

CCQM WG on Electrochemical Analysis and Classical Chemical Methods

CCQM-K173.1 - Assay of sodium carbonate

Final report

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Summary

The CCQM key comparison CCQM-K173.1 is a subsequent comparison to CCQM-K173. It was performed to demonstrate the capability of KRISS 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 KRISS were in good agreement with the reference value and may serve as evidence to support respective CMC claims.

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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
Korea Research Institute of Standards and Science	KRISS	KR	Kyungmin Jo	kyungmin.jo@kriss.re.kr

3 Time schedule

Preparation of Technical protocol	October 2023
Dispatch of samples:	December 2023
Reporting deadline:	15 March 2024
Draft A report:	Spring 2024
Discussion:	EAWG meeting, 22 April 2024
Draft B report:	November 2024

4 Description of samples

Samples for comparison were prepared and distributed by KRISS. The assay was expected to be in the range of 99.8 % to 100.1% of the theoretical value based on the sodium carbonate amount content.

The source material for the sample was commercially available pure sodium carbonate. The material was transferred to a cleaned 15 L low-density polyethylene carboy and homogenised for 10 hours using a 3D mixer at a speed of 15 rpm. The homogenised material was then bottled in glass bottles closed with Teflon-lined plastic screw caps. Each bottle contained approximately 40 g of material and was sealed in a plastic bag. The samples were shipped by air courier on 12 December 2023 and the samples arrived to their destination without damage on 19 December.

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4.1 Homogeneity

The homogeneity of the sample was assessed by KRIS using coulometric titration, using 2 g samples taken from each of 10 systematically selected bottles out of 250 in total. The results of the homogeneity test are shown in Figure 1. The between-sample standard deviation, which includes the contributions of both sample homogeneity and measurement repeatability, was 0.0051 %. This indicates that homogeneity is sufficient for the comparison.

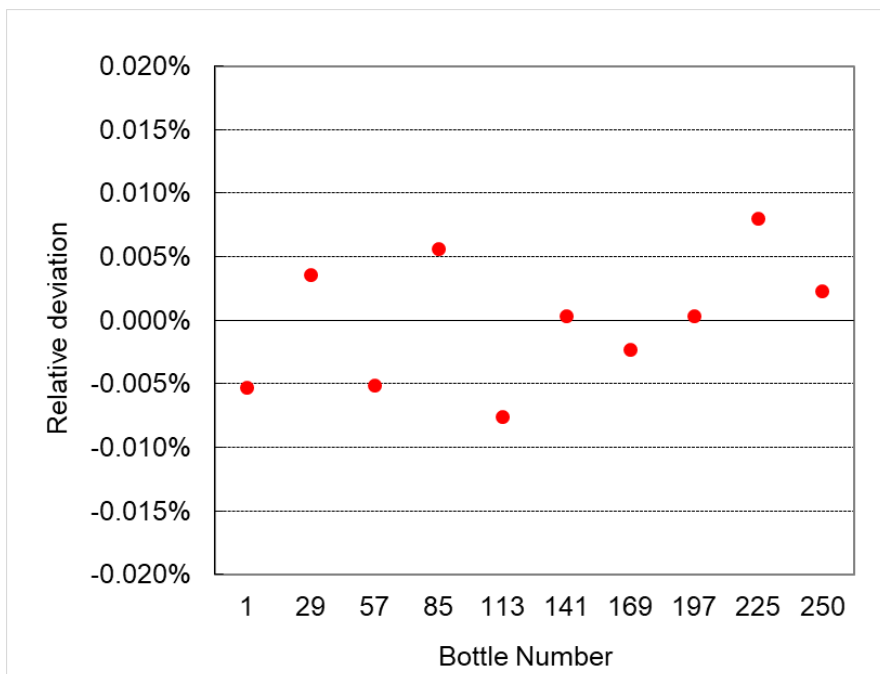


Figure 1. Results of the homogeneity test.

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 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 .
- Express the results 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 can be used by participants, but coulometric titration or titrimetry are recommended with back-titration implementation.

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6 Results

All participants sent their reports in time.

Table 2. Measurement dates and dates when the reports were sent to the coordinator (or to EAWG chair in the case of coordinator).

Institute	Measurement period	Date report sent
KRISS	20 Feb to 13 Mar 2024	15 Mar 2024
SMU	8 to 12 Jan 2024	23 Jan 2024 (PTB)

6.1 Methods of measurement

Measurement methods used by the participants are presented in Table 3; both used coulometric determination of excess acid after reaction with sodium carbonate. Additional information on the measurement methods is summarized in Table 4.

Table 3. 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	0.00037 mol/kg (66 %)
KRISS	Coulometry	Potentiometric, charge corresponding to pH 7	Maximum possible mass change of sample during weighing (for 2 min)	0.00066 mol/kg (48 %)

Table 4. Details on the coulometric titration.

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	1–1.6 %	2
KRISS	Horizontal	120	102	2	15–20 %	2

6.2 Reported Results

The reported values and uncertainties are summarized in Table 5 and also displayed graphically in Figure 2.

Table 5. Measurement results of CCQM-K173.1.

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	9.43279	0.00023	0.00045	0.00090	7	2
KRISS	9.43149	0.00052	0.00095	0.00187	7	2

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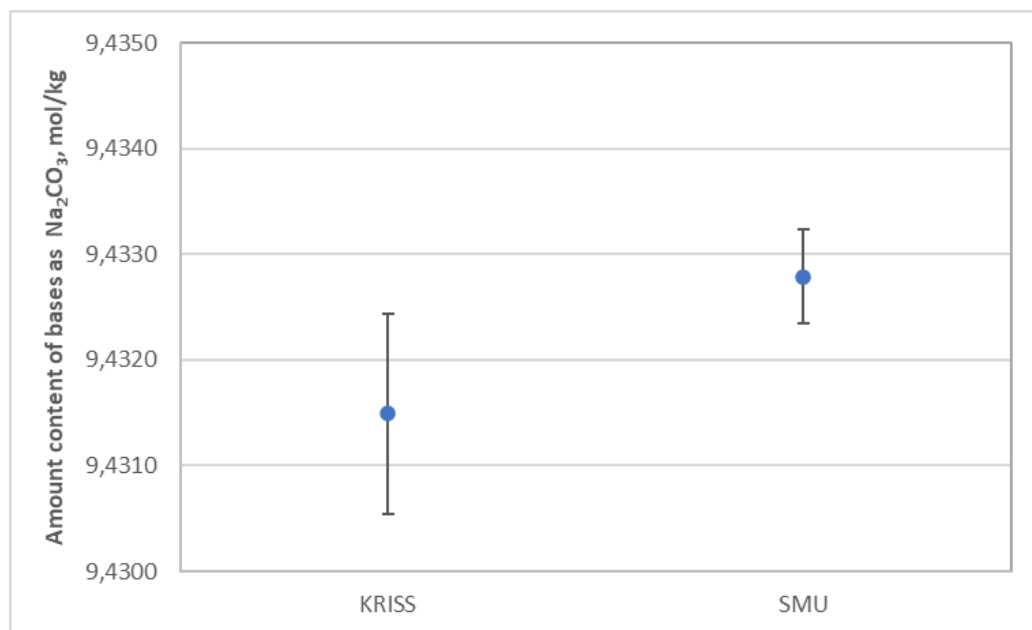


Figure 2. Measurement results of CCQM-K173.1. The error bars indicate the combined standard uncertainty.

6.3 Reported results calculated as mass fractions

Table 6 indicates the reported results explicitly in terms of mass fractions since these are often the preferred quantity in CMC submissions.

Table 6. 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	999.767	0.024	0.048	0.095	7	2
KRIS	999.628	0.055	0.101	0.199	7	2

The following formula has been used to calculate mass fractions from the reported results (using $M(\text{Na}_2\text{CO}_3) = 105.9884$ g/mol): $w_i = v_i \cdot M_i$

7 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.

8 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 the equation (1), based on assumption that the deviation of the coordinating laboratory's result from the reference value is constant.

$$D_{\text{NMI, K173.1}} = v_{\text{NMI, K173.1}} - v_{\text{SMU, K173.1}} + D_{\text{SMU, K173}} \quad (1)$$

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$D_{NMI, K173.1}$	Degree of equivalence of the participant of the subsequent comparison
$D_{SMU, K173}$	Degree of equivalence of SMU in CCQM-K173
$V_{NMI, K173.1}$	Result of NMI in CCQM-K173.1
$V_{SMU, K173.1}$	Result of SMU in CCQM-K173.1

For the calculation of uncertainty of the degrees of equivalence equation (2) was used, assuming no significant correlation between both SMU results. The meaning of the symbols is analogous to those above.

$$u^2(D_{NMI, K173.1}) = u^2(D_{SMU, K173}) + u^2(V_{NMI, K173.1}) + u^2(V_{SMU, K173.1}) \quad (2)$$

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

$$E_n(x_i) = \frac{D_i}{U(D_i)} \quad (3)$$

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 7. 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)
KRISS	9.43149	0.00187	-0.0027	0.0032	-0.85	0.00187
In terms of mass fraction						
KRISS	99.963 %	0.020 %	-0.029 %	0.034 %	-0.85	0.020 %

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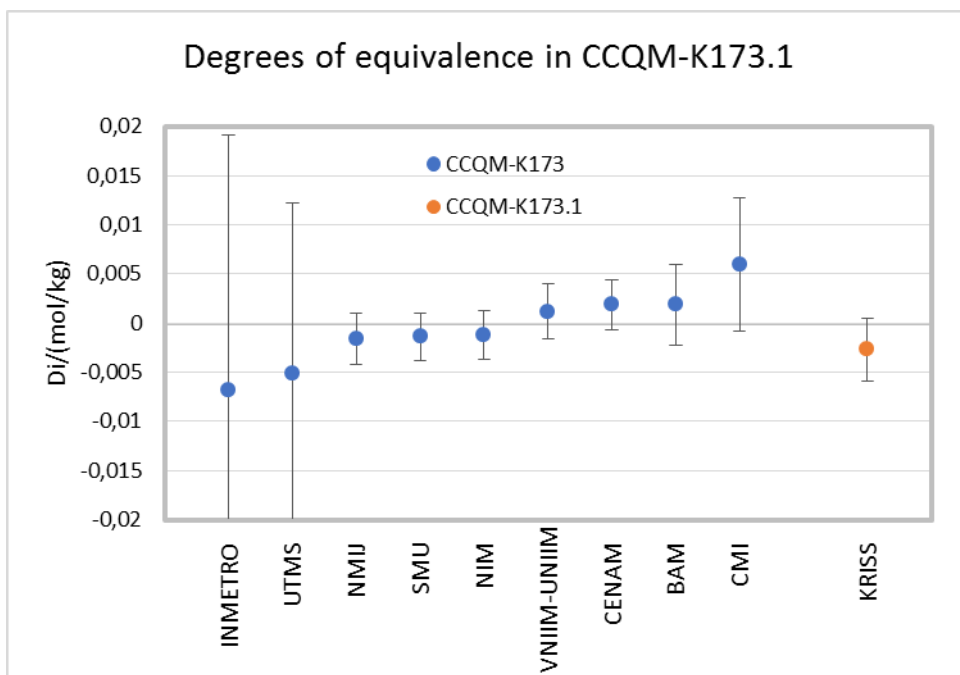


Figure 3. Degrees of equivalence for CCQM-K173/CCQM-K173.1 and their expanded uncertainties.

9 How Far Does the Light Shines statement

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.

Uncertainties claimed in the CMC submission must not be smaller than $U_{\min\text{CMC}}$ values stated in Table 7, 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 6.3 therefore specifies the results in terms of mass fractions and their calculation.

10 Acknowledgements

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

11 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>

CCQM WG on Electrochemical Analysis and Classical Chemical Methods

Key Comparison CCQM-K173.1

Assay of sodium carbonate

Technical protocol

Introduction

The CCQM key comparison CCQM-K173.1 is a subsequent comparison to CCQM K173. It will be performed to demonstrate the capability of KRISS 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.

Proposed time schedule

Preparation of Technical protocol	October 2023
Dispatch of samples:	December 2023
Reporting deadline:	15 March 2024
Draft A report:	Spring 2024
Discussion:	EAWG meeting, April 2024
Draft B report:	November 2024



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.

Description of the sample

Samples for comparison will be prepared and distributed by KRISS. 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 was assessed by KRISS using coulometric titration with a sample size of about 2 g and found to be adequate for comparison with the between-bottle relative standard deviation of 0.0051 %.

INSTRUCTIONS AND SAMPLE DISTRIBUTION

Each participant will receive one numbered bottle containing about 20 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-K173.1, 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 KRISS contact person by e-mail. If there is any damage, please contact KRISS immediately, and KRISS 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 $\text{Mg}(\text{ClO}_4)_2$, 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.

Reporting

The report should be sent by e-mail to the coordinating laboratory by 15 March 2024 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 CO₂...). 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, CO₂ 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.

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.

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.



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