean	4.0864	0.0009	4.0951	0.0007	4.1160	0.0006
Median	4.0867	0.0010	4.0952	0.0003	4.1158	0.0002
Weighted Mean U[1]	4.0873	0.0006	4.0956	0.0005	4.1159	0.0006
Weighted Mean C[2]	4.0873	0.0009	4.0956	0.0007	4.1159	0.0005
DerSimonian-Laird[3]	4.0869	0.0009	4.0955	0.0007	4.1159	0.0004
Birge Ratio	1.484		1.202		0.890	

[1] uncorrected for observed dispersion (selected as KCRV), [2] corrected for observed dispersion, [3] according to NIST Consensus Builder [6].

EAWG (online meeting of December 5th, 2023) also decided to use the weighted mean uncorrected for observed dispersion as the KCRV for all measurement temperatures.

The KCRV and its standard uncertainty, $u(\mathrm{KCRV})$, were calculated for each measurement temperature using Equation 7 to Equation 9 [5]:

$$\mathrm{KCRV} = \sum_{i=1}^{m} w_i x_i \qquad \text{Equation 7}$$

where

$$w_i = \frac{\left(\frac{1}{u(x_i)}\right)^2}{\sum_{j=1}^{m}\left(\frac{1}{u(x_j)}\right)^2} \qquad \text{Equation 8}$$

and x_i, x_j are the pa^0 results.

$$\frac{1}{u^2(\mathrm{KCRV})} = \sum_{i=1}^{m} \frac{1}{u^2(x_i)} \qquad \text{Equation 9}$$

Calculation of the Degrees of Equivalence

The degree of equivalence for each participant, d_i, is given by Equation 10:

$$d_i = x_i - \mathrm{KCRV} \qquad \text{Equation 10}$$

For the results used in calculation of the KCRV, the standard uncertainty for the degree of equivalence, $u(d_i)$, is given by Equation 11:

$$u(d_i) = \sqrt{u^2(x_i) - u^2(\mathrm{KCRV})} \qquad \text{Equation 11}$$

For the results not used in the calculation of the KCRV (from secondary methods and CENAM), $u(d_i)$ is given by Equation 12:

$$u(d_i) = \sqrt{u^2(x_i) + u^2(\mathrm{KCRV})} \qquad \text{Equation 12}$$

The expanded uncertainties, $U(d_i)$, are calculated with a coverage factor, *k*, equal to 2.

The minimum standard uncertainties for CMC claims, $u(\mathrm{CMC_{min}})$, were calculated using the following procedure [7].

The best estimate x_i reported by an institute is assumed to be consistent with the KCRV if:

$$|d_i| \leq U(d_i) \qquad \text{Equation 13}$$

then, $u(\mathrm{CMC_{min}})$ is given by Equation 14:

$$u(\mathrm{CMC}_{\mathrm{min},i}) = u(x_i) \qquad \text{Equation 14}$$

The best estimate x_i is assumed to be inconsistent with the KCRV if:

$$|d_i| > U(d_i) \qquad \text{Equation 15}$$

then, $u(\mathrm{CMC}_{\mathrm{min}})$ is given by Equation 16:

$$u(\mathrm{CMC}_{\mathrm{min},i}) = \sqrt{u^2(d_i) + \left(\frac{d_i}{2}\right)^2} \qquad \text{Equation 16}$$

The expanded uncertainties, $U(\mathrm{CMC}_{\mathrm{min}})$, are calculated with a coverage factor, *k*, equal to 2.

The degrees of equivalence with expanded uncertainties are given in Table 10 to Table 12 and in Figure 16 to Figure 18. The $U(\mathrm{CMC}_{\mathrm{min}})$ values are also given in the tables.

Table 10. Degrees of equivalence with expanded uncertainties (*k*=2) at 15 °C.

Acronym	d_i	$U(d_i)$	$U(\mathrm{CMC}_{\mathrm{min}})$
BFKH	−0.0020	0.0055	0.0056
BIM	−0.0039	0.0042	0.0044
CENAM	−0.0043	0.0346	0.0346
CMI	0.0003	0.0019	0.0022
INMETRO	0.0034	0.0023	0.0041
NIM	−0.0028	0.0034	0.0036
NMIJ	−0.0006	0.0025	0.0028
VNIIFTRI	−0.0004	0.0034	0.0036

Table 11. Degrees of equivalence with expanded uncertainties (*k*=2) at 25 °C.

Acronym	d_i	$U(d_i)$	$U(\mathrm{CMC}_{\mathrm{min}})$
BFKH	0.0001	0.0047	0.0048
BIM	−0.0005	0.0043	0.0044
SNSU-BSN	−0.0041	0.0047	0.0046
CENAM	0.0076	0.0266	0.0266
CMI	−0.0002	0.0017	0.0020
IBMETRO	−0.0049	0.0103	0.0102
INMETRO	0.0033	0.0024	0.0041
INTI	0.0190	0.0360	0.0360
LATU	0.0010	0.0034	0.0032
NIM	−0.0025	0.0034	0.0036
NMIJ	−0.0008	0.0024	0.0026
UME	−0.0032	0.0057	0.0058
VNIIFTRI	−0.0004	0.0032	0.0034

Table 12. Degrees of equivalence with expanded uncertainties (*k*=2) at 37 °C.

Acronym	d_i	$U(d_i)$	$U(\mathrm{CMC_{min}})$
BFKH	−0.0003	0.0053	0.0054
BIM	0.0023	0.0043	0.0044
CENAM	0.0418	0.0342	0.0540
CMI	−0.0001	0.0014	0.0018
INMETRO	0.0017	0.0028	0.0030
NIM	−0.0027	0.0034	0.0036
NMIJ	−0.0004	0.0023	0.0026
VNIIFTRI	−0.0001	0.0034	0.0036

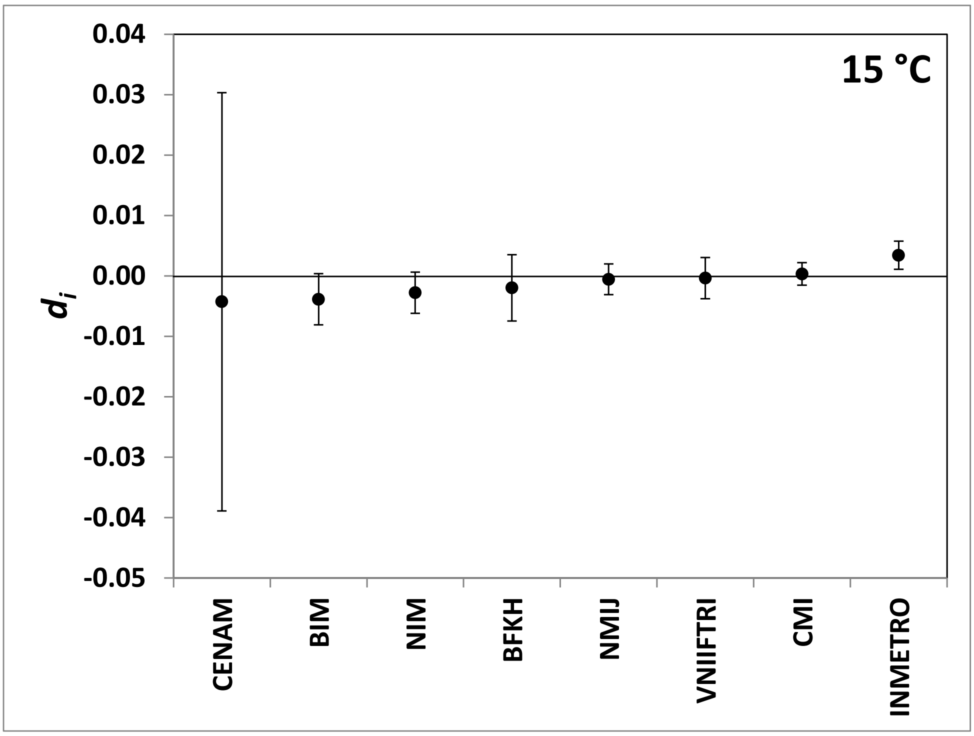

Figure 16. Degrees of equivalence with expanded uncertainties (*k*=2) at 15 °C.

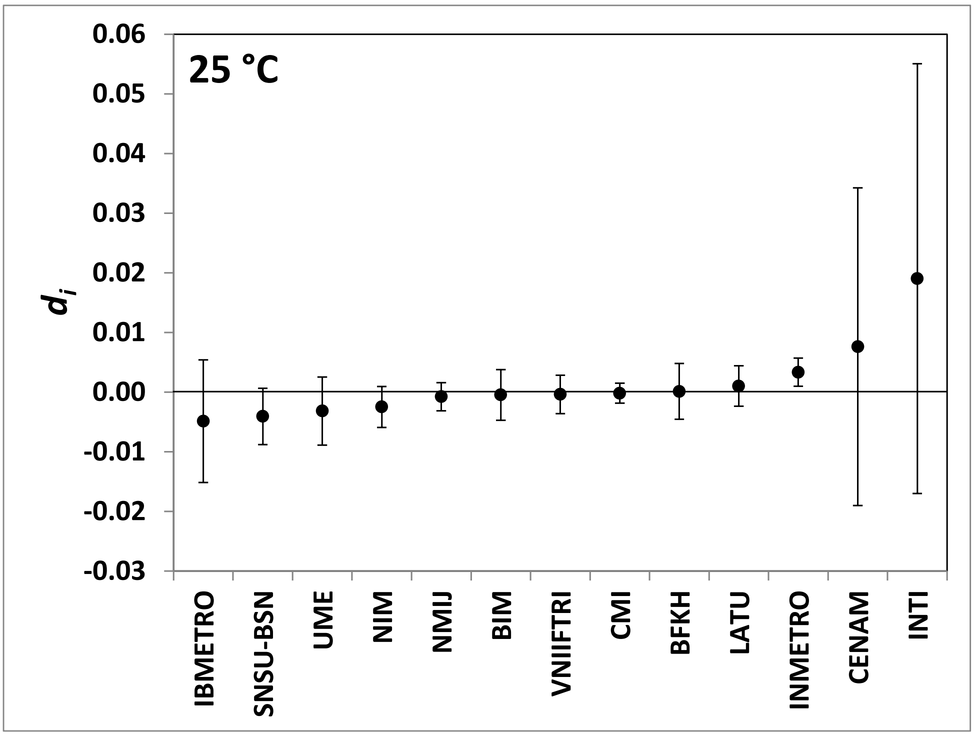

Figure 17. Degrees of equivalence with expanded uncertainties (k=2) at 25 °C.

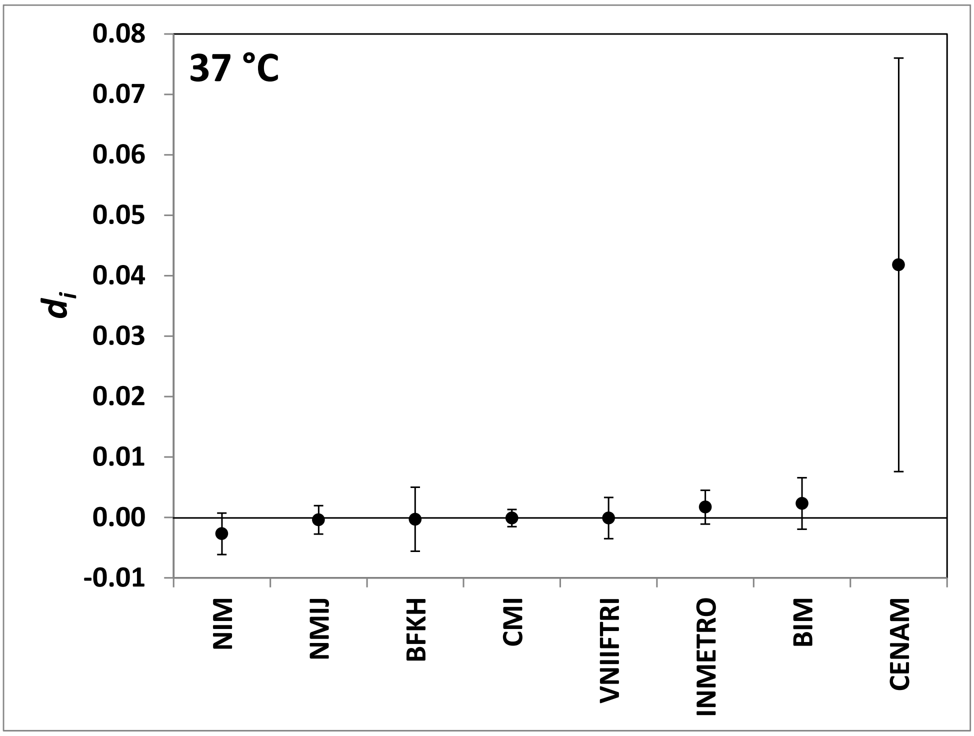

Figure 18. Degrees of equivalence with expanded uncertainties (k=2) at 37 °C.

Conclusion

Comparability of measurement results was successfully demonstrated by many participating NMIs for the measurement of pH of a phthalate buffer within related expanded uncertainties from 15 °C to 37 °C. It is expected that the performance of each participant in the present key comparison is representative for measurement of pH of a phthalate buffer with the same technique as used in the present comparison. Due to the lack of results, no conclusion was possible for the comparability of measurement at 5 °C and 50 °C.

How far the Light Shines

Phthalate buffer solution is widely used in an acid pH range and is an "extended capability" buffer in primary Harned cell measurements. Participants that successfully took part in the CCQM-K91.2022 key comparison have demonstrated their capability to measure the pH of phthalate buffers with the method applied in this comparison (see Table 1), in the pH range from 3.6 to 4.6, and in the temperature range from 15 °C to 37 °C. The corresponding measurement uncertainties for each temperature must be assessed in reviewing CMC claims. Participants that successfully took part in this key comparison may use this key comparison to support CMCs in other ranges in accordance with the requirements specified in section 3 of the CMC guidelines of EAWG [7].

Acknowledgment

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