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Ural Scientific Research Institute for Metrology – Affiliated Branch of the
D.I.Mendeleyev Institute for Metrology (VNIIM -UNIIM)

Report of the CCQM-K173

Assay of Sodium Carbonate

Final report

Bing Wu¹ and Alena Sobina²

¹National Institute of Metrology, P. R. China (NIM)

No.18, Bei San Huan Dong Lu, Chaoyang District, Beijing China, 100029,

²Ural Scientific Research Institute for Metrology – Affiliated Branch of the

D.I.Mendeleyev Institute for Metrology (VNIIM -UNIIM)

4, Krasnoarmeyskaya Street, Ekaterinburg, Russian Federation, 620075

With participation of:

BAM: Sebastian Recknagel, René Meinhardt

CENAM: Griselda Rivera-Sánchez, José Luis Ortiz-Aparicio

CMI: Matilda Rozikova

INMETRO: Paulo Paschoal Borges, Sidney Pereira Sobral

NIM: Bing Wu, Tao Zhou, Jianying Zhang

NMIJ: Toshiaki Asakai

UMTS: Andrey Glebov, Aleksandr Melnikov, Vladimir Gavrilkin, Anton Petrenko, Volodymyr Tkachenko

SMU: Michal Máříšský, Zuzana Hanková

VNIIM –UNIIM: Alexandr Shimolin, Alena Sobina

Beijing, Ekaterinburg, November 2022



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1. ABSTRACT

The CCQM-K173 Assay of Sodium Carbonate key comparison was jointly organized by the Inorganic Analysis (IAWG) and Electrochemical Analysis and Classical Chemical methods (EAWG) working groups of CCQM to test the abilities of the national metrology institutes (NMIs) to measure the purity or amount content of solid bases. They are important challenges for reference material producers, providers of other measurement services, such as proficiency testing schemes. Evidence of successful participation in formal, relevant international comparisons is needed to support calibration and measurement capability claims (CMCs) made by NMIs and designated institutes (DIs).

Nine NMIs participated in this key comparison CCQM-K173. National Institute of Metrology P. R. China (NIM) and Ural Research Institute for Metrology - Affiliated Branch of the D.I.Mendeleyev Institute for Metrology (VNIIM-UNIIM), Russian Federation, acted as the coordinating laboratories of the comparison.

The measurement methods used by the participants for measuring the amount content of bases expressed as sodium carbonate were coulometry and titrimetry.

In general, good overlap of results was observed, the suitability of coulometry and titrimetry for assay of high purity materials was demonstrated. The majority of results were split in two groups differing from each. This bias was however covered by the stated uncertainty estimates. Various effects have been evaluated that may cause it. However, the reason for the bias has not been identified clearly.



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2. INTRODUCTION

The CCQM-K173 key comparison is the next step in realization the long-term strategy of CCQM (IAWG+EA WG) on purity determination of the high pure substances (e.g. CCQM-K34, CCQM-K48.2014, CCQM-K96, CCQM-K152&P192).

Pure materials are very important reference materials to establish traceability in chemical metrology. Respective studies and comparisons of pure materials are important activities in the Electrochemical Analysis and Classical Chemical Methods Working Group and Inorganic Analysis Working Group in particular. Acid-base analysis is made almost exclusively by titration methods, and sodium carbonate is widely used as a chemical standard for acid-base titrimetry.

The objective of this comparison was to determine the amount content of bases (mol/kg) expressed as Na_2CO_3 . Participants were free to choose the analytical procedure.

Scope:

The comparison tested the capabilities and methods used for assay of high purity substances and underpins claims of calibration and measurement capabilities of the institutes.

For coulometry or titrimetry, good results indicate good performance in assaying bases. CCQM-K173 supports CMC claims for the measurement of the amount content of solid base materials.



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3. LIST OF PARTICIPANTS

The participating NMIs and contact persons are given in Table 1.

Table 1 List of participants

Institution	Country	Contact person
BAM Bundesanstalt für Materialforschung und -prüfung	Germany	Sebastian Recknagel
CENAM Centro Nacional de Metrología	Mexico	José Luis Ortiz-Aparicio
CMI Czech Metrology Institute	Czech Republic	Matilda Rozikova
INMETRO Instituto Nacional de Metrologia, Qualidade e Tecnologia	Brazil	Paulo Paschoal Borges
INTI Instituto Nacional de Tecnología Industrial	Argentina	Hernan Lozano & Mabel Puelles
NIM National Institute of Metrology of P.R.China	China	Bing Wu
NIST National Institute of Standards and Technology	USA	Jason F. Waters
NMIJ National Metrology Institute of Japan	Japan	Toshiaki Asakai
SE "UKRMETRTESTSTANDART" (UMTS) "ALL-UKRAINIAN STATE RESEARCH AND PRODUCTION CENTER FOR STANDARDIZATION, METROLOGY, CERTIFICATION AND CONSUMERS' RIGHTS PROTECTION"	Ukraine	Anton Petrenko
SMU Slovak Institute of Metrology	Slovakia	Michal Mariassy
VNIIM-UNIIM Ural Scientific Research Institute for Metrology (since 2020 UNIIM - Affiliated Branch of the D.I.Mendeleyev Institute for Metrology)	Russia	Alena Sobina



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4. TIME SCHEDULE

Date	Action
March 2021	Sample Preparation and Homogeneity Testing
IAWG&EAWG joint meeting, April 2021	Discussion of the technical protocol
April 2021	Call for participation to EAWG & IAWG members
The end of May 2021	Deadline for registration
Mid-June 2021	Dispatch of the samples
29 September 2021	Deadline for Submission of Results
Autumn meeting, 2021	Preliminary Discussion of Results
EAWG meeting October 2022	Draft A report

5. SAMPLES

5.1 Sample preparation

The source of the sample was from a 5 kg batch of commercially available pure sodium carbonate powder. After being homogenized, a 400 g portion was selected from the middle fraction of the batch and was homogenized again in a large bottle. This homogenised portion was then transferred to 20 glass bottles closed with plastic caps for the comparison. Impurities were determined by using ICP-MS method.

The amount content of bases, expressed as sodium carbonate in mol/kg, was the measurand. The assay was in the range of 99.8 % to 100.1% of the theoretical value based on the sodium carbonate amount content.



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Any method or combination of methods could be used by the participants, however, coulometric titration or titrimetry were recommended in conjunction with the implementation of back-titration.

The recommended minimum sample amount for analysis was 150 mg.

5.2 Sample drying

The material should be dried at $(275 \pm 5)^\circ\text{C}$ for 4h 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 another desiccant, and cooled to room temperature before weighing.

The dried material was 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. To this end, a density value of 2.533 g/cm^3 was used for the sodium carbonate sample.

5.3 Homogeneity Assessment of Study Material

Twelve bottles, selected at random, were tested by VNIIM-UNIIM for homogeneity. To this end, two independent samples of each bottle were analyzed by coulometric titration. Data obtained were evaluated by one-way ANOVA. Summary results of homogeneity assessment for the samples of sodium carbonate are given in the table 2 and 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	0,000173	11	1,6E-05	0,30	0,97	2,7
Within groups	0,000634	12	5,3E-05			
Total	0,000807	23				

Within groups, $CV_{w_{th}}$ $CV_{w_{th}} = MS_{w_{th}}/\bar{X} \cdot 100\%$	0,0073 %
Between groups, $CV_{b_{tw}}$ $CV_{b_{tw}} = MS_{b_{tw}}/\bar{X} \cdot 100\%$	0,0040 %
Total analytical variability, CV $CV = \sqrt{(CV_{w_{th}})^2 + (CV_{b_{tw}})^2}$	0,0083 %
Probability of falsely rejecting the hypothesis that all samples have the same measurand value	2,7 %

Homogeneity of sodium carbonate for CCQM-K173

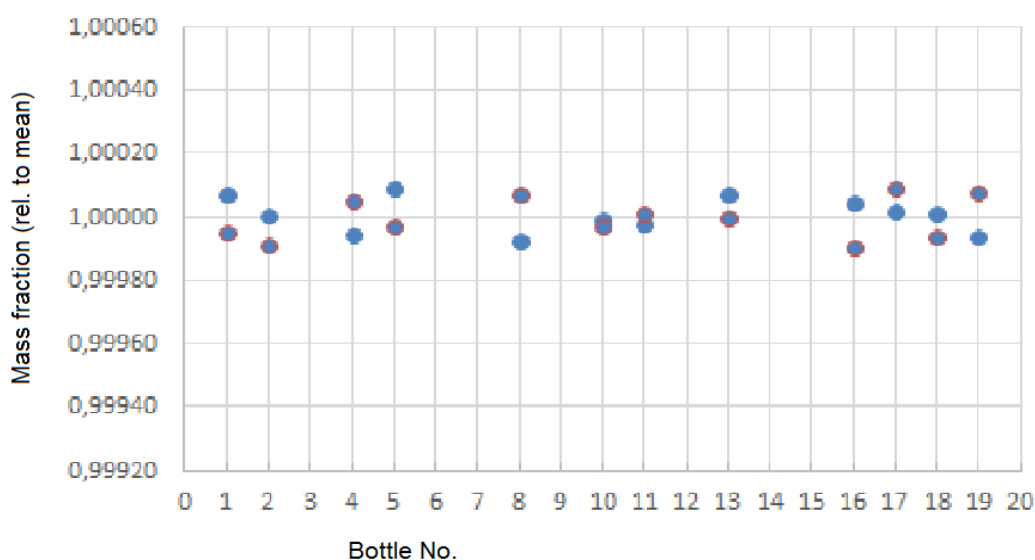


Figure 1. Homogeneity evaluation for assay of sodium carbonate



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Standard uncertainty of inhomogeneity was estimated by the formulas recommended by ISO Guide 35^[1]

$$u_h = \frac{MS_{btb} - MS_{wth}}{n} \quad (1)$$

$$u_h = \sqrt{\frac{MS_{wth}}{n}} \cdot \sqrt{\frac{2}{\nu_{MS_{wth}}}} \quad (2)$$

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 0.0033 %. 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.

5.4 Stability Assessment of Study Material

Sodium carbonate is known to be a stable material which is convenient for storage and transportation. Typical shelf-life of CRMs of sodium carbonate is from 5 to 10 years. The main factor of instability of the sample material is absorbing water and carbon dioxide (CO₂) from the air which may form a hard cake containing hydrated sodium carbonate (Na₂CO₃) and/or sodium bicarbonate (NaHCO₃) on extended storage. Drying as described before expels absorbed water and carbon dioxide yielding pure Na₂CO₃. So the main factor of instability (NaHCO₃ formation) is eliminated by proper heating before measurement.

5.5 Distribution

NIM has received 12 bottles samples from VNIIM-UNIIM on 14 June 2021. And then nine bottles samples have been dispatched to other participants from NIM by Fedex on 22nd June 2021. All participants have received the sample until 22nd July 2021 except INTI. INTI wasn't able to release the sample from their customs since Na₂CO₃ is a substance declared as a chemical precursor for the manufacture of narcotic drugs in Argentina and required a special authorization that they didn't get. On 3rd Feb 2022 INTI had just released the sample from their customs and was still interested in



participating in this comparison to claim acid-base CMCs. But it was impossible to prolong as results were disclosed at the EAWG/IAWG meetings in autumn 2021. At the request of NIST, the deadline was extended from the 15th September to 29th September 2021. Finally, nine participants submitted the measurement result protocols.

The dispatch dates and receipt dates are given in Table 3.

Table 3 Sample sent dates, receipt dates and report dates

Institute	Sample No.	Sample dispatch date	Sample receipt date	Date report sent
BAM	1	22-Jun-21	2-Jul-21	30-Aug-21
CENAM	2	22-Jun-21	2-Jul-21	15-Sep-21
CMI	3	22-Jun-21	22-Jul-21	4-Oct-21
INMETRO	4	22-Jun-21	29-Jun-21	15-Sep-21
INTI	5	22-Jun-21	/	/
NIM	6	7-Jun-21	14-Jun-21	15-Sep-21
NIST	7	22-Jun-21	20-Jul-21	/
NMIJ	8	22-Jun-21	28-Jun-21	16-Aug-21
SE "UKRMETRTE STSTANDART" (UMTS)	10	22-Jun-21	8-Jul-21	11-Oct-21
SMU	9	22-Jun-21	1-Jul-21	15-Sep-21
VNIIM-UNIIM	/	/	/	15-Sep-21



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6. INSTRUCTIONS TO PARTICIPANTS

The instructions sent to the participants by e-mail consisted of the technical protocol, the registration form, the return receipt form and the results report template.

The technical protocol (appendix A) contained background information and timing of the comparison. Information on sample homogeneity and sample preparation for measurements was given. The participants were free to choose the measurement procedure, however, the coulometric titration or titrimetry method were recommended for this comparison. The participants were requested to express the results as amount content of sodium carbonate [mol/kg] and to provide uncertainty evaluation according to JCGM 100:2008^[2].

The results report template contained entries related to the measurement results, a detailed uncertainty evaluation and a description of the measurement procedures.

7. METHODS OF MEASUREMENT

The measurement methods used by the participants are shown in Table 4.

Table 4 Measurement methods and approaches used by the participants of CCQM-K173

NMI	Measurement method	Measurement date	Additional information
INMETRO	Coulometric HCl-back titration	6-9 Sep	-
UMTS	Coulometric HCl-back titration	5-9 Oct	Mass fraction of 30 impurities using ICP-OES
NMIJ	Coulometry+Titrimetry (H ₂ SO ₄ ,NaOH)	12 Jul	
SMU	Coulometric HCl-back titration	25-30 Aug	-
NIM	Coulometric HCl-back titration &coulometry back titration with electrolysis generated H ⁺	9-20 Aug, 1 Sep	Mass fraction of 15 impurities using HR-ICP-MS



NMI	Measurement method	Measurement date	Additional information
VNIIM-UNIIM	Coulometric back titration with generated H ⁺	16-22 Mar, 23-25 Aug	Mass fraction of 7 impurities using IC, 17 impurities using ICP-MS
CENAM	Coulometric HCl-back titration	14 Sep	
BAM	Titrimetry	8-16 Jul	-
CMI	Coulometric HCl-back titration	22-24 Sep	

The measurement methods used by the participants to measure the amount content of bases expressed as sodium carbonate were constant current coulometry and titrimetry. All participants reported more or less details on their coulometric and titrimetric procedures. Some details on measurement procedures from the reports as well as main uncertainty sources are given in Table 5 and Table 6.

Note: CENAM also reported, as additional information, a value obtained by HCl titrimetry, traceable to reference material SRM-723e from NIST.

Table 5 Some parameters of the coulometric measurement procedures

Analytical method - detailed description	INMETRO	UMTS	NMIJ	SMU
Cell characteristics:				
Type of the coulometric cell (vertical/horizontal)	vertical	horizontal	horizontal	vertical
Number of chambers (working + auxiliary + intermediate + ... = ?)	3	4	4 (two intermediate compartments)	3 (1 intermediate chamber)
Volume of the electrolyte in the working camera, mL	300	200	80	250
Working electrolyte composition	1.0 mol/kg KCl	1 mol/L KCl	1 mol/L KCl	48 g/L KCl
Auxiliary electrolyte composition	1.0 mol/kg KCl	1 mol/L KCl	1 mol/L KCl	75 g/L KCl
Main current value, mA	200	30	100	200
The value of the working electrode surface, cm ²	1	1	45 mm (wide) * 120 mm (long), 80 mesh (not plate)	Pt wire, ca 7 cm ²



The material of auxiliary electrode (Pt / Ag / Cu / other)	Ag	Ag	Ag	Ag
Electrolyte temperature (if registered), °C	25	20 ± 2	room temperature	23.0
End-point detection method	potentiometric	glass pH-electrode	combined pH glass electrode	potentiometric
End-point estimation method	nonlinear regression	multi-parametric	inflection point estimated by using a third order polynomial approximation	nonlinear LSQ EP calculation
Type of generating (anodic/cathodic/variable) at main generating	cathodic	cathodic	cathodic	cathodic
Procedure characteristics:				
Generating current value of the pretitration (if applicable), mA	2	4 and 0,5	5	1.6
Single impulse time of the pretitration (if applicable), s	2.4		3	2 and 2.4
Purging the electrolyte by inert gas (over the electrolyte/ through the electrolyte)	through the electrolyte	no information	over the electrolyte	through the electrolyte
The inert gas flow rate value, L/min	Not measured	0.02	0.05	0.12
Method for determining the absence of CO ₂ in electrolyte (measuring / by character of indicating signal / other)	by character of indicate signal	glass pH-electrode	measuring	CO ₂ eliminated by the procedure; titration curve slope check
Major uncertainty sources	current efficiency, electrolyte impurities, CO ₂ removal	weighing, amount content of HCl	drying conditions, repeatability of coulometric determinations for sulfuric acid, switching	spray losses on sample preparation, amount content of HCl, weight of Na ₂ CO ₃



Analytical method - detailed description	NIM	VNIIM-UNIIM	CENAM	CMI
Cell characteristics:				
Type of the coulometric cell (vertical/horizontal)	horizontal	vertical	vertical	vertical
Number of chambers (working + auxiliary + intermediate + ... = ?)	4 (two intermediate compartments)	4	working+ intermediate (agar)+auxiliary	3 (1 intermediate compartments)
Volume of the electrolyte in the working camera, mL	150	300	200	250
Working electrolyte composition	1 mol/L NaCl	0.5M Na ₂ SO ₄	1.0 mol/L KCl	0.5 M KCl
Auxiliary electrolyte composition	1 mol/L KCl	0.5M CuSO ₄	1.0 mol/L KCl	1 M KCl
Main current value, mA	101.81068	100	100 mA	200 mA
The value of the working electrode surface, cm ²	102 rectangular sheet	84	0.33	7
The material of auxiliary electrode (Pt / Ag / Cu / other)	Ag	Cu	Ag	Ag
Electrolyte temperature (if registered), °C	room temperature	65	ambient temperature (19 °C)	-
End-point detection method	combined pH glass electrode	combined pH glass electrode	potentiometric glass electrode	potentiometric
End-point estimation method	calculation of the inflection point by solving the 2nd derivative accord. to the time (it is also the maximum of the 1st derivative)	polynomial 3 degrees	cubic equation	nonlinear regression
Type of generating (anodic/cathodic/variable) at main generating	cathodic	variable	cathodic	cathodic



Procedure characteristics:				
Generating current value of the pretitration (if applicable), mA	10.18127	3	3	2
Single impulse time of the pretitration (if applicable), s	2	10	3	2
Purging the electrolyte by inert gas (over the electrolyte/ through the electrolyte)	through the electrolyte	through the electrolyte	argon ultrapure	through the electrolyte
The inert gas flow rate value, L/min	0.2~0.3	0.3	aproximately 5-8 mL/s	
Method for determining the absence of CO ₂ in electrolyte (measuring / by character of indicating signal / other)	by character of indication signal	by character of indication signal	by character of indication signal	by character of indication signal
Major uncertainty sources	concentration of HCl, end-point determination, weighing of HCl, instability of current	weighing, impurities, Cu diffusion, impermeability (CO ₂)+diffusion,	amount content of HCl, weighing Na ₂ CO ₃	amount content of HCl, weighing Na ₂ CO ₃ and HCl



Table 6 Some parameters of the titrimetric measurement procedures

Parameter	BAM	CENAM
Certified reference material	NIST SRM-351a, sodium carbonate	The gravimetric titration with a certified reference material from NIST (Tris(hydroxymethyl)aminomethane, SRM-723e) and CENAM (HCl, CMR-6200074j) like calibrator and from NIST (sodium carbonate, SRM-351a) like control.
Purging the electrolyte by inert gas	The gas flushing with argon from above	No information
The method	Direct titration	HCl-back titration
End-point indication method	potentiometric (calculation of the inflection point by solving the 2nd derivative accord.)	potentiometric
C(HCl) for titration	0.2 mol/kg	0.1mol/kg
Mass of Na ₂ CO ₃ , g	0.19	9 (Aqueous Sodium Carbonate Solution prepared)
Major uncertainty sources	weighing, CRM	Amount content of HCl, mass of diluted Tris(hydroxymethyl)aminomethane used in the final titration

8. RESULTS AND DISCUSSION

8.1 Measurement results for amount content of sodium carbonate

Results of the amount content of sodium carbonate and corresponding uncertainties reported by the participants are summarized in Table 7. According to the χ^2 consistency check, the results of 9 participants were inconsistent. There were two groups of results with small uncertainties which hardly overlapped (see Figure 2).



Table 7 Results for amount content of bases expressed as Na_2CO_3

<i>Institute</i>	<i>Result</i> <i>/mol.kg⁻¹</i>	<i>n</i>	<i>SD</i> <i>/mol.kg⁻¹</i>	<i>u_c</i> <i>/mol.kg⁻¹</i>	<i>U</i> <i>/mol.kg⁻¹</i>	<i>k</i>
INMETRO	9.4252	6	0.0102	0.0129	0.0258	2
UMTS	9.4269	6	0.0131	0.0085	0.0171	2
NMIJ	9.43042	7	0.00127	0.00068	0.0014	2
SMU	9.43060	8	0.00044	0.00041	0.0008	2
NIM	9.43082	12	0.00135	0.00051	0.0010	2
VNIIM-UNIIM	9.4332	9	0.00082	0.00085	0.0017	2
CENAM	9.43386	6	0.00090	0.00060	0.0012	2
BAM	9.4339	8	0.00130	0.0017	0.0034	2
CMI	9.4380	6	0.00745	0.0032	0.0064	2
Consistency test	χ_{obs}^2	$\chi_{0.05,m-1}^2$	<i>m</i>	Conclusion		
	35.24	15.51	9	$\chi_{obs}^2 > \chi_{0.05,m-1}^2$	inconsistent	
	30.56	11.07	6	$\chi_{obs}^2 > \chi_{0.05,m-1}^2$	inconsistent	

Table 7a Additional Results

<i>Institute</i>	<i>Result</i> <i>/mol.kg⁻¹</i>	<i>n</i>	<i>SD</i> <i>/mol.kg⁻¹</i>	<i>u_c</i> <i>/mol.kg⁻¹</i>	<i>U</i> <i>/mol.kg⁻¹</i>	<i>k</i>
CENAM(titrn-info)	9.43441	18	0.00211	0.00146	0.0029	2

CMI had realised that they did a calculation error. The result after correction accompanied with the expanded uncertainty was (9,433214±0,002946) mol/kg. Since the error had been identified only after disclosure of the KC results, it was not possible to correct the value, neither for KCRV nor for DoE calculation. For this reason the result of CMI was excluded from KCRV calculation.

Furthermore, an investigation of M. Mariassy from SMU showed that the large uncertainties reported by INMETRO and UKRMETRTESTSTANDART (UMTS) were due to repeatability issues. It must therefore be assumed that these institutes have



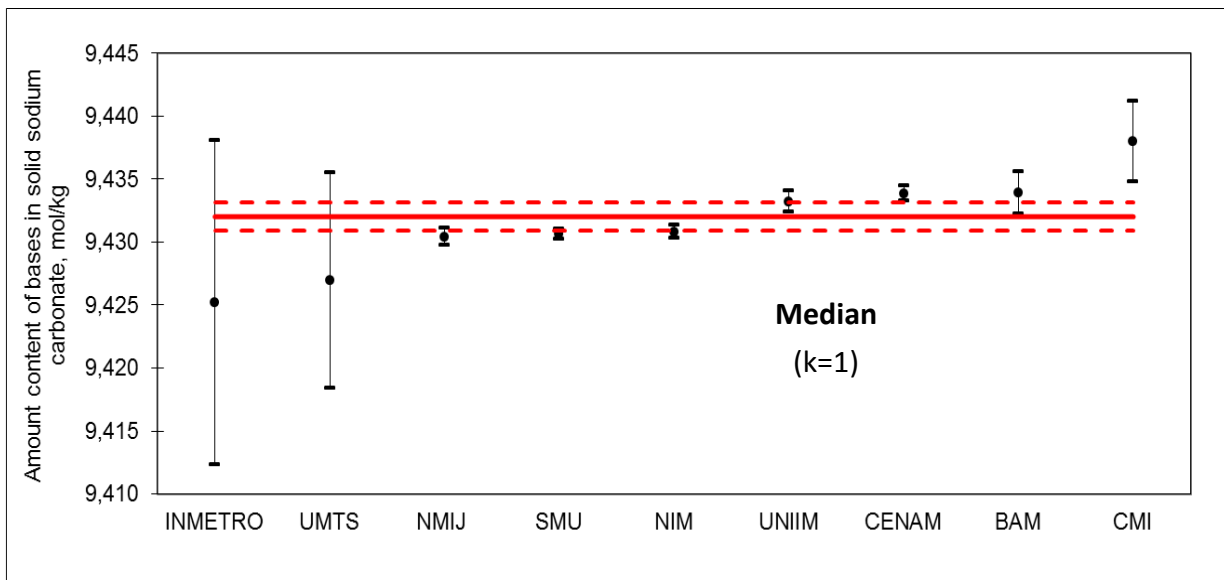
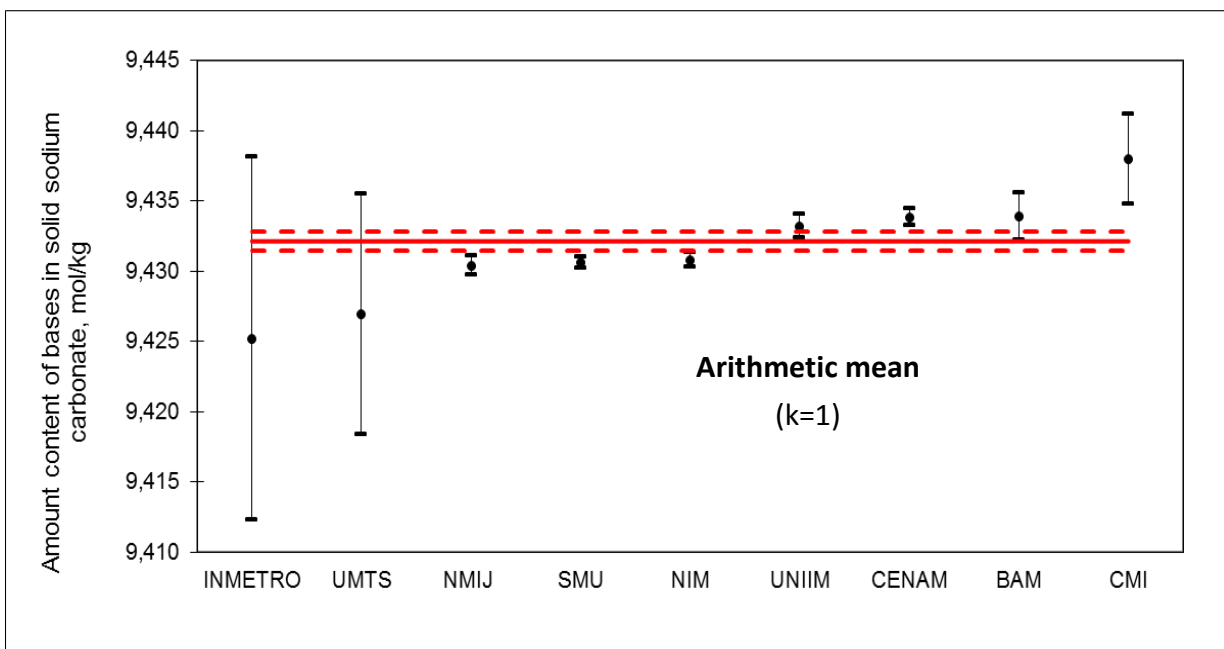
faced some technical problems during the measurement. Consequently, their results were excluded from KCRV calculation as well. INMETRO and UMTS have agreed to this decision. INMETRO later discovered that there was a malfunction of a valve for deaeration of the solution. Consistency χ^2 test showed that the results of 6 participants (except CMI, INMETRO and UMTS) were also inconsistent (Table 7).

Table 8 shows various KCRV estimators calculated from the results remaining for KCRV calculation (NMIJ, SMU, NIM, VNIIM-UNIIM, CENAM, BAM). All results are shown in Figure 2, together with the reported standard uncertainties.

Table 8 Possible estimators of the KCRV

<i>Candidate KCRV</i>	<i>Amount content</i>	<i>Mass fraction expressed as Na₂CO₃</i>	<i>Standard uncertainty</i>	<i>Expanded uncertainty</i>
	(molkg ⁻¹)	(kgkg ⁻¹)	(molkg ⁻¹)	(molkg ⁻¹)
<i>Arithmetic mean</i> (\bar{x})	9,4321	0,99970	0,00069	0,0014
<i>Median*</i>	9,4320	0,99968	0,00114	0,0023
<i>Uncertainty- weighted mean</i>	9,4315	0,99963	0,00061	0,0012

Note: *It was proposed to use the *median of the results of the 6 participants* as the KCRV.



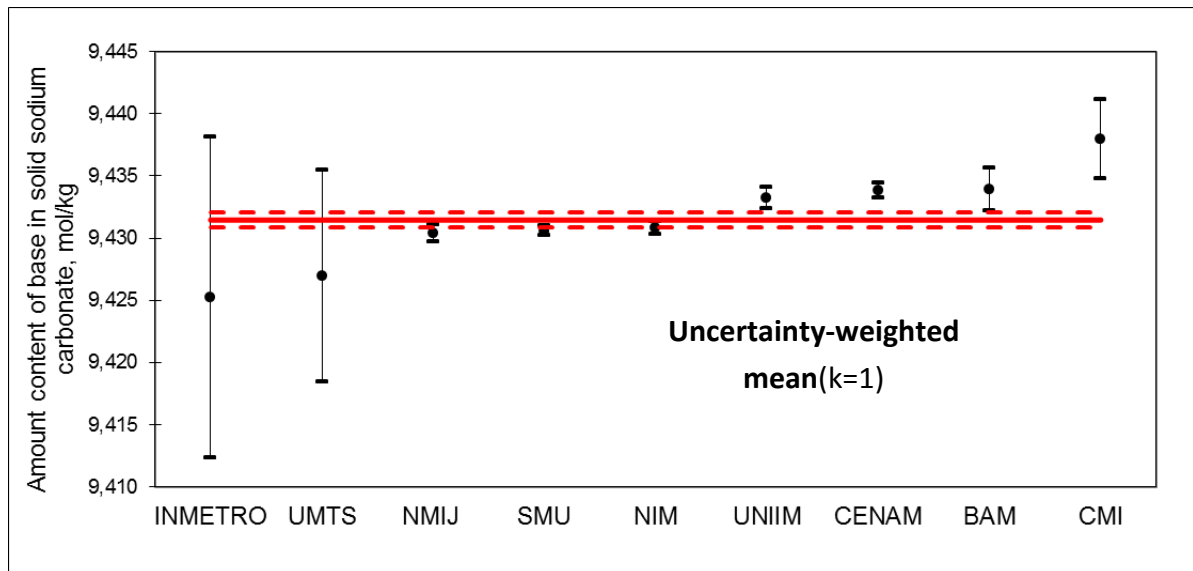


Figure 2. Results of CCQM-K173 and different KCRV estimators (each bar indicates the combined standard uncertainty)

8.2 Algorithm for comparison data treatment

A consistency check was performed according to the CCQM guidance note ^[3] using the algorithm shown below

$$\bar{x}_u = \frac{\sum_{i=1}^m \frac{x_i}{u(x_i)^2}}{\sum_{i=1}^m \frac{1}{u(x_i)^2}} \quad (3)$$

$$\chi_{obs}^2 = \sum_{i=1}^m \left(\frac{x_i - \bar{x}_u}{u(x_i)} \right)^2 \quad (4)$$

where x_i is the result of the value of i NMI, $u(\bar{x})$ is the standard uncertainty of \bar{x} , m is number of participants of the key comparison.

After calculations using formulas (3), (4) χ_{obs}^2 with $m-1$ and with $\chi_{0.05, m-1}^2$ the 95 percentile of χ^2 with $m-1$ of freedom ($\chi_{0.05, m-1}^2$ - has been taken from Microsoft Excel) were compared,



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If $\chi_{obs}^2 < m-1$ it is normally safe to proceed with the assumption that the results are mutually consistent and that the uncertainties account fully for the observed dispersion of values.

If $m-1 < \chi_{obs}^2 < \chi_{0.05,m-1}^2$ the data does not provide strong evidence that the reported uncertainties are inappropriate, but it remains a risk that additional factors are contributing to the dispersion. Referring to the prior working group decision on presumptive consistency we proceed accordingly.

If $\chi_{obs}^2 > \chi_{0.05,m-1}^2$ the data should be considered mutually inconsistent.

Candidates of the key comparison reference value (KCRV) were estimated following the CCQM guidance note ^[3] using different approaches. Results and uncertainties were taken from the participants' reports as they were. Formulas for calculation are shown below.

KCRV estimators:

Arithmetic mean

$$\bar{x} = \frac{1}{m} \sum_{i=1}^m x_i \quad (5)$$

$$u^2(\bar{x}) = \frac{\sum_{i=1}^m (x_i - \bar{x})^2}{m(m-1)} \quad (6)$$

where x_i is the result of the value of i NMI, $u(\bar{x})$ is the standard uncertainty of \bar{x} .

Median

$$med(x) = \left. \begin{cases} \frac{1}{2}(x'_{m/2} + x'_{m/2+1}), & m \text{ even} \\ x'_{(m+1)/2}, & m \text{ odd} \end{cases} \right\} \quad (7)$$



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$$u^2(\text{med}(x)) = \frac{\pi}{2m} \hat{\sigma}^2 \quad (8)$$

$$\hat{\sigma} = 1.483 \text{med}(|d_i|) \quad (9)$$

Where $d_i = x_i - \text{med}(x)$.

Uncertainty-weighted mean

$$\bar{x}_u = \sum_{i=1}^m w_i x_i \quad (10)$$

$$w_i = \frac{1/u^2(x_i)}{\sum_{i=1}^m 1/u^2(x_i)} \quad (11)$$

$$\frac{1}{u^2(\bar{x}_u)} = \sum_{i=1}^m 1/u^2(x_i) \quad (12)$$

$$u_{corr}^2(\bar{x}_u) = \frac{\chi_{obs}^2}{m-1} u^2(\bar{x}_u) = \frac{\sum_{i=1}^m \left(\frac{x_i - \bar{x}_u}{u(x_i)} \right)^2}{m-1} u^2(\bar{x}_u) \quad (13)$$

where $u(x_i)$ is the standard uncertainty of x_i .

8.3 Impurity analysis

The impurities were analysed by NIM, UKRMETRTESTSTANDART (UMTS) and VNIIM-UNIIM. Their results were summarized in Table 9.



Table 9 Mass fraction of impurities by semi-quantitative measurement methods (in $mg \cdot kg^{-1}$)

<i>Institute (method)</i>	<i>NIM (HR-ICP-MS)</i>	<i>VNIIM-UNIIM (IC, ICP-MS)</i>	<i>UMTS (ICP-OES)</i>
<i>Impurities</i>			
F ⁻	/	<7	/
Cl ⁻	/	<7	/
NO ₂ ⁻	/	<15	/
NO ₃ ⁻	/	<6	/
Br ⁻	/	<8	/
SO ₄ ²⁻	/	<5	/
PO ₄ ³⁻	/	<30	/
Li	/	0.0040	1.098
Be	/	0.0005	<0.00044
B	/	/	<2
Mg	/	0.46	<0.11
Al	/	0.054	38.61
Si	/	/	<1
P	0.037	1.5	<0.4
K	0.245	6.39	194.6
Ca	6.84	26.4	31.73
Sc	0.154	/	/
Ti	/	/	54.88
V	0.003	0.029	<0.135
Cr	0.032	0.104	3.69
Mn	0.031	0.361	<0.014
Fe	/	4.43	<0.14
Co	/	0.022	<0.115
Ni	/	0.057	<0.25
Cu	/	0.257	<0.08
Zn	/	0.070	<0.065
As	0.641	/	5.388
Se	/	/	1.696
Rb	0.002	/	/
Sr	0.527	1.92	<0.0028



<i>Institute (method)</i>	<i>NIM (HR-ICP-MS)</i>	<i>VNIIM-UNIIM (IC, ICP-MS)</i>	<i>UMTS (ICP-OES)</i>
<i>Impurities</i>			
Mo	0.032	0.061	2.49
Ag	/	/	<0.75
Cd	0.012	/	<0.065
Sn	0.009	/	<0.2
Sb	/	/	<0.2
Ba	0.266	/	<0.005
Ta	0.053	/	/
Tl	/	/	<0.2
Pb	/	/	<0.8
Bi	/	/	2.095

8.4 Discussion

Sodium carbonate was chosen as an object for the key comparison for the first time so for some participants it was a challenge to implement a new measurement procedure and to evaluate its uncertainty.

Either constant current coulometry or titrimetry were used. However, there were no two identical measurement procedures. Titrimetry is known to have larger uncertainty than coulometry, but in this comparison titrimetric result by BAM was accompanied by rather small relative expanded uncertainty (0,036 %) and in opposite two coulometric results by INMETRO and UMTS were accompanied by uncommon large relative expanded uncertainty values (0,27 % and 0,18 % respectively). BAM implemented automatic potentiometric titrimetry with argon purging and the software calculation of the second equivalence point (inflection point) near the end-point. INMETRO and UMTS had a poor repeatability. Expanded uncertainties evaluated by the other participants were in the range from 0,009 % (SMU) to 0,068 % (CMI). The major sources of bias for each participant are given in the Table 5 for coulometry and in the Table 6 for titrimetry. The major type B uncertainty sources for the constant current coulometry were amount content of HCl, weighing, drying conditions of



Na₂CO₃, end-point determination, impurities, and current efficiency. The major type B uncertainty sources for titrimetry were content of HCl, weighing and CRM. Some of them are considered in more details below.

Sample preparation before weighing. Even though most participating NMIs had dried the sample before weighing according to the protocol (*dried at 275 °C for 4h*) without crushing or grinding the material), uncertainties in drying and weighing procedures were often underestimated. Weighing uncertainty depends on sample size, and sodium carbonate is hygroscopic, so, details of the procedures are important. But very little information was given. In most cases, this uncertainty source was not considered.

Current efficiency. Although current efficiency is easier to be achieved up to 100% in the coulometric titration of acids and back-titration of bases, it still has a noticeable effect on the measurement results. At the determination of carbonate by electrolytic generation of H⁺ with the coulometric method (platinum electrode and copper electrode, sodium sulphate aqueous solution as electrolyte solution), the current efficiency may be influenced by side reaction of persulfate formation, which is favoured by high sulphate concentration.

End-point calculation. Some participating NMIs regarded the uncertainty of end-point evaluation as one of the major uncertainty sources (sometimes it was considered as type A uncertainty). An important factor is the slope of titration curve. The slope of the titration curves for preliminary and final titrations are to be identical or at least very close to each other.

The influence of air and gas impurities. CO₂ from the air and/or purging gas (usually argon) acidifies the electrolyte. CO₂ removal is easier when external reaction of sodium carbonate with the acid is implemented compared to the implementation with the internal reaction in the coulometric cell.

It can be seen in Figure 2, that the results of the 6 institutes used to calculate the candidate KCRVs are apparently split into two groups that show a small, but distinct bias. The potential sources of the biases and the effect on the measurement result of the amount content of bases in solid sodium carbonate are listed in the table 10. However, a deep analysis of the measurement protocols ^[4] did not reveal a cause for the observed bias. It must also be considered that the number of results is relatively



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small. The apparent bias might well be just an arbitrary spread into two groups. In any case, it seems that the individual uncertainties stated by the institutes are underestimated to a certain extent. Slightly larger uncertainties would in fact provide more consistent results. Nevertheless, the overall spread of the results and the associated uncertainties can be accepted as being reasonably consistent, provided the KCRV and its uncertainty account for this observation. Therefore, the median is proposed as the best estimate for the KCRV.

Table 10 - Potential sources of bias in sodium carbonate assay by coulometry or titrimetry

Positive bias	Negative bias
HCl loss in reaction	Carbonate loss in reaction
Incorrect HCl concentration	Incorrect HCl concentration
Residual CO ₂ present in solution in final titration	Incomplete drying
Low current efficiency in H ⁺ generation	Water absorption before/during weighing

9. EQUIVALENCE STATEMENTS

The degrees of equivalence and their uncertainties are calculated according to the following equations:

$$d_i = x_i - med(x) \quad (14)$$

$$u^2(med(x)) = \frac{\pi}{2m} \hat{\sigma}^2 \quad (15)$$

$$u^2(d_i) = u^2(x_i) + u^2(med(x)) \quad (16)$$

$$U(d_i) = k \cdot u(d_i) \quad (17)$$



Where d_i is the degree of equivalence between the NMI result x_i and the median of the results, and $U(d_i)$ is the expanded uncertainty ($k = 2$) of the d_i calculated by combining the standard uncertainty $u(d_i)$ of the NMI result and the standard uncertainty $u(\text{med}(x))$. The equivalence statements for CCQM-K173 are shown in Table 11. The same data are graphically presented in Figures 3. To this end, the median of the results of the 6 participants (NMIJ, SMU, NIM, VNIIM-UNIIM, CENAM and BAM) mentioned above has been used as (proposed) KCRV.

Table 11 Equivalence statements of Na_2CO_3 amount content for CCQM-K173

Participant	Reported Value (x_i)	Standard combined uncertainty ($u(x_i)$)	d_i	$U(d_i)$	$d_i/U(d_i)$
	mol.kg ⁻¹	mol.kg ⁻¹	mol.kg ⁻¹	mol.kg ⁻¹	/
INMETRO	9.4252	0.0129	- 0.00681	0.02590	-0.26
UTMS	9.4269	0.0085	- 0.00507	0.01722	-0.29
NMIJ	9.43042	0.00068	- 0.00159	0.00265	-0.60
SMU	9.4306	0.00041	- 0.00141	0.00242	-0.58
NIM	9.43082	0.00051	- 0.00119	0.00250	-0.48
VNIIM-UNIIM	9.4332	0.00085	0.00119	0.00284	0.42
CENAM	9.43386	0.00060	0.00185	0.00257	0.72
BAM	9.4339	0.0017	0.00189	0.00409	0.46
CMI	9.4380	0.0032	0.00595	0.00679	0.88

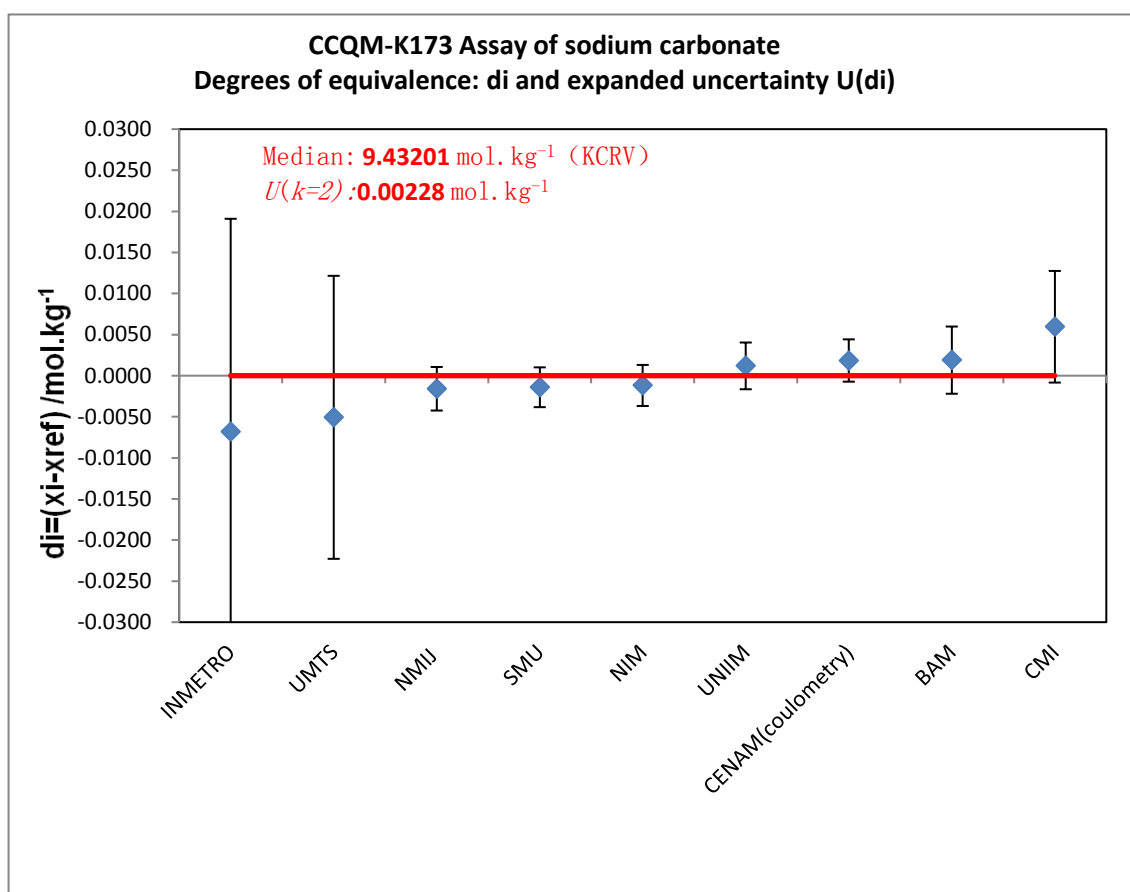


Figure 3. Degrees of equivalence d_i and expanded uncertainty $U(d_i)$ ($k=2$) for amount content of bases expressed as sodium carbonate

10. SCOPE OF THE COMPARISON (How far the light shines)

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.

11. CONCLUSION

The measurement capabilities of NMIs for amount content of bases in high purity sodium carbonate were demonstrated in this comparison. In general, results of participants were in good agreement. The median of 6 participants was proposed as the reference values of the key comparison (amount content of bases expressed as sodium carbonate 9.43201 mol/kg and associated expanded uncertainty ($k=2$) 0.00228 mol/kg). The suitability of coulometry and titrimetry for assay of high purity substances was again demonstrated.

12. ACKNOWLEDGEMENTS

The coordinating laboratories gratefully acknowledge Dr. M. Mariassy (SMU), Dr. S. Seitz (PTB), Dr. T. Asakai (NMIJ) for their contribution and support, discussing the results and report review. And thanks all of the analysts from the participant institutes for their contributions as well as the contact persons.

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CCQM-K173

Assay of Sodium Carbonate

Key Comparison

Technical protocol

April 2021

Bing Wu¹ and Alena Sobina²

¹National Institute of Metrology, P. R. China (NIM)
No.18, Bei San Huan Dong Lu, Chaoyang District, Beijing China, 100029,

²Ural Scientific Research Institute for Metrology – Affiliated Branch of the
D.I.Mendeleyev Institute for Metrology (VNIIM -UNIIM)

4, Krasnoarmeyskaya Street, Ekaterinburg, Russian Federation, 620075



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им. Д.И.Менделеева

Ural Scientific Research Institute for Metrology – Affiliated Branch of
the D.I.Mendeleyev Institute for Metrology (VNIIM -UNIIM)

INTRODUCTION

Pure materials are very important for traceability in chemical metrology. Pure material studies and comparisons are important activities in the Electrochemical Analysis and Classical Chemical Methods Working Group and Inorganic Analysis Working Group at all times. Acid-base analysis is made almost exclusively by titration methods; sodium carbonate is the most used reference material for this measurement.

This key comparison is organized jointly by EAWG and IAWG of CCQM to test the abilities of the NMIs to measure the purity or amount content of solid bases. They are important challenges for reference material producers, providers of other measurement services, such as proficiency testing schemes. Evidence of successful participation in formal, relevant international comparisons is needed to document calibration and measurement capability claims (CMCs) made by national metrology institutes (NMIs) and designated institutes (DIs).

The comparison will test the capabilities and methods used for assays of high purity materials and persistently underpin the claimed calibration and measurement capabilities of the institutes.

For coulometry or titrimetry, good results will indicate good performance in assaying bases.

TIMELINE

Table 1 Timeline

Date	Action
March 2021	Sample Preparation and Homogeneity Testing
IAWG&EAWG joint meeting, April 2021	Discussion of the technical protocol
April 2021	Call for participation to EAWG & IAWG members
The end of May 2021	Deadline for registration
Mid-June 2021	Dispatch of the samples



15 September 2021	Deadline for Submission of Results
Autumn meeting, 2021	Preliminary Discussion of Results
IAWG&EAWG joint meeting April 2022	Draft A report

Please note that the schedule will be subject to discussion in the April and May meetings of EAWG and IAWG. It might be necessary to adapt it due to the implications of the Covid-19 pandemic.

MEASURANDS

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

The assay is in the range of 99.8 % to 100.1% of the theoretical value based on the sodium carbonate amount content.

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

STUDY MATERIALS

The source of the sample is from a 5 kg batch of commercially available pure sodium carbonate. After being homogenized, a 400 g portion was selected from the middle fraction of the batch and was homogenized again in a large bottle. This homogenized portion was then transferred to 20 glass bottles closed with plastic caps for the comparison. The impurities were determined by ICP-MS.

Recommended Minimum Sample Amount

The recommended minimum sample amount for analysis is at least 150 mg.



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Dry Mass Determination

The material should be dried at $(275 \pm 5)^\circ\text{C}$ for 4h 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 2.533 g/cm^3 .

Homogeneity Assessment of Study Material

Twelve bottles, selected at random, were tested by VNIIM-UNIIM for homogeneity. To this end, two independent samples of each bottle were analyzed by coulometric titration. Data obtained were evaluated by one-way ANOVA. Summary results of homogeneity assessment for the samples of sodium carbonate are given in the table 1 and figure 1.

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

ANOVA Estimate	
Within-packet, CV_{wth} :	0,0073 %
Between-packet, CV_{btw} :	0,0040 %
Total analytical variability, CV:	0,0083 %
Probability of falsely rejecting the hypothesis that all samples have the same measurand value:	2,7 %



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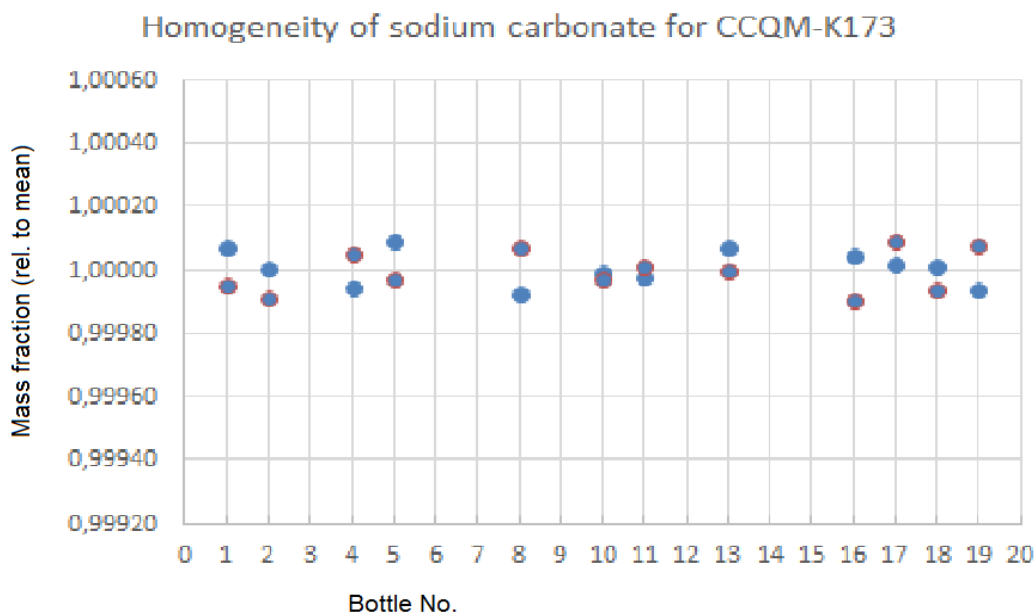


Figure 1. Homogeneity evaluation for assay of sodium carbonate

Stability Assessment of Study Material

Sodium carbonate is known to be a stable material during storage and transportation. Typical shelf-life of CRMs of sodium carbonate is from 5 to 10 years.

The material absorbs water and carbon dioxide (CO_2) from the air and may form a hard cake containing hydrated sodium carbonate (Na_2CO_3) and/or sodium bicarbonate (NaHCO_3) on extended storage. Drying as described before expels absorbed water and carbon dioxide yielding pure Na_2CO_3 .

Available Calibration Materials

Participants using coulometry establish the metrological traceability of their results to the SI using a direct realization via a primary method.



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Participants using titrimetry may establish the metrological traceability of their results to the SI using certified reference materials (CRMs) from an NMI/DI having the required CMC claims.

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, 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 NIM contact person by e-mail, fax or mail. If there is any damage, please contact us immediately, and NIM will send another bottle.

The sample should be stored in a dark, dry place at laboratory temperature in the original container until used.

The technical protocol and a template for the report will be sent by e-mail.

RESULTS

The report should be sent to the coordinating laboratories (**NIM and VNIIM-UNIIM**) **before 15 September 2021**, preferentially by e-mail. The coordinator will confirm the receipt of each report to the participant. If the confirmation does not arrive within one week, please contact the coordinator 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 boxes. If this is not possible, the format can be modified or the data can be reported in another form.

Information requested:



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1. The results will 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.
2. If the assay is determined from impurity analysis, results for all the elements/compounds sought must be included.
3. 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.
4. The complete measurement equation has to be given, as well as the values of the constants (suggested Faraday constant: $96485.33212 \text{ C mol}^{-1}$ (exact value without uncertainty)) 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.
5. 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. Thereported uncertainty should be expressed as a combined standard uncertainty and as an expanded uncertainty referred to a 95 % level of confidence.
6. 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.
7. 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.



USE OF CCQM-K173 IN SUPPORT OF CALIBRATION AND MEASUREMENT CAPABILITY (CMC) CLAIMS

How Far the Light Shines

Successful participation will demonstrate capabilities for an assay of high purity materials. Good result indicates good performance in assaying the purity (amount content of solid bases as well as their water solutions.

Considering the IAWG Core Capability Matrix, this material falls into the category of “Calibration materials and solutions”, and so will support CMCs for the analyte groups of “Inorganic species” (anion OH⁻ and cation H⁺), at the 1 mg/kg level and higher.

Core Capability table

Analyte groups	Matrix challenges						Calibration materials and solutions
	Water/aqueous	High Silica content (e.g. Soils, sediments, plants, ...)	High salts content (e.g. Seawater, urine, ...)	High organics content (e.g. high carbon) (e.g. Food, blood/serum, cosmetics, ...)	Difficult to dissolve metals (Autocatalysts, ...)	High volatile matrices (e.g. solvents, fuels, ...)	
Group I and II: Alkali and Alkaline earth (Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba)							
Transition elements (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ag, Cd, Ta, W, Au, Hg, Al, Ga, In, Tl, Pb, Po)							
Platinum Group elements (Ru, Rh, Pd, Os, Ir, Pt)							
Metalloids / Semi-metals (B, Si, Ge, As, Sb, Te, Se)							
Non-metals (P, S, C, N, O)							
Halogens (F, Cl, Br, I)							
Rare Earth Elements (Lanthanides, Actinides)							
Inorganic species (elemental, anions, cations)							K173: OH ⁻ , H ⁺
Small organo-metallics							
Proteins							
Nanoparticles							

Low level (e.g. below 50 µg/kg)
High level (e.g. above 50 µg/kg)



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ВНИИМ
им. Д.И.Менделеева

Ural Scientific Research Institute for Metrology – Affiliated Branch of
the D.I.Mendeleyev Institute for Metrology (VNIIM -UNIIM)

Contact Details

Please send the completed report form by e-mail not later than 15 September, 2021 to:

Bing Wu

National Institute of Metrology (NIM)

No. 18, Bei San Huan Dong Lu, Chaoyang District,

Beijing, P.R.China, 100029

Tel.: +86 10 64225471 Fax: +86 10 64294060

E-mail: wubing@nim.ac.cn

Alena Sobina

Ural Scientific Research Institute for Metrology – Affiliated Branch of the
D.I.Mendeleyev Institute for Metrology (VNIIM -UNIIM)

4, Krasnoarmeyskaya Street

Ekaterinburg, Russian Federation, 620075

Tel.: + 7 343 355 49 22 Fax: +7 343 355 49 22

E-mail: sobinaav@uniim.ru