CCQM WG on Electrochemical Analysis and Classical Chemical Methods

CCQM-K96.2023.1 – Assay of potassium dichromate

Final report

Kyungmin Jo, Min-Ah Oh, Alena Sobina, Alexandr Shimolin

30 April 2025

Summary

The CCQM key comparison CCQM-K96.2023.1, a subsequent comparison to CCQM-K96.2023, was conducted to demonstrate the capability of VNIIM-UNIIM to measure the amount content of oxidants. KRISS served as the coordinating laboratory, with its results linking to the original comparison. Participating institutes may use a method of their choice, but coulometry with potentiometric or amperometric endpoint determination is expected to be used in most cases. The results from VNIIM-UNIIM were in good agreement with the reference value, providing evidence to support the respective CMC claims.

Table of Contents

CCQM-K96.2023.1

1 Coordinating laboratory and contact person

(Main contact)
Kyungmin Jo
Korea Research Institute of Standards and Science (KRISS)
267 Gajeong-ro, Yuseong-gu, Daejeon, Republic of Korea
Tel: +82 42 868 5621
Email: kyungmin.jo@kriss.re.kr

(Alternative contact)
Min-Ah Oh
Email: minah.oh@kriss.re.kr

2 List of participants

The list of participants is given in Table 1.

Table 1. List of participants.

Acronym	Institute	Country	Contact person	Email
KRISS	Korea Research Institute of Standards and Science	Korea	Kyungmin Jo	kyungmin.jo@kriss.re.kr
VNIIM-UNIIM	Ural Research Institute for Metrology – Affiliated Branch of the D.I.Mendeleyev Institute for Metrology	Russia	Alena Sobina	sobinaav@uniim.ru

3 Time schedule

Invitation: October 2023
Registration deadline: 31 October 2023
Dispatch of samples: November 2023
Reporting deadline: 29 February 2024
Draft A report: October 2024
Discussion: EAWG meeting, October 2024
Draft B report: December 2024

4 Description of samples

Sample for comparison was prepared and distributed by KRISS. At the request of the participants, it was from the same batch as that used in the original comparison (CCQM-K96.2023).[a] The source material was commercially available pure potassium dichromate. The material was transferred into a cleaned 10 L low-density polyethylene carboy and homogenized for 10 hours using a 3D mixer at a speed of 15 rpm. After homogenization, the material was filled into glass bottles, which were then sealed with Teflon-lined plastic screw caps. Each bottle contained approximately 20 g of powder and was enclosed in a plastic bag. The

samples were shipped by air courier on 18 October 2023 and arrived at their destination undamaged on 28 November.

[a] *To ensure the independence of measurements between the original (CCQM-K96.2023) and subsequent bilateral (CCQM-K96.2023.1) comparisons, KRISS performed two independent measurements on samples taken from two different bottles of the same batch. Additionally, to preserve the confidentiality of the measurement results from both comparisons, the results of the bilateral comparison were revealed only after the results of the original comparison had been disclosed.*

4.1 Homogeneity

Homogeneity was assessed by KRISS using constant-current coulometric titration, using 0.3 g samples taken from each of 10 bottles selected at regular intervals out of a total of 89. The results of the homogeneity test are presented in Figure 1. The between-sample standard deviation, accounting for both sample homogeneity and measurement repeatability, was 0.0011 %. This demonstrates that the homogeneity is adequate for the comparison.

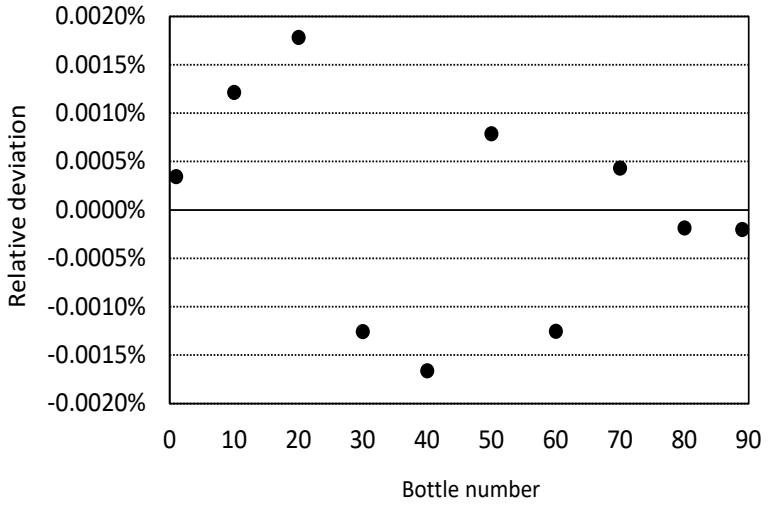

Figure 1. Result of the homogeneity test.

5 Instructions for measurement

The sample should be dried at 110 °C for 2 hours without crushing or grinding. Once dried, it must be stored in a desiccator containing silica gel (or other appropriate desiccants) and cooled to room temperature before weighing. The sample mass should be corrected for air buoyancy, with the sample density being 2676 kg/m^3. A minimum of 0.3 g of the sample is required for each measurement.

Any method, or combination of methods, could be employed for the comparison. It was expected that each institute would use the highest-level method available, such as coulometry or titrimetry. Participants were requested to report the results as the amount content of oxidants in the sample in the unit 'mol kg^{-1}', and to provide an uncertainty evaluation in accordance with JCGM 100:2008 [1].

6 Results and discussion

The measurement period and the dates when the reports were sent are provided in Table 2. VNIIM-UNIIM submitted their results slightly later than the original deadline, as they wanted to examine some influencing factors more thoroughly.

Table 2. Measurement dates and report submission dates.

Institute	Bottle number	Measurement period	Date report sent
KRISS	89	22 – 26 Jan 2024	31 Jan 2024
VNIIM-UNIIM	61	27 – 29 Feb 2024	18 Mar 2024

6.1 Methods of measurement

Measurement methods used by the participants are presented in Table 3; both used constant-current coulometry using either horizontal or vertical cells. The details of the measurement methods are summarized in Table 4 to Table 6. Pre-titration was performed in all coulometric measurements using the same electrolyte, and a continuous supply of high-purity inert gas (e.g., Ar or N_2) was maintained throughout the entire titration process.

Table 3. Measurement methods used by the participants.

Institute	Measurement method	Cell type	Cell volume /mL
KRISS	Constant-current coulometry	Horizontal, 2 Intermediate compartments (ICs)	100 – 120
VNIIM-UNIIM		Vertical, 1 IC	300

Table 4. Details of measurement parameters.

Institute	Sample mass/g	Cathode	Anode	Main current /mA	Current density[a] /(mA/cm^2)
KRISS	0.3	Pt plate (4 cm × 10 cm)	Pb rod (5 mm dia., 15 cm)	102	1.3
VNIIM-UNIIM	0.3	Pt nets (85 cm^2)	Pt nets (85 cm^2)	200	2.4

[a] The value was calculated by taking into account the geometric area of the electrode.

Table 5. Details of measurement parameters (continued).

Institute	Endpoint indication	Endpoint estimation	When the sample was introduced	Electrolyte pre-treatment
KRISS	Amperometry, 0.41 V vs. Hg/Hg_2SO_4	LR, x-intercept	After main titration	Yes[a]
VNIIM-UNIIM	Biamperometry	LR, x-intercept	Before main titration	Yes

[a] Measurements were performed by reusing the electrolyte.

6.2 Reported Results

The reported values and uncertainties are summarized in Table 6 and also displayed graphically in Figure 2. The main sources of uncertainty and their contributions are shown in Table 7.

Table 6. Measurement results of CCQM-K96.2023.1.

Institute	Value /mol kg^{-1}	*n*	SD /mol kg^{-1}	u_c /mol kg^{-1}	*U* /mol kg^{-1}	*k*
KRISS	3.399021	6	0.000063	0.000103	0.000286	2.8
VNIIM-UNIIM	3.398588	8	0.000364	0.000202	0.000404	2

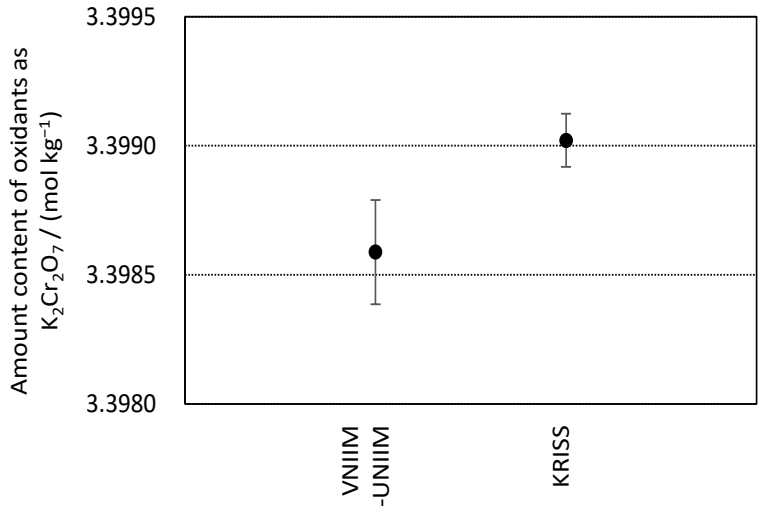

Figure 2. Measurement results of CCQM-K96.2023.1. The error bars indicate the combined standard uncertainty (*k* = 1).

Table 7. Major uncertainty sources and their contribution.

Institute	Major uncertainty source (contributions)
KRISS	Reproducibility (intermediate precision) (77 %), EP determination for final titration (12 %)
VNIIM-UNIIM	Sample diffusion (46 %), reproducibility (41 %), sample mass (11 %)

6.3 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 from the reported results (using $M(K_2Cr_2O_7)$ = 294.185 g/mol): $w_i = v_i M(K_2Cr_2O_7)$

Table 8. Measurement results in terms of mass fractions.

Institute	Value w_i g kg^{-1}	*n*	SD g kg^{-1}	$u(w_i)$ g kg^{-1}	$U(w_i)$ g kg^{-1}	*k*
KRISS	999.941	6	0.018	0.030	0.084	2.8
VNIIM-UNIIM	999.814	8	0.107	0.059	0.119	2

7 Estimators for the Key Comparison Reference Value (KCRV)

The results were linked to the key comparison reference value of CCQM-K96.2023 through the results of KRISS, which served as the linking laboratory.

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

The DoE of the participant in this comparison was calculated using the results of the coordinating laboratory (v_{KRISS}) and participating institute (v_{NMI}) as well as the DoE of KRISS in CCQM-K96.2023 ($\mathrm{DoE}_{\mathrm{KRISS,\ K96.2023}}$), according to the equation (1).

$$\mathrm{DoE}_{\mathrm{NMI}} = \mathrm{v}_{\mathrm{NMI}} - \mathrm{v}_{\mathrm{KRISS}} + \mathrm{DoE}_{\mathrm{KRISS,K96.2023}} \quad (1)$$

Equation (2) was used to calculate the DoE of the participant, assuming that the results of the coordinating laboratory and participant were not correlated.

$$u^2(\mathrm{DoE}_{\mathrm{NMI}}) = u^2(\mathrm{v}_{\mathrm{NMI}}) + u^2(\mathrm{v}_{\mathrm{KRISS}}) + u^2(\mathrm{DoE}_{\mathrm{KRISS,K96.2023}}) \quad (2)$$

The DoE of the participant is given in Table 9. The table also presents the uncertainty-weighed DoE (E_n value), which is calculated using equation (3).

$$E_n(x_i) = \frac{\mathrm{DoE}_i}{U(\mathrm{DoE}_i)} \quad (3)$$

A result is considered consistent with the KCRV if $|E_n(x_i)| \leq 1$. Table 9 also shows minimal expanded uncertainties U_{minCMC} consistent with the proposed KCRV, which makes the submission and review of CMC easier. If a result is consistent with the KCRV, U_{minCMC} is equivalent to the expanded uncertainty reported by the institute (see the Annex).

Figure 3 shows the DoEs and their expanded uncertainties for the results of the participating institutes in the CCQM-K96.2023 and CCQM-K96.2023.1 comparisons.

Table 9. Degrees of equivalence with corresponding expanded uncertainties.

Institute	Value /mol kg^{-1}	U /mol kg^{-1}	DoE_i /mol kg^{-1}	$U(\mathrm{DoE}_i)$ /mol kg^{-1}	$\mathrm{DoE}_i/U(\mathrm{DoE}_i)$	U_{minCMC} /mol kg^{-1}
VNIIM-UNIIM	3.398588	0.000404	−0.000093	0.000605	−0.15	0.000404
In terms of mass fraction						
VNIIM-UNIIM	99.9814 %	0.0119 %	−0.0027 %	0.0178 %	−0.15	0.0119 %

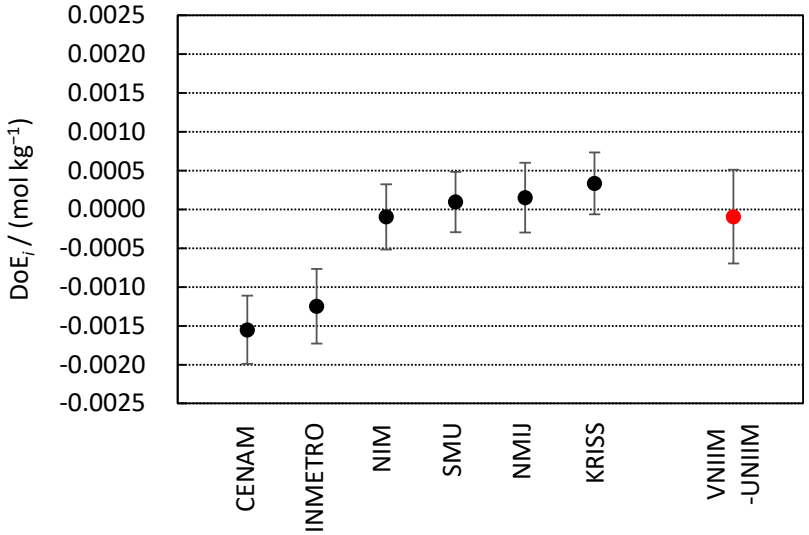

Figure 3 Degrees of equivalence for CCQM-K96.2023 (black solid circle) and CCQM-K96.2023.1 (red solid circle) with corresponding expanded measurement uncertainties (k = 2).

9 How Far the Light Shines statement

The comparison supports the capabilities to measure the amount content of oxidants in high-purity potassium dichromate. Good results will demonstrate good performance in assaying high-purity oxidants, where participants can apply the principles of oxidation-reduction titration in a similar manner. The uncertainties claimed in the CMC submission must not be smaller than the U_{minCMC} values stated in Table 9, unless exceptions stated in the EAWG-CMC guidelines can be applied. The measurement results, DoE and its uncertainty, along with U_{minCMC} values, are also presented as mass fractions in Table 9, as the respective CMCs are often submitted in terms of mass fraction rather than amount content.

10 References

[1] 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).

[2] 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).

Annex

Calculation of U_{minCMC}

1. If a result is consistent with the KCRV ($|E_n(x_i)| \leq 1$)

In this case, U_{minCMC} is equivalent to the expanded uncertainty reported by the institute ($U(x_i)$).

2. If a result is inconsistent with the KCRV ($|E_n(x_i)| > 1$)

Equation (4) was used to calculate $u(\text{DoE}_i)$ in the original comparison (CCQM-K96.2023).

$$u^2(\text{DoE}_i) = \left(1 - \frac{2}{m}\right) u^2(x_i) + u^2(\text{KCRV}) \tag{4}$$

where m is the number of result contribute to determining the KCRV.
If the result of the participating institute is inconsistent with the KCRV, then $u(\text{DoE}_i)$ must be increased to make the results consistent. To achieve this, the uncertainty reported by the institute must be greater than the initially reported uncertainty, and this adjusted uncertainty (i.e., U_{minCMC}) is calculated using equation (5) with $k = 2$ being the coverage factor.

$$U^2_{\text{minCMC}}(x_i) = 2(u^2(\text{DoE}_{i,\text{adj}}) - u^2(\text{KCRV}))/(1 - \frac{2}{m}) \tag{5}$$

where $u(\text{DoE}_{i,\text{adj}})$ is the adjusted uncertainty required the make the results consistent.

Appendix

Technical protocol

Key comparison CCQM-K96.2023.1

Assay of potassium dichromate

Purpose

The CCQM-K96.2023.1 is a follow-up comparison of the CCQM-K96.2023. The comparison is organized by Korea Research Institute of Standards and Science (KRISS) and takes the form of a bilateral comparison between KRISS and Ural Scientific Research Institute for Metrology – Affiliated Branch of the D.I. Mendeleev Institute for Metrology (VNIIM-UNIIM). The results of KRISS will be used to link the results of the participating institutes with the results of CCQM-K96.2023.

Proposed schedule

Invitation:	October 2023
Registration deadline:	31 October 2023
Dispatch of samples:	November 2023
Reporting deadline:	29 February 2024
Draft A report:	October 2024
Discussion:	EAWG meeting, autumn 2024
Draft B report:	December 2024

Measurand

Measurand for the comparison is the amount content of oxidants expressed as potassium dichromate. The nominal value of the measurand is 3.4 mol/kg.

Description of the sample

The source material is commercially available pure potassium dichromate. The material was homogenized for 10 hours at 15 rpm using a 3D powder mixer and then filled into glass bottles with Teflon-lined plastic screw caps.

The homogeneity of the sample was measured by coulometry using a 0.3 g sample taken from each of 10 bottles that were systematically selected from 89 bottles. The between-sample standard deviation, which includes the contribution of both sample homogeneity and measurement repeatability, was 0.0011 %. This result indicates that the homogeneity is adequate for the comparison.

Distribution and actions after receipt of the samples

Each participant will receive one numbered bottle containing approximately 20 g of the material. Shipment to all participants will be carried out at the same time. The bottles will be packed in a cardboard box and shipped via courier. The contents will be labeled as ‘potassium dichromate’ for research purposes and will be accompanied by the material safety data sheet (MSDS). The participants will be informed of the date of sample dispatch along with the shipment tracking number. Please be attentive to possible customs delays.

After receiving the samples, please inspect the bottles for any damage and notify the coordinating laboratory via e-mail regarding the receipt of the sample. If any damage is found, report it immediately to the coordinating laboratory, detailing the encountered situation. The sample should be stored in its original container at laboratory temperature until it is used.

Instruction for measurement

Sample material should be dried at 110 °C for 2 hours without crushing or grinding the material. After drying it should be stored 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 the sample is 2.676 g/cm^3. The minimum sample mass for each measurement is at least 0.3 g.

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

Reporting

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

1. Information regarding participating institution and participants

- Institutional name and acronym
- Institutional address
- Name(s) of analyst(s)

2. Information regarding the sample

- Bottle number
- Date of receipt of the sample

3. Information regarding the measurement

- Date(s) of measurement
- At least six individual measurement results

  The final mean value is automatically calculated in a spreadsheet. Please also provide the temperature, relative humidity, and atmospheric pressure in your laboratory at the time of each mass measurement, as well as the air density used for each buoyancy correction.

- Complete uncertainty budget for the measurement results

  The uncertainty budget must include both instrumental sources of uncertainty (e.g., mass, time, voltage, resistance, etc.) as well as chemical sources (e.g., endpoint determination, equilibria, CO_2 or O_2 interferences, impurities in the electrolyte and electrode, etc.). The uncertainty evaluation should comply with the ISO document JCGM 100:2008 *Guide to the Expression of Uncertainty in Measurement* (GUM). The uncertainty components, along with a summary of how they are calculated, must be included. The reported uncertainty should be expressed as a combined uncertainty and as an expanded uncertainty referred to a 95 % level of confidence.

- Analytical method and a detailed description of the measurement procedure

  If you use coulometry, the following information should be included: Measuring instruments used, cell description, volume of the electrolyte in the working chamber, number of titration stages 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 method of adding the sample.

- Complete measurement equation 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.

While not essential, information on impurities present in the sample is welcome.

The report should be sent by e-mail to the coordinating laboratory **before 29 February 2024**. **However, the deadline will be extended on an individual basis to ensure that all participants have a measurement and reporting period of three months from the receipt of the sample.** The coordinator will confirm the receipt of each report. If you do not receive confirmation within one week, please contact the coordinator to identify the issue.

Key comparison reference value (KCRV)

The KRISS measurement results will serve as the key comparison reference value (KCRV) for linking the participants' results to the CCQM-K96.2023.

How far the light shines statement

Participants who successfully take part in the CCQM-K96.2023.1 key comparison demonstrate their ability to measure the amount content of oxidants in high-purity potassium dichromate. Good results will indicate a good performance in assaying high-purity oxidants, wherein the principles of oxidation-reduction titration used by participants can be applied similarly.

Contact person and coordinating laboratory

Kyungmin JO (kyungmin.jo@kriss.re.kr)

Korea Research Institute of Standards and Science (KRISS)

Alternative contact:

Min-Ah OH (minah.oh@kriss.re.kr), KRISS