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CCQM WG on Electrochemical Analysis and Classical Chemical Methods

CCQM-K169–Assay of sodium oxalate

Final Report

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with participation of

BFKH: Daniel Nagy
CENAM: Griselda Rivera-Sánchez, José Luis Ortiz-Aparicio
INMETRO: Paulo Paschoal Borges, Sidney Pereira Sobral
NIM: Bing Wu, Tao Zhou, Jingbo Chao
VNIIM–UNIIM: Alexandr Shimolin

09 July 2026

Summary

The CCQM-K169 Assay of Sodium Oxalate key comparison was jointly organized by the Electrochemical Analysis and Classical Chemical methods (EAWG) and Inorganic Analysis (IAWG) working groups of CCQM to test the abilities of the national metrology institutes (NMIs) to measure the amount content of reductants in high purity substances as well as assaying high purity salts to be used as primary standards. Reductants have not been measured in comparisons for assay of high purity salts yet. Five NMIs participated in this key comparison CCQM-K169. The comparison was initiated by NMIJ (Japan), but it was postponed due to COVID-19 pandemic.

Later, NMIJ had to withdraw from participating and piloting. Finally, VNIIM-UNIIM (Russia) acted as a coordinating laboratory. Participating institutes could use a method of their choice. Constant-current coulometry and/or gravimetric titrimetry were used.

The spread of the results is larger than typically observed in key comparisons of high purity salts' assays. It may be related to a new analyte (reductants have never been measured in key comparisons before), complicated measurement procedure, a small number of participants, and because at least two labs experienced in assaying sodium oxalate did not participate. Nevertheless, four out of five NMIs were in reasonable agreement with the key comparison reference value.

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2 List of participants

The list of participants is given in Table 1.

Table 1. List of participants

Acronym	Institute	Country	Contact person	Email
BFKH	Government Office of the Capital City Budapest	Hungary	Daniel Nagy	nagy.daniel2@bfkh.gov.hu
CENAM	Centro Nacional de Metrología	Mexico	José Luis Ortiz-Aparicio	jortiz@cenam.mx
INMETRO	Instituto Nacional de Metrologia, Qualidade e Tecnologia	Brazil	Paulo Paschoal Borges	ppborges@inmetro.gov.br
NIM	National Institute of Metrology P.R.China	China	Bing Wu	wubing@nim.ac.cn
VNIIM-UNIIM	D.I.Mendeleyev Institute for Metrology (VNIIM) Ural Research Institute for Metrology – Affiliated Branch of the D.I.Mendeleyev Institute for Metrology (VNIIM-UNIIM)	Russia	Alena Sobina	sobinaav@uniim.ru

3 Time schedule

Action	Date
Announcement of study (by NMIJ)	3 November 2020 on IAWG/EAWG meeting
First call for participants (by NMIJ)	February 2022
Registration deadline (by NMIJ)	31 March 2022
Second call for participants (by VNIIM-UNIIM)	April-May 2023
Registration deadline (by VNIIM-UNIIM)	30 June 2023
Dispatch of the samples (by VNIIM-UNIIM with assistance of NIM)	March-April 2024
Reporting deadline	31st August 2024
First discussion	October 2024 on EAWG meeting
Draft A1 report	Fall 2025
Draft B report	Spring 2026

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4 Samples

4.1 Description of samples

The samples for the comparison were prepared by the coordinating laboratory using commercially available high-purity sodium oxalate. A portion of ~150 g of material has been homogenized and bottled into glass bottles closed with plastic screw caps. Each bottle contained about 20 g of the sample. The bottle labels indicated “CCQM-K169 Assay of sodium oxalate, sample for comparison”, CAS number 62-76-0, net weight of the sample, bottle number.

Six bottles in card tubes, packed into a cardboard box, were sent on 28 February 2024 by air courier from VNIIM-UNIIM to NIM China, who kindly agreed to deliver samples to the other participants. Shipment to BFKH, CENAM and INMETRO was performed by NIM on 26 March 2024. The tracking number was sent by e-mail to the contact person of each laboratory. Each participant received a uniquely numbered bottle containing about 20 g of the sample undamaged.

4.2 Homogeneity

Seven bottles prepared for comparison were measured by VNIIM-UNIIM to verify homogeneity of the batch. Two independent masses of 0.3 g from each bottle were analysed by coulometric titration using Ce(IV) as a titrant. The obtained data were evaluated by one-way ANOVA. From an analysis of variances (ANOVA), the standard deviation of the repeatability, the standard deviation of within-bottle homogeneity and the standard uncertainty due to between-bottle homogeneity were evaluated (u_h=0.000771 mol/kg which corresponds to the relative value 0.0103%). The obtained value of the relative standard uncertainty due to between-bottle homogeneity is less than the relative standard deviation of the participants which varies from 0.013 % to 0.0481 % and less than the relative expanded uncertainty reported by the participants which varies from 0.016 % to 0.084 %. A summary of the ANOVA results is given in the table 2 and figure 1.

Table 2. ANOVA results of the homogeneity assessment for the amount content of reductants expressed as sodium oxalate (in mol/kg)

Source of variation	SS	df	MS
Between groups	$1{,}108 \cdot 10^{-5}$	6	$1.847 \cdot 10^{-6}$
Within groups	$4{,}607 \cdot 10^{-6}$	7	$6.581 \cdot 10^{-7}$
Total	$1.569 \cdot 10^{-5}$	13	

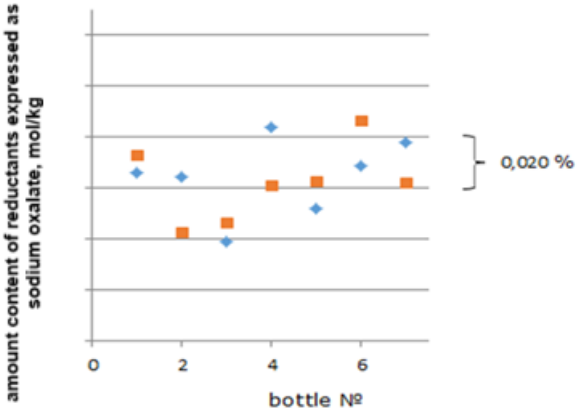

Fig. 1. Result of the homogeneity test. Squares and diamonds indicate the two measurements from the corresponding bottles.

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4.3 Stability

Sodium oxalate is known to be a stable material during storage and transportation. Typical shelf-life of CRMs of sodium oxalate is 5 years. Measurement results obtained by the piloting laboratory during homogeneity study and during the period of measuring after dispatching samples to the participants have confirmed stability of the study material.

The samples of sodium oxalate were found to be adequate for the key comparison.

5 Correspondence with institutes

Participating NMIs INMETRO, NIM, CENAM and VNIIM-UNIIM provided measurement reports on time. The pilot laboratory sent its measurement report to the EAWG Chair to ensure its integrity. BFKH requested a one-month extension of the deadline for report submission.

In this comparison, the technical protocol contained for the first time a list of obligatory uncertainty sources to be considered by the participants based on the EAWG CMC guide [1]. According to it, the pilot laboratory checked the reports, and asked all participants to revise their reports and include all obligatory uncertainty sources. INMETRO was additionally asked to check its report for numerical errors (because the result was significantly lower than those of the other participants), but without being informed of the magnitude or sign of the apparent anomaly.

Finally, all participants had sent revised reports with the obligatory uncertainty sources before the results were disclosed at the EAWG meeting. The revised reports of NIM, CENAM and BFKH contained the same values and corresponding uncertainties for the measurand as in the original reports. Two participants (INMETRO and CENAM) provided revised reports with corrected results (values and corresponding uncertainties) due to following reasons:

- INMETRO applied a third order polynomial to determine the end-point of the gravimetric titration of sodium oxalate and corrected both the result and measurement uncertainty;
- CENAM found a numerical error, due to a wrong link in the spread sheet used for the calculation. Consequently, masses indicated in the first report did not correspond to the preparation of the Ce (IV) diluted solution but corresponded erroneously to the preparation of the potassium dichromate diluted solution. As a consequence of these corrections, the values of oxalate amount content obtained were also modified, as well as the corresponding uncertainty calculation.

No new measurements were carried out by INMETRO and CENAM to correct their results. According to the EAWG CMC guide, and in accordance with CIPM-MRA guidelines G-11, if numerical mistakes are found before disclosing results and no new measurement results were used, a correction can be accepted. EAWG discussed and decided that

- corrections of the result and corresponding uncertainty based on changing the method of calculation the titration end-point were not allowed, so the corrected result of INMETRO was declined and the initial data were used for further evaluation;
- corrections of the result and corresponding uncertainty due to correcting the linking (numerical) error was accepted, so the corrected result of CENAM was taken for the further evaluation.

The results taken into account for the evaluation of the comparison are presented in the Table 5.

6 Instructions for measurement

The material had to be dried at 105 °C for 2 h without crushing or grinding the material. After drying, it should be placed in a desiccator with silica gel or other desiccants, and cooled to room temperature before weighing.

The mass of the sample should be corrected for air buoyancy. The density of sodium oxalate was 2.34 g cm^{-3}.

The minimum sample mass for each measurement was 0.3 g.

Any method or combination of methods could be used for the comparison, but coulometry or titrimetry were recommended.

Some issues concerning challenges of the measurement were discussed in a Web-conference of the participants of CCQM-K169 on 26th September 2023. It was recommended

- to use Ce (IV) as the titrant,
- that participants must investigate the dependence their measurement procedure and quantify uncertainties accordingly if permanganate is used as the titrant,
- other methods may be added to the report as additional information, even though the primary result must be clearly identified.

Participants were requested to report the results as the amount content of reductants in the sample in the unit 'mol/kg', and to provide an uncertainty evaluation in accordance with JCGM 100:2008 [2].

7 Results and discussion

The measurement period and the dates when the reports were sent are provided in Table 3.

Table 3. Measurement dates and report submission dates

Institute	Bottle number	Sample receipt date	Measurement period	Date report sent	Date revised report sent
BFKH	6	10 April 2024	20 September 2024 – 26 September 2024	30 September 2024	15 October 2024
CENAM	1	18 April 2024	25 – 26 August 2024	02 September 2024	27 September 2024
INMETRO	4	17 April 2024	15 – 19 August 2024	30 August 2024	30 September 2024
NIM	5	6 March 2024	17 April 2024 – 02 August 2024	28 August 2024	02 September 2024
VNIIM-UNIIM	1-7	-	05 September 2023 – 29 April 2024	12 August 2024	-

7.1 Methods of measurement

Measurement methods used by the participants to measure the amount content of reductants expressed as sodium oxalate were constant-current coulometry (VNIIM-UNIIM), gravimetric titrimetry (CENAM), and constant-current coulometry in conjunction with gravimetric titrimetry (INMETRO, NIM, BFKH). The participants' reports varied in the level of provided details regarding the described methods. Summary information about the used methods is presented in Figure 2 and Table 4.

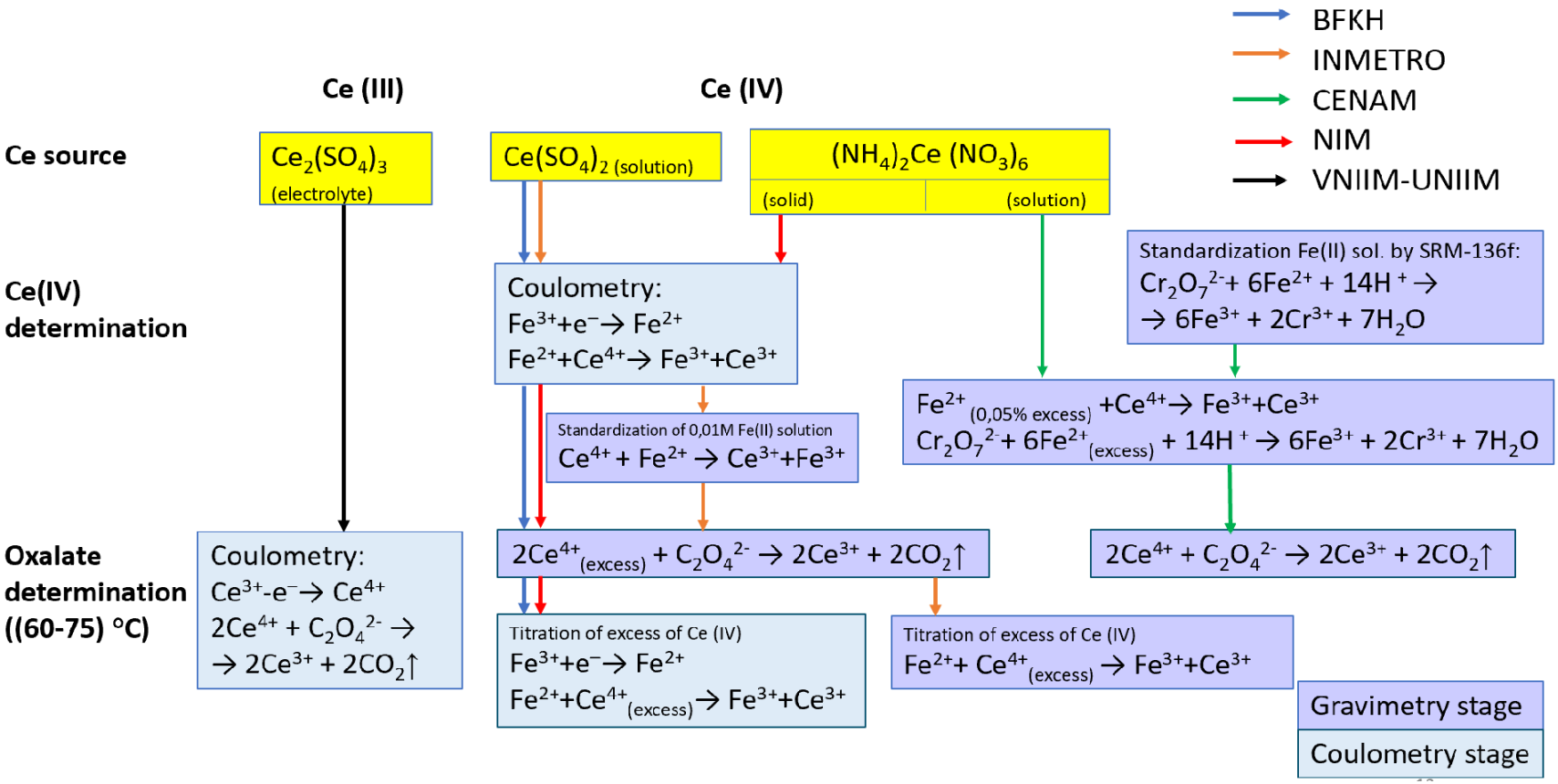

Fig.2 Stages and reactions of the measurement procedures used by participating NMIs

Table 4. Measurement methods and description of the measurement procedures used by the participants of CCQM-K169

Participant's acronym	Measurement method	Additional information
BFKH	Coulometric titration & gravimetric titration (2 stages): 1. coulometric titration of Ce(IV) by electrogenerated Fe(II) from Fe(III); 2. gravimetric titration of oxalate by an excess of Ce(IV) being coulometrically titrated by electrogenerated Fe(II) from Fe(III).	-
CENAM	Gravimetric titration (2 stages): 1. gravimetric standardization of Fe(II) solution by SRM-136f of potassium dichromate; 2. gravimetric titration of oxalate by an excess of Ce(IV) being gravimetrically titrated by standardized Fe(II) solution	-
INMETRO	Coulometric titration & gravimetric titration (3 stages): 1. coulometric titration of Ce(IV) solution by electrogenerated Fe(II) from Fe(III); 2. gravimetric standardization of Fe(II) solution by Ce(IV) solution characterized by coulometric titration; 3. gravimetric titration of oxalate by an excess of Ce(IV) being gravimetrically titrated by standardized Fe(II) solution	-
NIM	Coulometric titration & gravimetric titration (2 stages): • coulometric titration of Ce(IV) by electrogenerated Fe(II) from Fe(III); • gravimetric titration of oxalate by an excess of Ce(IV) being coulometrically titrated by electrogenerated Fe(II) from Fe(III).	72 impurities detected by semi-ICP-MS. 2 anion impurities measured by ion chromatography
VNIIM-UNIIM	Coulometric titration (1 stage): • coulometric titration with electrogenerated Ce(IV) from Ce(III)	Mass fraction of 48 impurities measured by ICP-MS

7.2 Reported Results

The reported values and their uncertainties are shown in Table 5 and displayed in Figure 3.

Table 5. Measurement results of amount content of reductants expressed as sodium oxalate in CCQM-K169. n indicates number of measurements, RSD indicated relative standard deviation.

Participant's acronym	Amount content of reductants expressed as sodium oxalate, x_i, mol·kg^{-1}	n	RSD, %	Combined standard uncertainty, $u_c(x_i)$, mol·kg^{-1}	Coverage factor k	Expanded uncertainty, U, mol·kg^{-1}	$U_{relative}$, %
INMETRO	7.453472	6	0.021	0.000686	2.52	0.001728	0.023
NIM	7.45967	11	0.013	0.000695	2.0	0.00139	0.019
CENAM(*)	7.4630216	6	0.019	0.0009347	2.57	0.002403	0.032
VNIIM-UNIIM	7.46093	17	0.014	0.000583	2.0	0.00117	0.016
BFKH	7.4667095	6	0.0481	0.0031489	2.0	0.0062978	0.084

(*) corrected result (see section 5)

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NIM and VNIIM-UNIIM carried out additional measurements of the impurity content. NIM reported that 72 impurities were measured by inductively coupled plasma mass spectrometry (semi-ICP-MS), results were given for those which value was larger than 0.7 mg/kg. Anion impurities were tested by ion chromatography (IC). VNIIM-UNIIM provided data for 48 impurities. Data on impurities analysis are given in Table 6. The other participants did not provide any information about impurities.

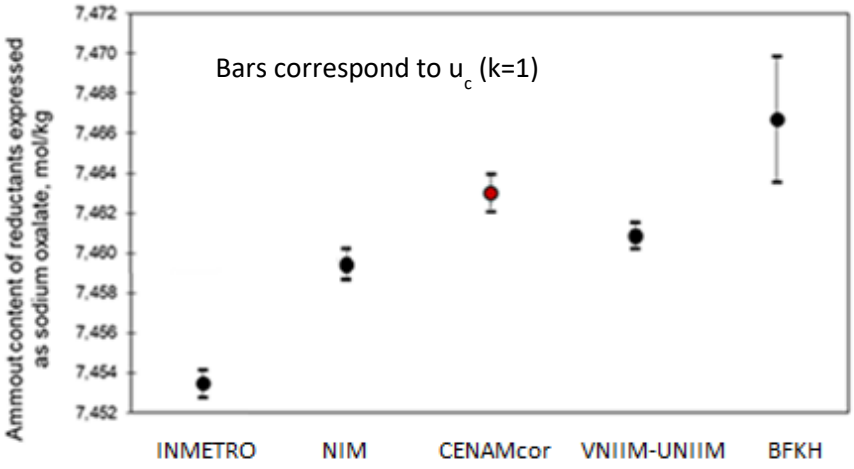

Fig. 3. Measurement results of CCQM-K169. The error bars indicate the combined standard uncertainty (k = 1). The originally reported result of lab 3 has been corrected (see section 5).

The list of uncertainty sources to be considered was provided in the Technical Protocol of CCQM-K169. Table 6 contains information on whether the mandatory sources were taken into account by the participant, as well as major uncertainty sources.

Table 6. Uncertainty sources must be considered according to the Technical Protocol and the considered uncertainty sources by the participants

Uncertainty sources must be considered	Considered in the uncertainty budget of the participant				
Participant's acronym	BFKH	CENAM	INMETRO	NIM	VNIIM-UNIIM
All quantities of the measurement equation	yes	yes	yes	yes	yes
Current efficiency	no	non applicable for gravimetric titration	yes	yes	negligible
End point determination, including mathematical model used to fit titration curves	yes	yes	yes	yes	yes
Migration of analyte or titrant into intermediate chamber /counter compartment	negligible	non applicable for gravimetric titration	yes	yes	yes
Impurities in electrolyte and purging gas	yes	non applicable for gravimetric titration	yes	yes	yes
O_2 sensitivity	no	The effect of oxygen was significant on the concentration of Fe(II). The diminution of the Fe(II) concentration was accounted for the measurement of Ce(IV).	yes (for coulometric stage), no (for two gravimetric stages)	yes	yes
Reaction kinetics	not relevant for Ce(IV)/Ce(III) and Fe(II)/Fe(III)				
Stoichiometry	not relevant for Ce(IV)/Ce(III) and Fe(II)/Fe(III)			yes	not relevant for Ce(IV)/Ce(III) and Fe(II)/Fe(III)
Major uncertainty sources	End-point determination, reproducibility	Amount content of Ce(IV), reproducibility, end-point determination, weighing	Reproducibility, concentration Ce(IV) solution, weighing	End-point determination, purity of ammonium cerium (IV) nitrate, reproducibility, weighing, instability of current	Migration of analyte or titrant into intermediate chamber, reproducibility, weighing, electrolyte impurities

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Table 7. Mass fraction of impurities in the sample of sodium oxalate reported by the participants

Impurity	NIM				VNIIM-UNIIM			
	Mass fraction value, $mg \cdot kg^{-1}$	Expanded uncertainty (k=2), $mg \cdot kg^{-1}$	Relative expanded uncertainty	Analytical method used	Mass fraction value, $mg \cdot kg^{-1}$	Expanded uncertainty (k=2), $mg \cdot kg^{-1}$	Relative expanded uncertainty	Analytical method used
Mg	2.1	0.9	43%	ICP-MS	2.3	0.3	13%	ICP-MS
Si	21.5	21.5	100%	ICP-MS	<10	-	-	ICP-MS
K	12.2	1.4	11%	ICP-MS	1	0.3	30%	ICP-MS
Sr	0.7	0.3	43%	ICP-MS	1.6	0.4	25%	ICP-MS
Ti	0.8	0.6	75%	ICP-MS	1.4	0.2	14%	ICP-MS
NO3	20.5	6.2	30%	IC	/	/	/	/
Cl	6.2	3.1	50%	IC	/	/	/	/
Li	/	/	/	/	<0.03	/	/	ICP-MS
B	/	/	/	/	<1	/	/	ICP-MS
Al	/	/	/	/	0.04	0.01	25%	ICP-MS
P	/	/	/	/	4.4	0.4	9%	ICP-MS
Ca	/	/	/	/	14	3	21%	ICP-MS
Sc	/	/	/	/	<0.05	/	/	ICP-MS
V	/	/	/	/	<0.01	/	/	ICP-MS
Cr	/	/	/	/	0.022	0.002	9%	ICP-MS
Mn	/	/	/	/	0.26	0.05	19%	ICP-MS
Fe	/	/	/	/	0.48	0.05	10%	ICP-MS
Co	/	/	/	/	<0.01	/	/	ICP-MS
Ni	/	/	/	/	0.12	0.03	25%	ICP-MS
Cu	/	/	/	/	0.17	0.06	35%	ICP-MS
Zn	/	/	/	/	0.08	0.015	19%	ICP-MS
Ga	/	/	/	/	<0.01	/	/	ICP-MS
Ge	/	/	/	/	<0.05	/	/	ICP-MS
As	/	/	/	/	0.15	0.02	13%	ICP-MS
Se	/	/	/	/	0.11	0.03	27%	ICP-MS
Br	/	/	/	/	2.1	0.3	14%	ICP-MS
Rb	/	/	/	/	<0.01	/	/	ICP-MS
Y	/	/	/	/	<0.01	/	/	ICP-MS
Zr	/	/	/	/	0.33	0.08	24%	ICP-MS
Nb	/	/	/	/	2.5	0.1	4%	ICP-MS
Mo	/	/	/	/	0.44	0.14	32%	ICP-MS
Ag	/	/	/	/	<0.01	/	/	ICP-MS

Impurity	NIM				VNIIM-UNIIM			
	Mass fraction value, $mg \cdot kg^{-1}$	Expanded uncertainty (k=2), $mg \cdot kg^{-1}$	Relative expanded uncertainty	Analytical method used	Mass fraction value, $mg \cdot kg^{-1}$	Expanded uncertainty (k=2), $mg \cdot kg^{-1}$	Relative expanded uncertainty	Analytical method used
Cd	/	/	/	/	<0.01	/	/	ICP-MS
In	/	/	/	/	<0.01	/	/	ICP-MS
Sn	/	/	/	/	2.3	0.6	26%	ICP-MS
Sb	/	/	/	/	0.08	0.01	13%	ICP-MS
Te	/	/	/	/	<0.03	/	/	ICP-MS
I	/	/	/	/	<0.04	/	/	ICP-MS
Ba	/	/	/	/	0.04	0.005	13%	ICP-MS
La	/	/	/	/	<0.01	/	/	ICP-MS
Ce	/	/	/	/	<0.01	/	/	ICP-MS
Hf	/	/	/	/	0.26	0.03	12%	ICP-MS
Ta	/	/	/	/	1.5	0.3	20%	ICP-MS
W	/	/	/	/	2.9	0.7	24%	ICP-MS
Pt	/	/	/	/	<0.05	/	/	ICP-MS
Au	/	/	/	/	<0.05	/	/	ICP-MS
Hg	/	/	/	/	<0.01	/	/	ICP-MS
Tl	/	/	/	/	<0.01	/	/	ICP-MS
Pb	/	/	/	/	0.017	0.006	35%	ICP-MS
Bi	/	/	/	/	0.15	0.03	20%	ICP-MS

7.3 Reported results calculated as mass fractions

Table 8 shows the reported results in terms of mass fractions, as they are often the preferred quantity in calibration and measurement capability (CMC) submissions. The following formula was used to calculate mass fractions, W_i, $g \cdot kg^{-1}$, from the reported results:

$$W_i = v_i \cdot M(Na_2C_2O_4), \quad (1)$$

where v_i is the result of the i-th NMI for amount content of reductants expressed as sodium oxalate, $mol \cdot kg^{-1}$;

M ($Na_2C_2O_4$) is molar mass of sodium oxalate, $g \cdot mol^{-1}$($M(Na_2C_2O_4)$ = 133.9983 $g \cdot mol^{-1}$ [4]).

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Table 8. Measurement results in terms of mass fractions. n indicates a number of measurements, RSD indicates relative standard deviation

Participant's acronym	Mass fraction of reductants expressed as sodium oxalate, $g \cdot kg^{-1}$	n	RSD, %	Combined standard uncertainty, u_c, $g \cdot kg^{-1}$	k	Expanded uncertainty, U, $g \cdot kg^{-1}$	$U_{relative}$, %
INMETRO	998.75	6	0.021	0.092	2.52	0.23	0.023
NIM	999.58	11	0.013	0.090	2	0.18	0.019
VNIIM-UNIIM	999.75	17	0.014	0.077	2	0.15	0.016
CENAM(*)	1000.03	6	0.019	0.13	2.57	0.32	0.032
BFKH	1000.53	6	0.048	0.42	2	0.84	0.084

(*) corrected result (see section 5)

8 Discussion

The spread of the results does not correspond with the stated measurement uncertainties. The result reported by INMETRO, which was associated with a rather small uncertainty, is significantly lower than those of the other participants. A possible explanation for this deviation is the dissolution of sodium oxalate in hot acidic solution, leading to losses of oxalate. Another contributing factor may be the neglect of oxygen influence during the stages of gravimetric titration. Uncertainty due to oxygen sensitivity was listed as mandatory in the Technical Protocol. INMETRO considered this contribution only during the coulometric titration of Ce(IV) (stage 1), where the effect of oxygen was mitigated by inert gas purging, but did not evaluate it for the other two stages, where no preventive measures were taken. It is therefore likely, that INMETRO has underestimated the measurement uncertainty. The evaluation of the reports, and a subsequent discussion at the EAWG meeting did not reveal any further reasons for the spread of the results. Thus, further evaluation of the KC, i.e. KCRV and DoE estimation, is based on the assumption of unconsidered uncertainty contributions (dark uncertainty).

Useful outcomes from the pilot laboratory's preliminary work and from analysis of participants' reports are given below:

1. For sodium oxalate assay it is recommended to use Ce(IV) as titrant (due to simple one-stage reaction for electron transferring compared to complex multistage reaction of permanganate with oxalate depending on conditions (H^+ concentration, Mn^{2+} concentration, temperature). If permanganate is used as titrant, then the analyst must investigate the dependence the measurement procedure and quantify uncertainties accordingly.
2. It is important to prevent the solution from air oxygen influence at any stage of measurement procedure by inert gas purging.
3. It is strongly recommended to use initial titration procedure in the coulometric titration as well as gravimetric titration.

4. It is recommended not to dissolve sodium oxalate in hot acid due to undesirable processes of decomposition of oxalic acid under high temperature and to minimize time of sodium oxalate solution being heated without titrant Ce (IV) to avoid oxidizing of oxalate by oxygen from the air.

9 Estimators for the Key Comparison Reference Value (KCRV)

Only independent results can be used to calculate estimators for the KCRV. Hence, measurement results from institutes that established metrological traceability using measurement standards from other institutes usually are excluded from the KCRV calculation. In this comparison four participants used coulometry, which provides metrological traceability to the SI units kg, A, s. CENAM used gravimetric titrimetry applying the certified reference material of potassium dichromate NIST SRM 136f as a source of traceability. However, if the NMI providing traceability does not participate in the comparison the secondary result can be taken into account in KCRV calculation. Therefore, all five results of this comparison are considered as independent, and are used for KCRV calculation. The consistency test based on χ^2-criteria [3] likewise suggests that data are over dispersed (see Table 9).

Table 9. Results of the consistency test for the data given in Table 6

χ	χ_{obs}	m	$\chi_{obs}>\chi_{0.05,m-1}$	Conclusion: data are over dispersed
9.49	101.27	5		

The arithmetic mean, the uncertainty weighted mean corrected for the observed dispersion, the median and DerSimonian-Laird estimators have been calculated. The KCRV estimators are shown in Table 10 and Figure 4. Formulas are given in the Annex A [3]. Additionally, the NIST Decision Tree was applied for KCRV estimation, results are also given in Table 10. All estimators agree fairly well and have comparable uncertainties. Figure 5 shows the results exemplarily in relation to the median and its uncertainty.

Table 10. Candidate estimators for the KCRV, calculated according to CCQM/2013-22 [3], and NIST Decision Tree [5].

KCRV estimator	**Value, mol·kg^{-1}**	***u*, mol·kg^{-1}**	**u_{rel}, %**
Arithmetic mean	7.46076	0.00218	0.0292
Median [a]	**7.46093**	**0.00174**	**0.0233**
Uncertainty-weighted mean, corrected for the observed dispersion	7.45908	0.00174	0.0233
DerSimonian-Laird	7.46028	0.00204	0.0273
Hierarchical Gauss-Gauss (by NIST Decision Tree)	7.46051	0.00173	0.0232
[a]Median was proposed as the KCRV.			

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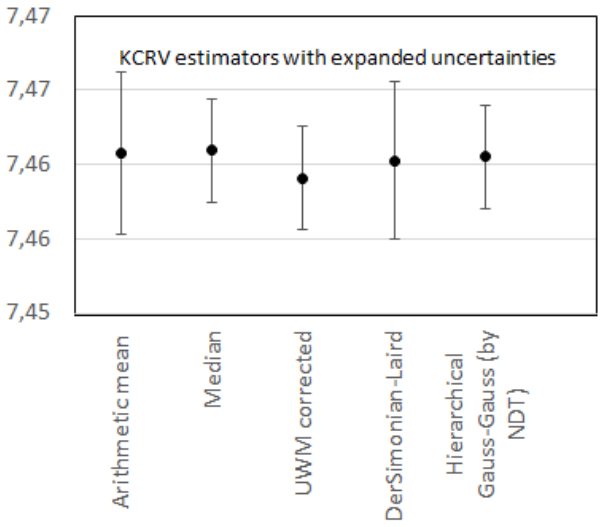

Fig. 4. Candidate estimators for the KCRV and their expanded uncertainties, calculated according to CCQM/2013-22 [3] and NIST Decision Tree [5].

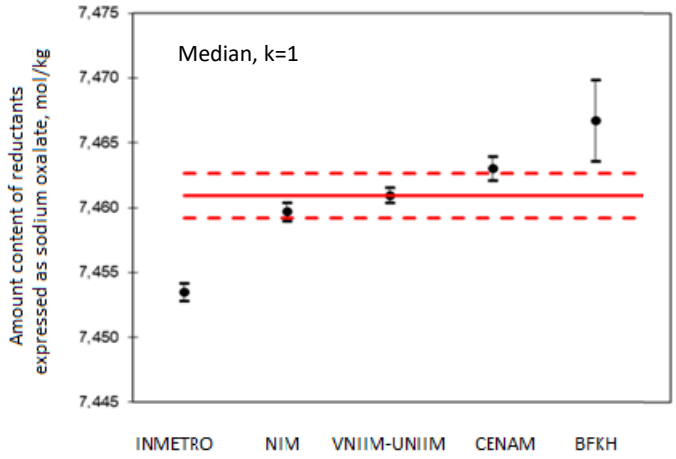

Fig. 5. The results of CCQM-K169 with the median as the KCRV estimator. The error bars represent the standard uncertainty (k = 1). The KCRV estimator is depicted as the solid red line, accompanied by its standard uncertainty indicated by the dashed red line.

Even though the spread of all results shows over-dispersion, it must be considered that there is indication that the result of INMETRO could be biased (see section 8) and that the result of BFKH has an appropriately large uncertainty with respect to its deviation from the estimators. Thus, it is reasonable to assume that the results of NIM, VNIIM-UNIIM and CENAM represent the KCRV more appropriately. Nevertheless, there is no technical reason to exclude the results of INMETRO and BFKH. Therefore, results of NIM, CENAM, VNIMM-UNIIM and BFKH are considered mutual consistent and the result of INMETRO is considered an outlier. This fits into category C of figure 1 of CCQM2013-22 [3], “generally consistent results with a small number of outlying values” with the median being an appropriate KCRV estimator. Note that 5 viable results are sufficient to calculate an appropriate MAD (see Annex 2, section 2.3) for the median and its uncertainty. Thus, the median is proposed to be used as KCRV estimator.

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

The DoE_i of result x_i of institute *i* and its uncertainty was calculated according to CCQM/2013-22 [3] with respect to the median as best estimate for the KCRV (see the Annex B):

$$\mathrm{DoE}_i = x_i - x_{\mathrm{ref}} \quad (2)$$

where DoE_i is the degree of equivalence between the participant's result (x_i) and the KCRV (x_{ref}).

When using the median as the KCRV estimator, the formula for the special case from section 2.3 of the CCQM/2013-22 guidance note (page 26) was applied to calculate $u(DoE_i)$, as shown below

$$u^2(\mathrm{DoE}_i) = (1 - \frac{2}{m})u^2(x_i) + u^2(\mathrm{KCRV}) \quad (3)$$

where $u(KCRV)$was calculated according to eq. (B.6);

$u(x_i)$ is standard uncertainty claimed by the *i*-th participant;

m is a number of participants' results taken for KCRV calculation.

$$U(\mathrm{DoE}_i) = 2 \cdot u(\mathrm{DoE}_i) \quad (4)$$

The results of degrees of equivalence (DoE) with corresponding expanded uncertainties are listed in Table 11 and shown on the Figure 6.

Table 11. Degrees of equivalence with corresponding measurement uncertainties (with the median chosen as KCRV).

Institute	Value, mol·kg^{-1}	U, mol·kg^{-1}	DoE_i, mol·kg^{-1}	$U(DoE_i)$, mol·kg^{-1}	E_n ($DoE_i/U(DoE_i)$)	U_{minCMC}, mol·kg^{-1}	$U_{\mathrm{minCMC\ rel}}$, %
INMETRO	7.45347	0.00173	-0.00746	0.00364	-2.05	0.00852	0.114
NIM	7.45967	0.00139	-0.00126	0.00364	-0.35	0.00139	0.019
VNIIM-UNIIM	7.46093	0.00117	0.00000	0.00359	0.00	0.00117	0.016
CENAM	7.46302	0.00240	0.00209	0.00377	0.56	0.00187	0.025
BFKH	7.46671	0.00630	0.00578	0.00599	0.96	0.00630	0.084

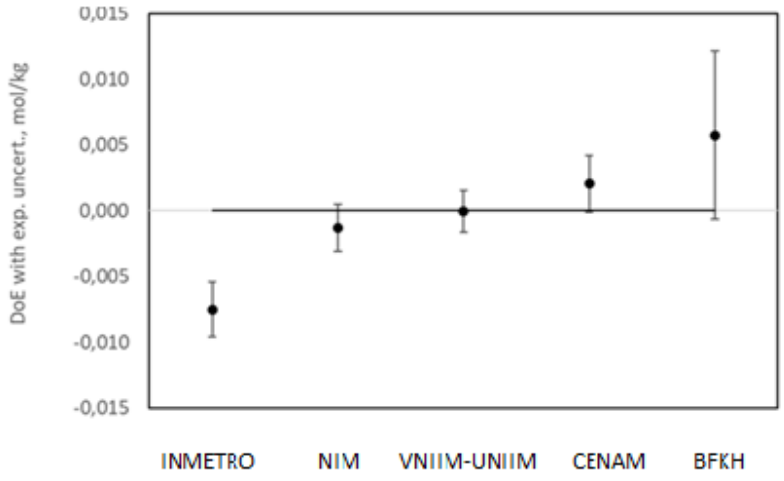

Fig. 6 Degrees of equivalence for CCQM-K169 with corresponding expanded measurement uncertainties (k = 2).

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Consistencies of the results were assessed by E_n values, calculated as

$$E_n(x_i) = \frac{\mathrm{DoE}_i}{U(\mathrm{DoE}_i)} \quad (5)$$

A result is considered consistent with the KCRV if $|E_n(x_i)| \leq 1$.

Table 11 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. U_{minCMC} were estimated due to following considerations:

1) If a result is consistent with the KCRV, U_{minCMC} is equivalent to the expanded uncertainty reported by the institute$U(x_i)$ for k=2 (if the expanded uncertainty was reported for k≠2, than $U_{\mathrm{minCMC}}= 2u(x_i)$).

2) If a result is inconsistent with the KCRV, it is assumed that the inconsistency is the result of underestimated or unknown uncertainty contributions, provided that failure of the measurement setup or the sample can be excluded. This comparison may therefore support CMC claims even if a respective result is inconsistent with the KCRV. However, the expanded uncertainty of the CMC claim at the 95 % level of confidence must be equal or larger than U_{minCMC}.

Up to now, CCQM/2013-22 gives no advice on how to calculate estimates for U_{minCMC} when the reported result is inconsistent. Here, the calculation is based on eq. (5) when $|En(x_i)| = 1$, i.e.,

$$DoE_i = U(DoE_i) = k \cdot u(DoE_i) \quad (6)$$

with $k = 2$ being the coverage factor.

Formulas given below are not general, they are related to KCRV estimator and its corresponding formula for $u(DoE_i)$. For the median used as KCRV estimator with the corresponding formula for $u(DoE_i)$ (see eq. (3)), eq. (6) will have a view

$$DoE_i = U(DoE_i) = 2 \cdot u(DoE_i) = 2 \cdot \sqrt{(1 - \frac{2}{m})u^2(x_i) + u^2(KCRV)}, \quad (7)$$

where m is a number of participants' results taken for KCRV calculation.

$$\frac{DoE_i^2}{4} = (1 - \frac{2}{m})u^2(x_i) + u^2(KCRV) \quad (8)$$

$U_{\min CMC}(x_i)$ for institute i can be calculated from eq. (8) by replacing $u(x_i)$ by $u_{\min CMC}(x_i)$according to the equation

$$U_{\min CMC}(x_i) = 2 \cdot u_{\min CMC}(x_i) = 2 \cdot \sqrt{\frac{\frac{DoE_i^2}{4} - u^2(KCRV)}{(1 - \frac{2}{m})}} \quad (9)$$

Finally, U_{minCMC} for participant #1 was calculated by eq. (9). The uncertainty of CMC claims must be equal or larger to U_{minCMC}.

It should be noted that the NIST decision tree / consensus calculator was also applied to calculate the uncertainties of the DoEs, based on a hierarchical Gauss estimator. However, the corresponding uncertainties that would have been assigned to NIM, CENAM and VNIIM-UNIIM were rather large compared to their reported uncertainties and their spread. They did not adequately reflect the performance of the participants. Therefore, this approach was abandoned. Likewise, the uncertainties of participants NIM, CENAM and VNIIM-UNIIM are smaller than the uncertainty of the

KCRV, which would suggest that their minimum uncertainties should be increased to better reflect the performance of the community, e.g. by using the uncertainty of the KCRV as minimal CMC uncertainty. However, for the reasons mentioned in sections 8 and 9, the results of these participants are considered more likely to represent the KCRV. Penalizing them with significantly larger minimum CMC uncertainties compared to their reported values would be inappropriate. Therefore, it was decided to use the reported uncertainties as minimum uncertainties, provided that the corresponding results are consistent with the KCRV.

11 How Far Does the Light Shines statement

The comparison provides support for the capabilities to measure the amount content of reductants in high-purity sodium oxalate. Good results achieved using coulometry or gravimetric titrimetry, or a combination of both methods, provide evidence for the capabilities to determine the amount content of reductants in pure salts in the range from 0.999 to 1 kg/kg, as well as in their aqueous solutions. It may also provide indirect support for assay of oxidants.

Institutes that have successfully participated in the key comparison can reasonably claim CMCs, usually in service category 1, for high purity chemicals as well as their water solutions for sample sizes similar to those used in this comparison according to EAWG CMC guideline [1]. The uncertainties claimed in the CMC submission must not be smaller than the U_{minCMC} values stated in Table 11, unless exceptions stated in the EAWG-CMC guidelines can be applied.

12 Acknowledgments

The authors are grateful to:

- Dr. T. Asakai from NMIJ, Japan, for initiation this comparison, which covers the new category of analytes (reductants) for high purity substances, and for preparing first version of technical protocol;
- Prof. L. Ma, B. Wu from NIM, China, for assist in dispatching samples of sodium oxalate which is considered as harmful substance;
- Dr. S. Seitz (PTB), Dr. M. Mariassy (SMU), Dr. T. Asakai (NMIJ) for the valuable input into discussion concerning the comparison.

13 References

[1] EAWG guideline for claims of Calibration and Measurement Capabilities (available at https://www.bipm.org/documents/20126/147095532/EAWG-GD-01+CMC+guidelines+v16/9bae1493-31f2-7de7-5faf-e02edef33d9c).

[2] JCGM 100:2008 Evaluation of measurement data - Guide to the expression of uncertainty in measurement (GUM) JCGM (available at https://www.bipm.org/en/committees/jc/jcgm/publications).

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

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Annex A
KCRV estimators

1. Arithmetic mean (see page 23 of the CCQM/2013-22 for detailed information)

Value	$$\bar{x} = \frac{1}{m}\sum_{i=1}^{m} x_i$$ where m is the number of institutes accepted for KCRV calculation and x_i is the reported value of each institute.	(A.1)
Standard uncertainty	$$u(\bar{x}) = \frac{s(x)}{\sqrt{m}}$$ where $s(x)$ is the (sample) standard deviation of the reported values x_1, ... , x_m given by	(A.2)
	$$s^2(x) = \frac{1}{m-1}\sum_{i=1}^{m}(x_i - \bar{x})^2$$	(A.3)

2. Median (see page 25 and 26 of the CCQM/2013-22 for detailed information)

Value	For m being even, $$\mathrm{med}(x) = \frac{1}{2}(x'_{\frac{m}{2}} + x'_{\frac{m}{2}+1})$$ where x'_1, .. , x'_m denote the reported values arranged in increasing order. For m being odd,	(A.4)
	$$\bar{x} = x'_{\frac{(m+1)}{2}}$$	(A.5)
Standard uncertainty	$$u^2(\mathrm{med}(x)) = \frac{\pi}{2m}\hat{\sigma}^2$$ where $\hat{\sigma}$ is a robust estimate of standard deviation, usually based on the median absolute deviation (MAD) multiplied by 1.483. (This corrected estimate is sometimes called MAD_E.)	(A.6)

3. Uncertainty-weighted mean (see page 24 and 25 of the CCQM/2013-22 for detailed information)

Value	$$\bar{x}_u = \sum_{i=1}^{m} w_i x_i$$ where	(A.7)
	$$w_i = \frac{1/u^2(x_i)}{\sum 1/u^2(x_i)}$$	(A.8)
Standard uncertainty	Case 2. Corrected for observed dispersion $$u^2_{\mathrm{corr}}(\bar{x}_u) = \frac{\chi^2_{\mathrm{obs}}}{m-1}u^2(\bar{x}_u)$$ where	(A.9)
	$$\chi^2_{\mathrm{obs}} = \sum_{i=1}^{m}\frac{(x_i - \bar{x}_u)^2}{u^2(x_i)}$$	(A.10)

4. DerSimonian-Laird procedure(see page 28 and 29 of the CCQM/2013-22 for detailed information)

Graybill-Deal mean	$\bar{x}_u = \frac{1}{W_1}\sum_{i=1}^{p} w_i x_i, \quad w_i = 1/u_i^2, \ i = 1,\ldots,p, \qquad W_1 = \sum_{i=1}^{p} w_i.$	(A.11)
Interlaboratory variance	$\lambda = \max\left[0, \ \frac{\sum_{i=1}^{p} w_i (x_i - \bar{x}_u)^2 - p + 1}{W_1 - W_2 / W_1}\right], \quad W_2 = \sum_{i=1}^{p} w_i^2.$	(A.12)
DerSimonian-Laird mean x_{DL}	$x_{\mathrm{DL}} = \sum_{i=1}^{N} \tilde{w}_i x_i, \qquad \tilde{w}_i = \frac{(u_i^2 + \lambda)^{-1}}{\sum_{j=1}^{p} (u_j^2 + \lambda)^{-1}}.$	(A.13)
Standard uncertainty $u(x_{\mathrm{DL}})$	$u(x_{\mathrm{DL}}) = \left[\sum_{i=1}^{p} \tilde{w}_i^2 (x_i - x_{\mathrm{DL}})^2 / (1 - \tilde{w}_i)\right]^{1/2}.$	(A.14)

Annex B

CCQM

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

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CCQM WG on Electrochemical Analysis and Classical Chemical Methods

CCQM-K169

Assay of sodium oxalate

Technical Protocol

16 April 2024 / Version 2

1. Introduction

CCQM-K169 is an original key comparison (KC), jointly organized by IAWG and EAWG as the next comparison for pure salts. The previous jointly organized by IAWG and EAWG comparisons were CCQM-P7 for sodium chloride, potassium chloride and potassium dichromate, CCQM-K34, CCQM-K34.2016 for potassium hydrogen phthalate, CCQM-P112 for EDTA, CCQM-K48 (CCQM-K114) for potassium chloride, CCQM-K96 for potassium dichromate, CCQM-K152 for potassium iodate, CCQM-K173 for sodium carbonate. The analyzed substances are categorized as halides, acids, complexing agents, oxidants, and bases. Reductants have not been measured in comparisons yet. In 2020 this comparison was proposed by NMIJ, Japan, but later it was postponed due to pandemic of COVID-19 and in 2022 NMIJ withdrew their participating and piloting due to political reasons.

Sodium oxalate is one of the key materials used as a reductant in titrimetry. It has been used for the standardization of potassium permanganate that is also widely used for chemical analyses.

Measurand is the amount content of reductants expressed as sodium oxalate, mol/kg.

The assay is in the range of 99.5 % to 100.1 % based on the amount content of reductants.

The nominal value of the reductants is (7.4 – 7.5) mol/kg.

The comparison will test the abilities of the metrological institutes to measure the amount content of reductants in high purity substances as well as assaying high purity salts to be used as primary standards. The results may be used to underpin claimed calibration and measurement capabilities and respective metrological services of the institutes.

The comparison is open to the National Metrology Institutes (NMI) or Designated Institutes (DI) of members or associate states of the Meter Convention.

2. Coordinating laboratory and contact person

Main contact:
Alena Sobina
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CCQM-K169

Second contact:
Alexandr Shimolin. Tel.: + 7 343 217 29 27.
E-mail: alex-shimolin@uniim.ru
Co-piloting institute
NIM, China, has kindly agreed to assist in shipping samples for CCQM-K169 to the participants.
Contact person:
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.

3. Time schedule

Announcement of study (by NMIJ):	3 November 2020 in IAWG/EAWG meeting
First call for participants (by NMIJ):	February 2022
Registration deadline (by NMIJ):	31 March 2022
Second call for participants (by VNIIM-UNIIM):	April-May 2023
Registration deadline (by VNIIM-UNIIM):	30 June 2023
Dispatch of the samples (by VNIIM-UNIIM with assistance of NIM):	~~October-November 2023~~ March-April 2024
Reporting deadline:	~~31st March 2024~~ 31 August 2024
First discussion:	~~Spring~~ Fall-2024 in EAWG meeting
Draft A1 report:	~~Summer 2024~~ March 2025
Draft B report:	Fall 2025

4. Description of sample

The sample for the comparison is prepared by the coordinating laboratory using commercially available high-purity sodium oxalate. The material has been homogenized and bottled in glass bottles closed with plastic screw caps.

Each participant will receive one (two, if requested with explanation of the reason) separately-numbered bottle containing about 20 g of the sample. The bottle labels indicate CCQM-K169 Assay of sodium oxalate, sample for comparison, CAS number 62-76-0, net weight of the sample, bottle number. 6 bottles in card tubes packed into a cardboard box were shipped by air courier from VNIIM-UNIIM to NIM, China who kindly agreed to deliver samples to other participants. The tracking number will be sent by email to the contact person of the laboratory. The content is marked "sample for comparison" with value 1 USD (or 1 EUR) per bottle. Please be attentive to possible customs delay, etc. Shipment to all participants will be performed at the same time.

Homogeneity Assessment of Study Material

Seven bottles were randomly selected from the set of 9 bottles. Coulometric titration using Ce(IV) as a titrant was performed to test the homogeneity. From analysis of variance (ANOVA), the standard deviation of the repeatability, the standard deviation within-bottle (in)homogeneity and the standard uncertainty due to between-bottle (in)homogeneity were evaluated (u_h=0.011%). The sample mass used for the homogeneity test was 0.3 g.

Stability Assessment of Study Material

Sodium oxalate is known to be a stable material during storage and transportation. Typical shelf-life of CRMs of sodium oxalate is 5 years. Measurement results obtained by the piloting laboratory during homogeneity study and during the period of measuring after dispatching samples to the participants will be compared to confirm stability of the study material.

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The samples of sodium oxalate were found to be adequate for the key comparison.

5. Actions after receipt of samples

- The packaging material must be removed after arrival of the samples and the bottles must be inspected for visible damage.
- Confirm receipt of samples and report any damage to the coordinating laboratory by email as soon as possible after arrival.
- Store the bottles in the original container at laboratory temperature until they are used.

6. Instruction for measurement

The material should be dried at 105 °C for 2 h without crushing or grinding the material. After drying, it should be placed in a desiccator with silica gel or other desiccants, and cooled to room temperature before weighing.

The mass of the sample should be corrected for air buoyancy. The density of sodium oxalate is 2.34 g cm^{-3}.

The minimum sample mass for each measurement is 0.3 g.

Any method or combination of methods can be used for the comparison, but coulometry or titrimetry is recommended. Some issues concerning challenges of measurement procedures for an assay of sodium oxalate were discussed on the Web-con for participants of CCQM-K169 on 26th September 2023. It was recommended

- to use Ce(IV) as titrant,
- that participants must investigate the dependence their measurement procedure and quantify uncertainties accordingly if permanganate is used as titrant,
- other methods may be added to the report as additional information, even though the primary result must be clearly identified.

7. Reporting

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

The participants are requested to use the provided spreadsheet for reporting. The spreadsheet can be modified as required, but the report must include the following information:

- Name and address of the laboratory performing the measurements
- Name(s) of the operator(s)
- Date of receipt of the sample
- Identification of the samples (bottle numbers) measured
- Date(s) of measurement
- Measurement results

–There should be at least six individual assay results, each expressed in units of mol kg^{-1}.

–The final result, obtained from the mean value of individual results, should be reported. Ifseveral measurement methods are used, it must be clear which is the main result and which is only additional information.

–Mass of the sample used for individual assay (without buoyancy correction), temperature, relative humidity, and pressure in the laboratory at the time of weighing including the formula used for calculating the sample mass with buoyancy correction.

- Complete uncertainty budget according to the *Guide to the Expression of Uncertainty in Measurement* (GUM).

If coulometry is used, the uncertainty budget must include both instrumental sources of uncertainty as well as chemical ones. List of uncertainty sources to be considered is provided in the Annex to EAWG guideline for claims of Calibration and Measurement Capabilities (EAWG CMC guidelines), in the

CCQM-K169
section "Additional specification of coulometric analytes", which is available at https://www.bipm.org/en/committees/cc/ccqm/wg/ccqm-eawg.

The following uncertainty contribution must be considered in general:

- All quantities of the measurement equation, i.e. sample mass, electric charge (coulombs, or current and time, or voltage, resistance and time). Faraday constant is used as an accurate value without uncertainty.
- Current efficiency.
- End point determination, including mathematical model used to fit titration curves.
- Migration of analyte or titrant into intermediate chamber /counter compartment.
- Impurities in electrolyte and purging gas.

Special sources of uncertainty depending on the analyte to be considered are O_2 sensitivity, reaction kinetics, current efficiency, stoichiometry.

Please pay attention, that he coordinator must ask the participant for a revised measurement report if the requested uncertainty contributions have not been addressed. The final report of the CCQM-comparison must include a statement that all participants have provided an uncertainty budget according to the requirements of the Technical Protocol.

–The reported uncertainty should be expressed as both a combined standard uncertainty and an expanded uncertainty with the corresponding coverage factor (k) referring to a 95 % level of confidence. Note that $k = 2$ if an infinite number of degrees of freedom can be reasonably assumed.

• Detailed description of the measurement procedure used, including a photo of the experimental setup, if available

–If coulometry is used, include the following information: the measuring instruments used, cell description, volume of the electrolyte in the working chamber, number of titration stages and the current used for each stage, endpoint evaluation procedure, etc.

• Complete measurement equations and raw data of one measurement

–The complete measurement equation, along with the values of the constants used and variables (raw data) for at least one measurement, must be provided. The data should allow for the recalculation of the result of this measurement.

The report must be sent to the coordinating laboratory by e-mail before 31 August 2024. 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.

8. Key comparison reference value

The key comparison reference value (KCRV) will be calculated following the CCQM-13/22 guidelines. The choice of the best estimator will be based to the actual distribution of the results.

9. How Far Does the Light Shines statement

The comparison provides support for the capabilities to measure the amount content of reductants in high-purity sodium oxalate. Results achieved using coulometry or titrimetry (direct approach), or a combination of both methods, provide evidence for the capabilities to determine the amount content of reductants in pure salts in the range 0.999 to 1 kg/kg, as well as in their aqueous solutions. For indirect methods, it may also provide indirect support for assay of oxidants.

Institutes that have successfully participated in the key comparison can reasonably claim CMCs, usually in service category 1, for high purity chemicals according to EAWG CMC guidelines.

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CCQM-K169

CCQM WG on Electrochemical Analysis and Classical Chemical Methods

CCQM-K169 Assay of sodium oxalate

Measurement Report

Use the Excel template provided with the this technical protocol for reporting measurement results.