CIPM MRA
Comparison reports

CCQM-K173.2

Assay of sodium carbonate

KEY COMPARISON

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CCQM WG on Electrochemical Analysis and Classical Chemical Methods

CCQM-K173.2 - Assay of sodium carbonate

Final report

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12 November 2025

Summary

The CCQM key comparison CCQM-K173.2 is a subsequent comparison to CCQM-K173. It was based on a request of INMETRO for a bilateral comparison; KEBS and BFKH joined also to demonstrate their capability to measure the amount content of bases. The institutes could use a method of their choice, although the use of coulometry or titrimetry with potentiometric determination of the endpoint was expected. The result of SMU was used as a link to the original comparison CCQM-K173.

The results of KEBS and BFKH were in good agreement with the reference value; a probable reason for the slight deviation of INMETRO's result was suggested.

1 - Slovak Institute of metrology (SMU), Slovakia
2 - Instituto Nacional de Metrologia, Qualidade e Tecnologia (INMETRO), Brazil
3 - Government Office of the Capital City Budapest (BFKH), Hungary
4 - Kenya Bureau of Standards (KEBS), Kenya

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CCQM-K173.2

1 Coordinating laboratory and contact person

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2 List of participants

Table 1. List of participants.

Institute	Acronym	Country	Contact person	Email
Slovak Institute of Metrology	SMU	SK	Michal Mariassy	mariassy@smu.gov.sk
Instituto Nacional de Metrologia, Qualidade e Tecnologia	INMETRO	BR	Paulo Paschoal Borges	ppborges@inmetro.gov.br
Government Office of the Capital City Budapest	BFKH	HU	Daniel Nagy	nagy.daniel2@bfkh.gov.hu
Kenya Bureau of Standards	KEBS	KE	Tabitha Orwa Ahuya	orwat@kebs.org

3 Time schedule

Preparation of Technical protocol	February 2025
Dispatch of samples:	March 2025
Reporting deadline:	31 May 2025
Draft A report:	20 August 2025
Discussion:	by e-mail, August-September 2025
Draft B report:	September 2025
Draft B report approval:	EAWG meeting, October 2025

4 Description of samples

Samples for comparison were prepared and distributed by INMETRO. The assay was expected to be in the range of 99.7 % to 100.1% of the theoretical value based on the sodium carbonate amount content.
The source of the sample was from a 1 kg batch of commercially available pure sodium carbonate powder. After being homogenized, the material was transferred to 65 glass bottles closed with plastic caps for the comparison.

Each glass bottle contained approximately 15 g of material and was closed with a plastic stopper and screw cap.
The samples were shipped by air courier on 03 and 04 April 2025 and arrived at their destination without damage within two weeks (see table 2).

4.1 Homogeneity and stability

Six bottles, selected at random, were tested by INMETRO for homogeneity using coulometric titration. Three independent samples from each bottle were analyzed. Data obtained were evaluated by one-way ANOVA. Summary results of homogeneity assessment and figures of merit for the samples of sodium carbonate are given in Table 2 and Table 3, respectively, and in Figure 1.

Table 2. Results of the homogeneity assessment for amount content of bases expressed as sodium carbonate by ANOVA

Source of variation	*SS*	*df*	*MS*	*F*	*P-Value*	*F critical*
Between groups	1.863E-05	5	3.725E-06	0.67986	0.64725	3.10588
Within groups	6.575E-05	12	5.479E-06			
Total	8.438E-05	17				

Table 3. The figures of merit

Within groups (CV_{wth}) $CV_{wth} = \frac{MS_{wth}}{\bar{X}.100\%}$	0.0058%
Between groups (CV_{btw}) $CV_{btw} = \frac{MS_{btw}}{\bar{X}.100\%}$	0.0040%
Total analytical variability (CV) $CV = \sqrt{(CV_{wth})^2 + (CV_{btw})^2}$	0.0070%
Probability of falsely rejecting the hypothesis that all samples have the same measurand value	3.1%

Standard uncertainty of inhomogeneity was estimated by the formulas recommended by ISO 33405.

$$u_h = \frac{\mathrm{MS_{btn}} - \mathrm{MS_{wth}}}{n} \qquad (1)$$

$$u_h = \sqrt{\frac{\mathrm{MS_{wth}}}{n}} \cdot \sqrt[4]{\frac{2}{\nu_{\mathrm{MS_{wth}}}}} \qquad (2)$$

Formula (1) gave a negative value due to mean square between groups was less than mean square within groups. Standard uncertainty of inhomogeneity calculated by formula (2) was 0.0038 %. This meant that inhomogeneity of the sample was less than repeatability of the method used, so the inhomogeneity of the sample was considered as negligible. The homogeneity is sufficient for the comparison.

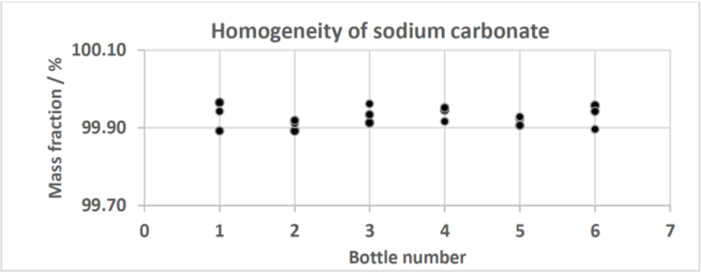

Figure 1. Results of the homogeneity test.

Sodium carbonate is a stable material in the absence of acid vapours. Water or carbon dioxide absorbed during storage are removed by sample drying.

5 Instructions for measurement

The instructions for participants were as follows (similar to those in CCQM-K173 [1]):

- The material should be dried at (275±5) °C for 4 h without crushing or grinding the material. After drying, it should be placed in a desiccator with silica gel, or $Mg(ClO_4)_2$, or another desiccant, and cooled to room temperature before weighing.
- The dried material is hygroscopic. Exposure of the dried material to the atmosphere should be minimized. Weighing should be performed rapidly or in closed vessels to minimize absorption of water.
- The mass of the samples should be corrected for buoyancy. The density of the sodium carbonate sample is about 2533 kg/m^3.
- Results should be expressed as the amount content of base expressed as sodium carbonate [measurand] with the unit ‘$mol\ kg^{-1}$’ and provide an uncertainty evaluation according to JCGM 100:2008 [2].
- The sample should be stored in a dark, dry place at laboratory temperature in the original container until used.
- The recommended minimum sample amount for analysis is at least 150 mg.
- The measurement should be conducted within six weeks after receipt of the sample.
- Measurand is the amount content of bases expressed as sodium carbonate, mol/kg.
- Any method or combination of methods could be used by the participants, but coulometric titration or titrimetry are recommended with back-titration implementation.

6 Communication with the participants

On May 26, the participants were reminded of the deadline for the reports.

On May 30, INMETRO requested an extension of one working day, which was granted.

On May 31, a request for clarification was sent to KEBS (source of traceability, units, etc.). No numerical information was given. A corrected report was sent on June 1.

The results were disclosed on June 10.

7 Results

All participants finished their measurements in time and all but one sent their reports before the deadline.

Table 4. Dates of sample receipt, measurement dates and dates when the reports were sent to the coordinator (or to EAWG chair in the case of coordinator).

Institute	Date of sample receipt	Measurement period	Date report sent
SMU	16 April 2025	14 to 15 May 2025	21 May 2025 (to PTB)

BFKH	10 April 2025	23 to 28 May 20225	30 May 2025
INMETRO	-	11 March to 4 April 2025	2 June 2025
KEBS	14 April 2025	15 May 2025	30 May 2025, corrected 1 June 2025

7.1 Methods of measurement

Measurement methods used by the participants are presented in Table 5; SMU, BFKH and INMETRO used coulometric determination of excess acid after reaction with sodium carbonate, KEBS used direct volumetric titration using visual indication. Additional information on the coulometric measurement methods is summarized in Table 6.

Table 5. Measurement methods used by the participating institutes.

Institutes (Acronym)	**Measurement method**	**Endpoint indication and estimation**	**Major uncertainty sources**	**Their contribution**
SMU	Coulometry	Potentiometric, non-linear regression	HCl amount content, spray losses on sample preparation	0.00057 mol/kg (99 %)
BFKH	Coulometry	Potentiometric, non-linear regression	Na_2CO_3 weighing and drying	0.0011 mol/kg (55 %)
INMETRO	Coulometry	Potentiometric, non-linear regression	HCl amount content	0.0007 mol/kg (83 %)
KEBS	Direct volumetric titration	Visual – methyl orange indicator	Endpoint repeatability	0.045 mol/kg (84 %)

Table 6. Details on the coulometric titrations.

Institutes (Acronym)	**Cell type**	**Cell volume / mL**	**Main current / mA**	**Current density / (mA cm^{-2})**	**Excess of acid added to carbonate**	**Sample mass / g**
SMU	Vertical	250	200	28	1 %	2
BFKH	Vertical	250	200	100	1.5 %	0.3
INMETRO	Vertical	250	200	44	5.5 %	0.5

7.2 Reported Results

The reported values and uncertainties are summarized in Table 7 and also displayed graphically in Figure 2.

Table 7. Measurement results of CCQM-K173.2. *n* is the number of measured samples and *k* is the coverage factor.

Institute	**Results v_i / mol kg^{-1}**	**Standard deviation / mol kg^{-1}**	**Standard uncertainty $u(v_i)$ / mol kg^{-1}**	**Expanded uncertainty $U(v_i)$ / mol kg^{-1}**	***n***	***k***
SMU	9.43310	0.00042	0.00060	0.00121	5	2
BFKH	9.4327	0.00086	0.0020	0.0041	6	2
INMETRO	9.4305	0.00087	0.0009	0.0017	7	2

KEBS	9.445	0.0060	0.054	0.11	6	2

Discussion:

The results show good overlap with the SMU value for BFKH and KEBS results, although the KEBS uncertainty is very high due to use of volumetric titration. KEBS reported the result as mass fraction of sodium carbonate; the reported values were recalculated to amount content using the molar mass of sodium carbonate used in the KEBS report.

The INMETRO result is slightly lower; examination of the report revealed that the acid used was assayed in November 2023. No stability term was included in the uncertainty budget. If concentration of acid gets higher due to evaporation of water, the result would tend to be low, in agreement with the negative DoE (see below). A check measurement may verify this assumption.

Some incorrect sensitivity coefficients were noted in the uncertainty budget of BFKH. Fortunately, the effect is not large - the use of the correct sensitivity coefficients would increase the claimed uncertainty by about 20%.

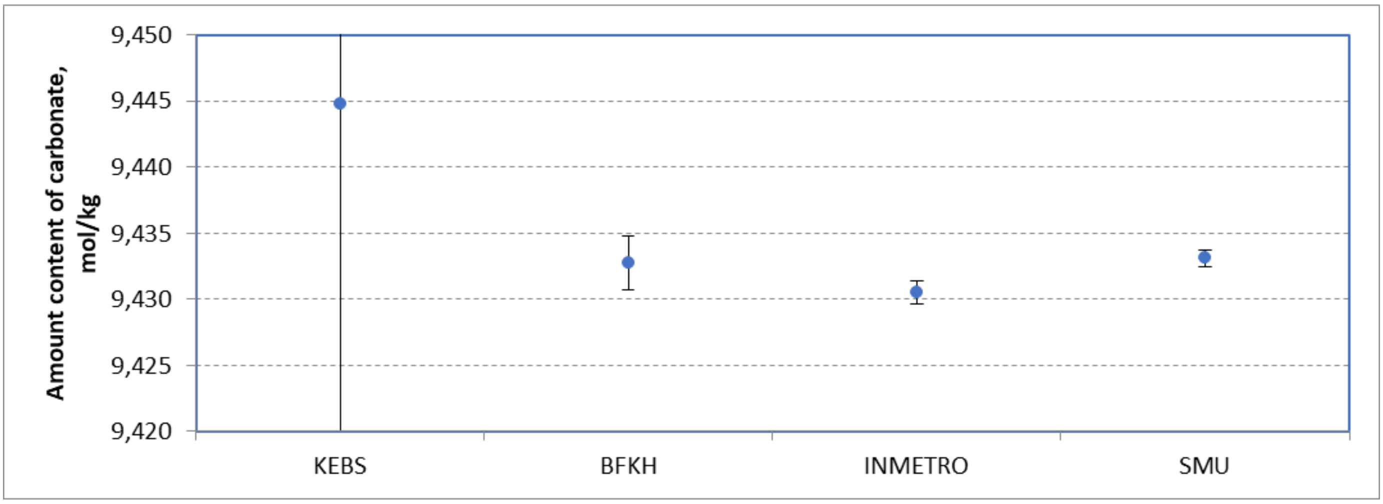

Figure 2. Measurement results of CCQM-K173.2. The error bars indicate the combined standard uncertainty.

7.3 Reported results calculated as mass fractions

Table 8 indicates the reported results explicitly in terms of mass fractions since these are often the preferred quantity in CMC submissions.

Table 8. Reported results in terms of mass fractions.

Institute	**Mass fraction w_i / g kg^{-1}**	**Standard deviation / g kg^{-1}**	**Standard uncertainty $u(w_i)$ / g kg^{-1}**	**Expanded uncertainty $U(w_i)$ / g kg^{-1}**	**n**	**k**
SMU	999.799	0.045	0.064	0.128	7	2
BFKH	999.758	0.091	0.22	0.43	6	2
INMETRO	999.523	0.092	0.091	0.18	7	2
KEBS	1011.15	0.63	5.7	11.3	6	2

The following formula has been used to calculate mass fractions from the reported results (using $M(Na_2CO_3)$ = 105.9884 g/mol; for KEBS 106 g/mol): $w_i = v_i \times M_i$

8 Estimators for the Key Comparison Reference Value (KCRV)

The results were linked to the key comparison reference value of CCQM-K173 through the results of SMU as the linking laboratory.

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

The degree of equivalence of the participants of the subsequent comparison relative to the original CCQM-K173 comparison was calculated using the results of the coordinating laboratory according to equation (3), based on the assumption that the deviation of the coordinating laboratory's result from the key comparison reference value is constant.

$$D_{\mathrm{NMI,\,K173.2}} = v_{\mathrm{NMI,\,K173.2}} - v_{\mathrm{SMU,\,K173.2}} + D_{\mathrm{SMU,\,K173}} \quad (3)$$

$D_{\mathrm{NMI,\,K173.2}}$	Degree of equivalence of the participant of the subsequent comparison
$D_{\mathrm{SMU,\,K173}}$	Degree of equivalence of SMU in CCQM-K173
$v_{\mathrm{NMI,\,K173.2}}$	Result of NMI in CCQM-K173.2
$v_{\mathrm{SMU,\,K173.2}}$	Result of SMU in CCQM-K173.2

Equation (4) was used for the calculation of the uncertainties of the degrees of equivalence, assuming no significant correlation between both SMU results. The meaning of the symbols is analogous to those above.

$$u^2(D_{\mathrm{NMI,\,K173.2}}) = u^2(D_{\mathrm{SMU,\,K173}}) + u^2(v_{\mathrm{NMI,\,K173.2}}) + u^2(v_{\mathrm{SMU,\,K173.2}}) \quad (4)$$

The degrees of equivalence are given in Table 7. The table also states the uncertainty weighted DoE (E_n value).

$$E_n(x_i) = \frac{D_i}{U(D_i)} \quad (5)$$

A result is considered consistent with the KCRV if $E_n(x_i) \leq 1$. Table 7 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 to the expanded uncertainty reported by the institute.
The degrees of equivalence are shown together with the original CCQM-K173 results in Figure 3.

Table 9. Degrees of equivalence for the measurement of the amount content of sodium carbonate with corresponding expanded uncertainties (k=2) and E_n numbers ($E_n=D_i/U(D_i)$). The last column lists the minimal expanded uncertainties U_{minCMC} (v_i) that are consistent with the KCRV.

Institutes *i*	**Result v_i/ (mol·kg^{-1})**	**Exp.uncert. U(v_i) (k=2)/ (mol·kg^{-1})**	**D$_i$ / (mol kg^{-1})**	***U*(D$_i$) / (mol kg^{-1})**	**E_n**	**U_{minCMC}(v$_i$)/ (mol·kg^{-1})**
BFKH	9.4327	0.0041	-0.0018	0.0049	-0.37	0.0041
INMETRO	9.4305	0.0017	-0.0040	0.0032	-1.25	0.00296
KEBS	9.445	0.11	0.0105	0.107	0.10	0.11 (*)

In terms of mass fraction						
BFKH	99.9758 %	0.043 %	-0.019%	0.052%	-0.37	0.043 %
INMETRO	99.9523 %	0.018 %	-0.043%	0.034%	-1.25	0.031 %
KEBS	100.1 %	1.1 %	0.11%	1.13%	0.10	1.1 % (*)

* Even though the source of traceability does not comply with MRA guidelines (see section 3.1 of the document CIPM MRA-G-13 – Calibration and measurement capabilities in the context of the CIPM MRA), the uncertainty statement of KEBS is acceptable for CMC submission, since the large value covers any foreseeable variation of the reagent used for titration.

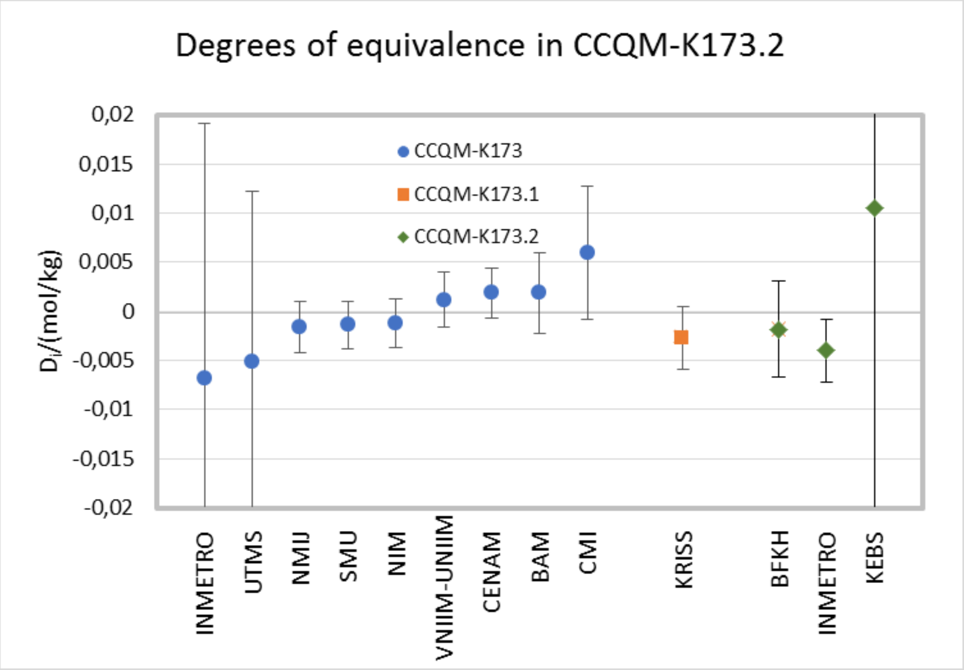

Figure 3. Degrees of equivalence for CCQM-K173/K173.1/K173.2 and their expanded uncertainties.

10 How Far Does the Light Shines statement

The comparison tested the capabilities and methods used for an assay of high purity sodium carbonate as one of the most widely used solid bases. A good result indicates good performance in assaying the purity (amount content) of solid bases like tris (tris(hydroxymethyl)aminomethane) and hydroxides and carbonates of alkali metals and alkaline earth metals with mass fraction not less than 99.8 % as well as their water solutions for sample sizes similar to those used in this comparison (equivalent to 3 to 40 mmol base). NMIs that used back titration implementation of coulometry or titrimetry may use this comparison for supporting CMCs of assay of liquid and solid strong acids and their solutions in the same ranges as well.
Uncertainties claimed in the CMC submission must not be smaller than U_{minCMC} values stated in Table 9, unless the exceptions stated in the EAWG-CMC guidelines can be applied.
Respective CMCs are often submitted as mass fraction rather than amount content. Section 7.3 therefore specifies the results in terms of mass fractions and their calculation.

11 Acknowledgements

The provision of samples and homogeneity testing by INMETRO is gratefully acknowledged by the coordinating laboratory.

12 References

[1] Bing Wu, Alena Sobina, et al.: Assay of sodium carbonate. 2023 Metrologia 60, Number 1A, 08004 DOI 10.1088/0026-1394/60/1A/08004

[2] JCGM 100:2008 GUM: Guide to the Expression of Uncertainty in Measurement, available at https://www.bipm.org/en/committees/jc/jcgm/publications

Appendix

CCQM WG on Electrochemical Analysis and Classical Chemical Methods

Key Comparison CCQM-K173.2

Assay of sodium carbonate

Technical protocol

1. Introduction

The CCQM key comparison K173.2 is a subsequent comparison to CCQM K173 requested by INMETRO. It will be performed to demonstrate the capability of INMETRO, BFKH and KEBS to measure the amount content of bases. The institutes can use a method of their choice, although the use of coulometry or titrimetry with potentiometric determination of the endpoint is expected.
The results of the key comparison may serve as evidence to support respective CMC claims.

2. Proposed time schedule

Preparation of Technical protocol	February 2025
Dispatch of samples:	March 2025
Reporting deadline:	31 May 2025
Draft A report:	15 July 2025
Discussion:	by e-mail, July-August 2025
Draft B report:	September 2025
Draft B report approval:	EAWG meeting, October 2025

3. MEASURAND

Measurand is the amount content of bases expressed as sodium carbonate, mol/kg.

Any method or combination of methods can be used by participants, but coulometric titration or titrimetry are recommended with back-titration implementation.

4. Description of the sample

Samples for comparison will be prepared and distributed by INMETRO. The assay is in the range of 99.8 % to 100.1% of the theoretical value based on the sodium carbonate amount content.
The homogeneity of the sample will be assessed by INMETRO using coulometric titration.

5. INSTRUCTIONS AND SAMPLE DISTRIBUTION

Each participant will receive one numbered bottle containing about 15 g of material. Shipment to all participants will be performed at the same time. The bottles will be shipped in a cardboard tube box by courier. The contents will be marked as a sample for comparison CCQM-K173.2, sodium carbonate, CAS # 497-19-8 and will be accompanied with the material safety data sheet (MSDS).
The participants will be informed of the date of dispatching of the samples. Participants must confirm the receipt of the sealed samples, by filling in the return receipt table and sending it to the INMETRO contact person by e-mail. If there is any damage, please contact INMETRO immediately, and INMETRO will send a replacement bottle.
The sample should be stored in a dark, dry place at laboratory temperature in the original container until used.
The recommended minimum sample amount for analysis is at least 150 mg.
The material should be dried at (275±5) °C for 4 h without crushing or grinding the material. After drying, it should be placed in a desiccator with silica gel, or $Mg(ClO_4)_2$, or other desiccant, and cooled to room temperature before weighing.
The dried material is hygroscopic. Exposure of the dried material to the atmosphere should be minimized. Weighing should be performed rapidly or in closed vessels to minimize absorption of water.
The mass of the samples should be corrected for buoyancy. The density of the sodium carbonate sample is about 2533 kg/m^3.
The measurement should be conducted within six weeks after receipt of the sample.
The technical protocol and a template for the report will be sent by e-mail.

6. Reporting

The report should be sent by e-mail to the coordinating laboratory by **31 May 2025** at the latest. The coordinating laboratory will confirm the receipt of each report. If the confirmation does not arrive within one week, please contact the coordinating laboratory to identify the problem.

A template for the report will be enclosed (Excel spreadsheet). If possible, the requested data should be entered into the corresponding cells. If this is not possible, the format can be modified or the data can be reported in another form.

Information requested:

1. Name and address of the laboratory performing the measurements
2. Name of the analyst(s)

3. Date of receipt of samples
4. Date(s) of measurement
5. The results should be reported as amount content [mol/kg] of bases expressed as sodium carbonate, to be accompanied by a full uncertainty budget. Information on impurities is welcome also from participants not using (100% - impurities) approach.
6. If the assay is determined from impurity analysis, results for all the elements/compounds sought must be included.
7. A detailed description of the measurement procedure is to be given (for coulometry this should include the following: cell description, volume of electrolyte in working chamber, the number of stages used in the titration and the current used for each stage, evaluation procedure for the endpoint, examples of the titration curve for initial and final endpoint determination), and the equipment used.
8. In order to further evaluate the effects of assay measurements, please report the details of the techniques used in the measurement procedure (the means of adding the sample, stirring, influence of CO_2, ...). A separate text file or official report may be used.
9. The complete measurement equation has to be given, as well as the values of the constants used and variables (raw data) for at least one measurement. The data should enable the recalculation of the result of this measurement. If trace element correction is used, the relevant data must be included here also.
10. At least six determinations should be performed. Please state all the individual results, not only the final mean value. The uncertainty budget must include instrumental sources of uncertainty (mass, time, voltage, volume ...) as well as chemical ones (endpoint estimation, equilibria, CO_2 interference, impurities, and purity of calibration standards ...) plus the relevant uncertainties for any trace element corrections. The uncertainty calculations should comply with the ISO document JCGM 100:2008 Guide to the Expression of Uncertainty in Measurement (2008) 1st ed., ISO, Geneva. Both Type A and Type B uncertainty components and a summary of how they are calculated have to be included. The reported uncertainty should be expressed as a combined standard uncertainty and as an expanded uncertainty referred to a 95 % level of confidence.
11. In order to facilitate comparisons of your measured masses (for assay measurements), please also provide either (1) the air density used for each buoyancy correction, or (2) the air temperature, humidity and pressure in your laboratory at the time of each mass measurement.

Participants performing titrimetric measurements are requested to provide additional information of their measurement setup in the “Additional information” data sheet of the reporting file.

7. Key comparison reference value

The results will be linked to the key comparison reference value of CCQM-K173 through the results of SMU as the linking laboratory.

8. How Far the Light Shines statement

The HFTLS statement is effectively the same as that in the original comparison:

The comparison tested the capabilities and methods used for assay of high purity sodium carbonate as one of the most widely used solid bases. Good result indicates good performance in assaying the purity (amount content) of solid bases like tris (tris(hydroxymethyl)-aminomethane) and hydroxides and carbonates of alkali metals and alkaline earth metals with mass fraction not less than 99.8 % as well as their water solutions for sample sizes similar to those used in this comparison (equivalent to 3 to 40 mmol base). NMIs that used back titration implementation of coulometry or titrimetry may use this comparison for supporting CMC of assay of liquid and solid strong acids and their solutions in the same ranges as well.

9. Contact person, coordinating laboratory and co-piloting laboratory

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