CCQM WG on Electrochemical Analysis and Classical Chemical Methods

CCQM-K96.2023 – Assay of potassium dichromate

Final report

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Summary

CCQM key comparison CCQM-K96.2023 (assay of potassium dichromate) is a repetition of the previous CCQM-K96 and CCQM-K96.1 key comparisons. This comparison was jointly organized by the CCQM Working Groups for Inorganic and Electrochemical Analysis (IAWG and EAWG) to evaluate the degree of equivalence of measuring the amount content of oxidants. The Korea Research Institute of Standards and Science (KRISS) served as the coordinating laboratory, with six national metrology institutes participating in the comparison. All participants employed constant-current coulometric titration for their analyses. The results from four of the six institutes were consistent, while those from two deviated from the others. Several potential causes of bias in the measurement results were investigated; however, the reason for the deviation was not clearly identified. Nevertheless, most participants who performed well in the earlier comparisons (CCQM-K96 and CCQM-K96.1) again demonstrated good agreement in this comparison.

CCQM-K96.2023

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CCQM-K96.2023

1   Coordinating laboratory and contact person

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2   List of participants

The list of participants for CCQM-K96.2023 is given in Table 1.

Table 1. List of participants.

Acronym	Institute	Country	Contact person	Email
CENAM	Centro Nacional de Metrología	Mexico	José Luis Ortiz-Aparicio, Griselda Rivera-Sánchez	jortiz@cenam.mx
CMI	Czech Metrology Institute	Czech Republic	Matilda Roziková	mrozikova@cmi.cz
INMETRO	Instituto Nacional de Metrologia, Qualidade e Tecnologia	Brazil	Paulo Paschoal Borges, Sidney P. Sobral	ppborges@inmetro.gov.br
KRISS	Korea Research Institute of Standards and Science	Korea	Kyungmin Jo, Min-Ah Oh	kyungmin.jo@kriss.re.kr
NIM	National Institute of Metrology, P. R. China	China	Bing Wu, Tao Zhou, Jianying Zhang	wubing@nim.ac.cn
NMIJ	National Metrology Institute of Japan	Japan	Yuya Hibino	hibino.yuya@aist.go.jp
SMU	Slovak Institute of Metrology	Slovakia	Michal Máriássy, Zuzana Hanková	mariassy@smu.gov.sk

3 Time schedule

Call for participants: May 2023
Registration deadline: 30 June 2023
Dispatch of samples: September 2023
Reporting deadline: 31 December 2023
Draft A report: March 2024
Discussion: EAWG spring meeting 2024
Draft B report: October 2024

4 Samples

4.1 Sample preparation

A 2 kg batch of commercially available pure potassium dichromate was the source material for the samples. This material was transferred to a cleaned 10 L low-density polyethylene carboy and homogenized for 10 hours using a 3D mixer at a speed of 15 rpm. The homogenised material was then filled in glass bottles which were subsequently closed with Teflon-lined plastic screw caps. Each bottle contained approximately 20 g of powder, and was sealed in a plastic bag.

4.2 Sample delivery

The sample bottles were shipped from KRISS on September 15th and 16th in a cardboard box via air courier. A spreadsheet template for reporting and a safety data sheet were provided by the time the samples were shipped. All samples arrived at their destination without damage. The dispatch and receipt dates for the sample, as well as the report submission date, are provided in Table 2. Due to the hazardous nature of the samples, customs clearance incurred delays, causing the majority of institutes to receive their samples later than scheduled. As a consequence, the measurement period was extended accordingly. CENAM, INMETRO, NIM, and SMU reported their results on time. KRISS and NMIJ reported their results a little later than the deadline due to technical problems encountered during the measurement, and because institutional and governmental approvals were required to release the results.

Table 2. Sample dispatch and receipt dates.

Institute	Bottle number	Dispatch date	Receipt date	Report submission date
CENAM	71	16 Sep 2023	22 Oct 2023	31 Dec 2023
CMI	79	15 Sep 2023	21 Sep 2023	Not submitted
INMETRO	59	16 Sep 2023	8 Dec 2023	28 Dec 2023
KRISS	81	-	-	18 Jan 2024
NIM	51	16 Sep 2023	13 Oct 2023	20 Dec 2023
NMIJ	69	16 Sep 2023	17 Nov 2023	15 Mar 2024
SMU	49	15 Sep 2023	4 Oct 2023	27 Nov 2023

4.3 Homogeneity

Homogeneity was assessed by KRISS using constant-current coulometric titration. To this end, 0.3 g samples were taken from each of 10 bottles selected at regular intervals out of a total of 89. As shown in Figure 1, the

between-sample standard deviation, which includes the contributions of both sample homogeneity and measurement repeatability, was 0.0011 %. This indicates that the homogeneity is sufficient for the comparison.
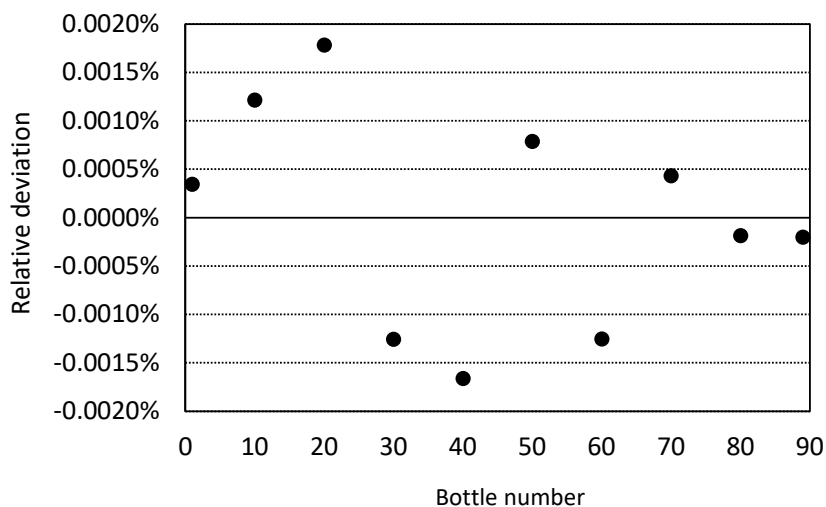

Figure 1. Result of homogeneity assessment.

4.4   Stability

Potassium dichromate is known to be a stable material, convenient for storage and transportation. The typical shelf-life of the certified reference material ranges from 10 to 20 years. KRISS has also confirmed in the past that the potassium dichromate reference material has remained stable in its stock for 10 years. Therefore, no further testing of stability was needed.

5   Correspondence with institutes

CMI requested an extension of the measurement period due to heavy workload at the end of the year. After discussions with the EAWG chair regarding reasonable limits for extending the measurement period, the coordinating laboratory concluded that extending the period by 4 weeks would not pose a problem, provided that the stability of the sample is guaranteed. Based on these discussions, the measurement period was extended by 4 weeks. However, due to technical issues encountered during the measurements, CMI was unable to submit the results within the extended deadline.

The results of CENAM and INMETRO differed significantly from those of most other participants. As a result, they were asked to check their results for possible typos, numerical errors, or transcription errors, without being informed about the magnitude and sign of the observed anomaly. INMETRO and CENAM confirmed that no such errors could be found, so that their originally reported results remain valid.

6   Instructions 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 2676 kg/m^3. The minimum sample mass for each measurement had to be 0.3 g at least.

Any method or combination of methods could be used for the comparison. It was expected that the highest-level method available at each institute, such as coulometry or titrimetry, was used. Lower-level methods were allowed. However, those results had to be reported only as additional information. The participants were requested to report the results as amount content of oxidants expressed as potassium dichromate with the unit 'mol kg^{-1}', and to provide an uncertainty evaluation according to JCGM 100:2008 [1].

7   Results and discussion

7.1   Methods of measurement

All participants used constant-current coulometry, using either horizontal or vertical cells, as indicated in Table 3. 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
CENAM		Vertical, 1 intermediate compartment (IC)	200
INMETRO		Vertical, 1 IC	250
KRISS	Constant-current coulometry	Horizontal, 2 ICs	100 – 120
NIM		Horizontal, 2 ICs	150
NMIJ		Horizontal, 2 ICs	80
SMU		Vertical, 1 IC	260 – 280

Table 4. Details of measurement parameters.

Institute	Sample mass/g	Cathode	Anode	Main current /mA	Current density[b] /(mA/cm^2)
CENAM	0.18[a]	Pt plate (1 cm × 1 cm)	Pt wire (0.5 mm dia., 80 cm)	100	50
INMETRO	0.5	Pt plate (5 cm × 6 cm)	Pt wire (0.3 mm dia., 50 mm)	300	5
KRISS	0.3	Pt plate (4 cm × 10 cm)	Pb rod (5 mm dia., 15 cm)	102	1.3
NIM	0.3	Pt wire (1.6 mm dia., 70 cm)	Pt plate (5 cm × 6 cm)	102	2.9
NMIJ	0.3	Pt mesh (8 cm × 2.5 cm)	Pt wire (1.5 mm dia., 30 cm)	50 – 150	-
SMU	0.5	Pt plate (94 cm^2)	Pt wire (9 cm^2)	300	3.2

[a] 0.1 mol/kg solution was prepared gravimetrically from the sample, and approximately 6 g of this solution was used for analysis.

[b] 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
CENAM	Amperometry, 0.45 V vs. Hg/Hg_2SO_4	Linear regression (LR), x-intercept	After main titration	-
INMETRO	Biamperometry	LR, x-intercept	Before main titration	Yes[a]
KRISS	Amperometry, 0.41 V vs. Hg/Hg_2SO_4	LR, x-intercept	After main titration	Yes[a]
NIM	Amperometry, 0.85 V vs. Hg/Hg_2Cl_2	LR, x-intercept	After main titration	Yes[a]
NMIJ	Potentiometry, Pt vs. Ag/AgCl	3rd order polynomial regression	After main titration	Yes[b]
SMU	Biamperometry	LR, x-intercept	Before main titration	Yes[c]

[a] Measurements were performed by reusing the electrolyte.

[b] The same amount of sample was used for pre-titration as was used for the assay.

[c] Electrolyte was pre-treated before the measurements.

Table 6. Details of measurement parameters (continued).

Institute	Estimated levels of total organic carbon (TOC) in the ultrapure water used
CENAM	2 ppb (measured in real-time monitoring)
INMETRO	< 10 ppb (available from the equipment manual)
KRISS	< 5 ppb (measured in real-time monitoring)
NIM	50 ppb – 100 ppb (measured using TOC measurement equipment)
NMIJ	2 ppb (measured in real-time monitoring)
SMU	1 ppb – 5 ppb (available from the equipment manual)

7.2 Reported Results

The reported values and uncertainties are summarized in Table 7 and depicted graphically in Figure 2. The main sources of uncertainty and their contributions are shown in Table 8. NIM analyzed the impurities of the sample using high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS), and the results are presented in Table 9. 68 impurities were detected, but only those with mass fractions greater than 1 mg/kg are displayed in the table.

Table 7. Measurement results of CCQM-K96.2023.

| Institute	Measurement date	Value /mol kg^{-1}	n	SD /mol kg^{-1}	u_c /mol kg^{-1}	U /mol kg^{-1}	k
CENAM	Dec 27 – 29, 2023	3.397167	6	0.000244	0.000147	0.000307	2.1
INMETRO	Dec 13 – 22, 2023	3.397473	6	0.000344	0.000183	0.000385	2.1
KRISS	Jan 10 – 17, 2024	3.399055	6	0.000032	0.000098	0.000273	2.8
NIM	Nov 21 – Dec 1, 2023	3.398623	10	0.000269	0.000121	0.000242	2
NMIJ	Feb 5 – 15, 2024	3.398872	10	0.000061	0.000157	0.000314	2
SMU	Nov 15 – 16, 2023	3.398815	5	0.000075	0.000065	0.000129	2
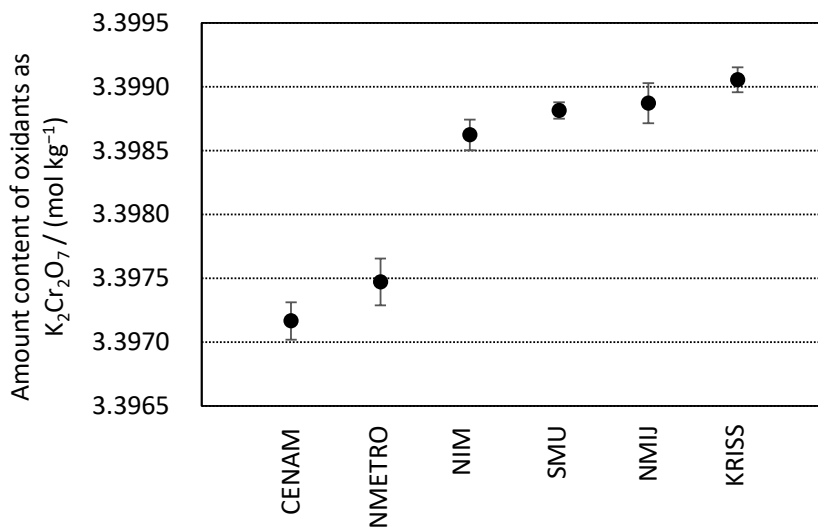
Figure 2. Measurement results of CCQM-K96.2023. The error bars indicate the combined standard uncertainty (k = 1).

Table 8. Major uncertainty sources and their contribution.

Institute	Major uncertainty source (contributions)
CENAM	Reproducibility (46 %), dichromate diffusion (21 %), voltage for main titration (16 %)
INMETRO	Reproducibility (59 %), current efficiency (15 %), incomplete rinsing (14 %)
KRISS	Reproducibility (intermediate precision) (84 %), charge for main titration (12 %)
NIM	Reproducibility (49 %), corrected time of pre-titration (23 %), Time of final titration (23 %)
NMIJ	Sample mass (88 %), current efficiency (10 %)
SMU	Sample diffusion (28 %), reproducibility (27 %), voltage for main titration (20 %)

Table 9. Mass fraction of impurities in the sample.

Element	Mass fraction, w_i/ (mg kg^{-1})	$u(w_i)$/ (mg kg^{-1})	Method
Na	160	1.25	HR-ICP-MS
Ga	4.04	0.72	HR-ICP-MS
Rb	5.58	0.07	HR-ICP-MS
Zr	3.33	0.05	HR-ICP-MS
Nb	3.87	0.14	HR-ICP-MS
Mo	2.36	0.06	HR-ICP-MS

7.3   Discussion

As seen in the Figure 2, two results deviate from the majority of the results. Table 10 lists a number of sources that could cause bias between results. Table 11 lists corresponding preventive measures. The reported results and measurement conditions from each participant were analyzed with respect to the effects mentioned in Tables 10 and 11 to discern underlying reasons for the observed deviation. No obvious bias or correlation of results could be identified. Likewise, neither CENAM nor INMETRO could find any other measurement error. Consequently, all results must be considered valid, and it must be concluded that some uncertainty contributions have been underestimated.

Table 10. Sources of measurement bias.

Source	Direction	Description
Dissolved O_2	+	Consumes electrogenerated titrant (Fe^{2+})
Reducible impurities	+	Causes an additional reduction reaction apart from titrant generation
Current efficiency	+	Causes more current to flow in practice than in theory
Oxide film on Pt cathode	+	Consumes electrogenerated titrant (Fe^{2+})
Sample loss	–	Reduces the total charge required for the reaction
Organic impurities	–	Consumes the sample (strong oxidizing agent) through reaction

Table 11. Measures to prevent measurement bias.

Source	Direction	Measures to prevent the bias
Dissolved O_2	+	Continuously supplies inert gas during measurement
Reducible impurities	+	Pre-treats or reuses the electrolyte
Current efficiency	+	Uses an appropriate level of current density
Oxide film on Pt cathode	+	Pre-treats or reuses the electrolyte, Reduces the electrode before the measurement
Sample loss	–	Establish procedures to prevent sample loss
Organic impurities	–	Pre-treats or reuses the electrolyte, Avoids contact between sample and organic matter when using the sample solution

8   Estimators for the Key Comparison Reference Value (KCRV)

Possible estimators and their uncertainties for the KCRV were calculated using results from all participants. They are summarized in Table 12, with visual representation provided in Figure 3. Formula are given in the Annex [2]. The results of the participants are shown in Figure 4 to Figure 6 in relation to each estimator.

Table 12. Candidate estimators for the KCRV, calculated according to CCQM/2013-22.

Estimator	Value /(mol kg^{-1})	u /(mol kg^{-1})	u_{rel}
Mean	3.398334	0.000328	0.0097 %
Median[a]	3.398719	0.000186	0.0055 %
Uncertainty-weighted mean, (Graybill-Deal)	3.398621	0.000253[b]	0.0074 %

[a] It was proposed as the KCRV.

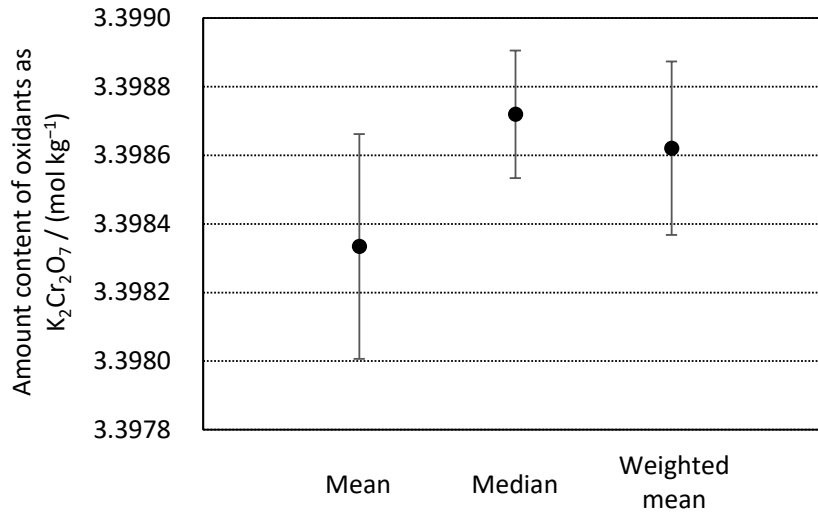[b] The uncertainty was corrected for observed dispersion.

Figure 3. Values and uncertainties of KCRV estimators for CCQM-K96.2023.
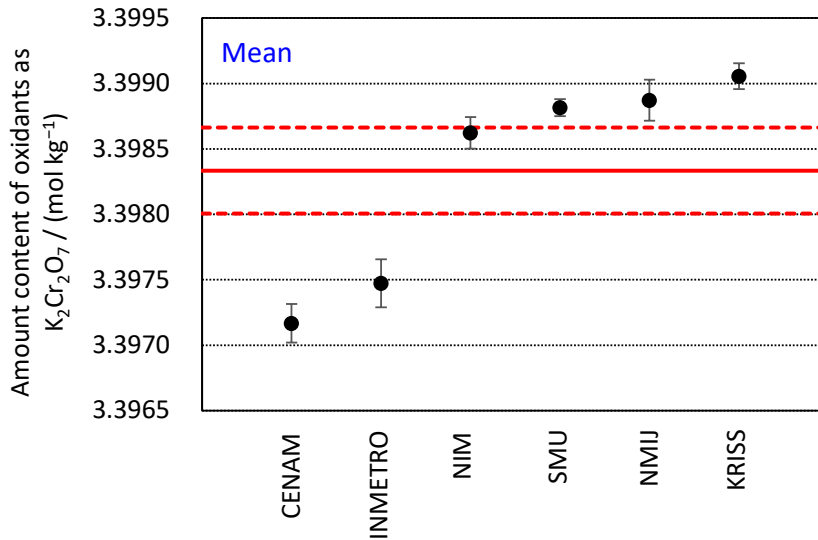The error bars indicate the standard uncertainty ($k = 1$).

Figure 4. The results of CCQM-K96.2023 with the arithmetic mean 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.
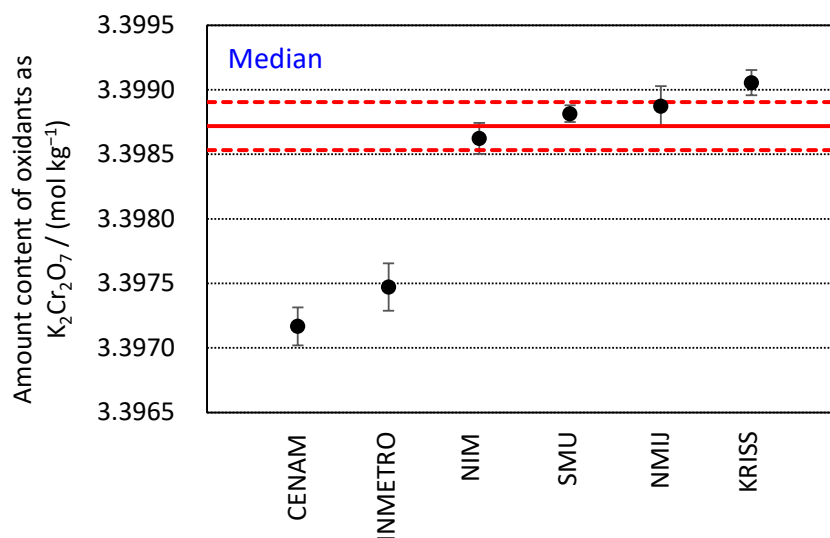
Figure 5. The results of CCQM-K96.2023 with the median as the KCRV estimator. The error bars represent the standard uncertainty ($k = 1$). The KCRV estimator is depicted as the solid red line, accompanied by its standard uncertainty indicated by the dashed red line.
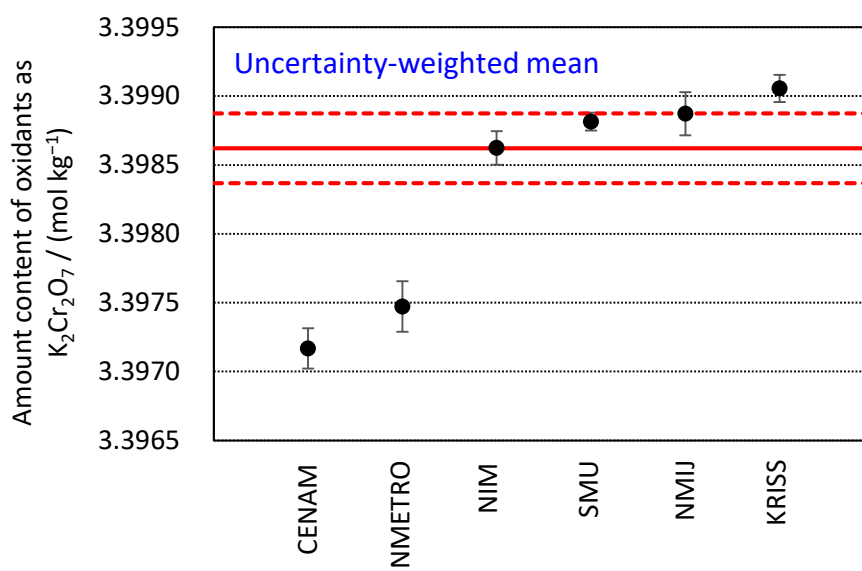

Figure 6. The results of CCQM-K96.2023 with the uncertainty-weighted mean as the KCRV estimator. The error bars represent the standard uncertainty ($k = 1$). The KCRV estimator is depicted as the solid red line, accompanied by its standard uncertainty indicated by the dashed red line.

The distribution of the results best fits into the category C (generally consistent results with a small number of outlying values) of Figure 1 of the CCQM/2013-22 document [2]. In this category, the arithmetic mean could be used if outlying values were excluded. However, there is no justification for excluding outliers in this comparison. Therefore, a robust statistical method should be used to estimate the KCRV, and a commonly used robust and simple estimator for this purpose is the median. Therefore, the median has been selected as the KCRV. Figure 5 suggests that the results of the majority of participants are consistent with the median within their expanded uncertainties, while the effect of the outliers is still reflected to some extent. All participants have agreed upon this choice.

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

The DoE_i of result x_i of institute i and its uncertainty is calculated according to CCQM/2013-22 with respect to the median as best estimate for the KCRV (see the Annex). The results are listed in Table 13. The table also states the uncertainty weighed DoE (E_n value).

$$E_n(x_i) = \frac{DoE_i}{U(DoE_i)} \tag{1}$$

A result is considered consistent with the KCRV if $|E_n(x_i)| \leq 1$. Table 13 also shows minimal expanded uncertainties U_{minCMC} consistent with the proposed KCRV, which makes the submission and review of claims of calibration and measurement capabilities (CMC) easier. If a result is consistent with the KCRV, U_{minCMC} is equivalent to the expanded uncertainty reported by the institute.

Regarding inconsistent results, it is assumed that they are the result of underestimated or unknown uncertainty contributions, provided that failure of the measurement setup or the sample can be excluded, as is the case here (see discussion above). 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. (1), i.e.,

$$DoE_i^2 \leq (k \cdot u(DoE_i))^2 \tag{2}$$

with $k = 2$ being the coverage factor. $U_{minCMC}(i) = 2 \cdot u_{minCMC}(i)$ for institute i can be calculated from eq. (2) by replacing $u(x_i)$ by u_{minCMC} in the formula for $u(DoE)$. It is important to note that the formula for $u(DoE)$ is different for different KCRV estimators. Using the median as the best estimate for the KCRV, we applied the 'special cases' formula from section 2.3 (page 26 in CCQM/2013-22) to calculate $u(DoE_i)$ and u_{minCMC}, respectively:

$$u^2(DoE_i) = \left(1 - \frac{2}{m}\right) u_{minCMC}^2(x_i) + u^2(median) \tag{3}$$

where m is the number of results contributing to the KCRV.

Moreover, in some cases, $u(DoE)$ does not depend on the uncertainties of the participants at all. Thus, if eq. (2) does not depend on the uncertainty of the concerned institute, the simple relation $U^2(DoE)=U^2(KCRV)+U_{minCMC}^2$ is used to calculate U_{minCMC}. It must be emphasized that it is possible under this condition that a calculated U_{minCMC} value is smaller than the originally reported uncertainty $U(x_i)$. In such cases, the larger value of the two values is used. Figure 7 shows the DoEs (in rising order) and their expanded uncertainties ($k = 2$).

Table 13. Degrees of equivalence with corresponding measurement uncertainties.

| Institute	Value /mol kg^{-1}	U /mol kg^{-1}	DoE$_i$ /mol kg^{-1}	$U(DoE_i)$ /mol kg^{-1}	DoE$_i$/$U(DoE_i)$	U_{minCMC} /mol kg^{-1}
CENAM	3.397167	0.000307	−0.00155	0.00044	−3.5	0.001846
INMETRO	3.397473	0.000385	−0.00125	0.00048	−2.6	0.001457
KRISS	3.399055	0.000273	0.00034	0.00040	0.8	0.000273
NIM	3.398623	0.000242	−0.00010	0.00042	−0.2	0.000242
NMIJ	3.398872	0.000314	0.00015	0.00045	0.3	0.000314
SMU	3.398815	0.000129	0.00010	0.00039	0.2	0.000129
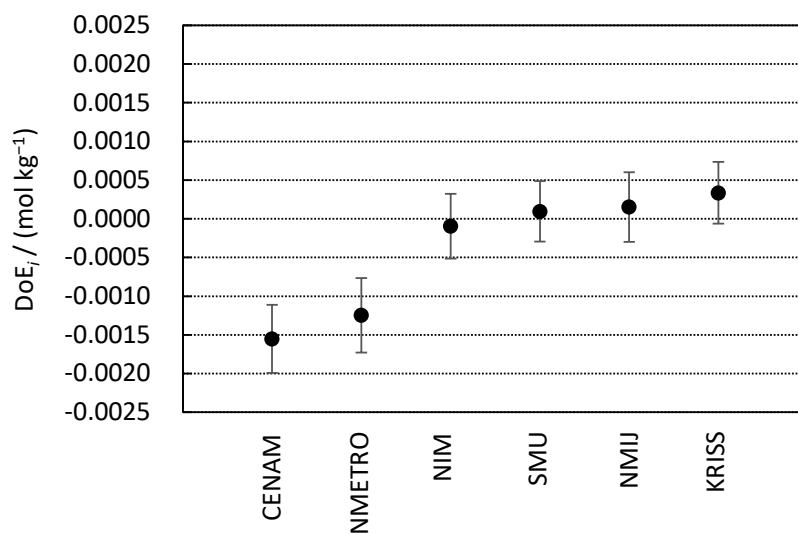
Figure 7. Degrees of equivalence with corresponding expanded measurement uncertainty ($k = 2$).

10   How Far Does the Light Shines statement

The comparison provides support for the capabilities to measure the amount content of oxidants in an assay of high purity potassium dichromate. Results achieved from coulometry (direct approach) provide evidence for the capabilities to assay the purity of pure salts in the range 0.995 to 1 kg/kg. The uncertainties claimed in the CMC submission must not be smaller than the U_{minCMC} values stated in Table 13, unless exceptions stated in the EAWG-CMC guidelines can be applied.

11   Acknowledgements

12   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).

CCQM-K96.2023

Annex

<u>KCRV estimators</u>

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.
Standard uncertainty	$$u(\bar{x}) = \frac{s(x)}{\sqrt{m}}$$ where $s(x)$ is the (sample) standard deviation of the reported values $x_1, \dots, x_m$ given by $$s^2(x) = \frac{1}{m-1}\sum_{i=1}^{m}(x_i - \bar{x})^2$$

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

Value	For m being even, $$\text{med}(x) = \frac{1}{2}\left(x'_{\frac{m}{2}} + x'_{\frac{m}{2}+1}\right)$$ where $x'_1, \dots, x'_m$ denote the reported values arranged in increasing order. For m being odd, $$\bar{x} = x'_{\frac{(m+1)}{2}}$$
Standard uncertainty	$$u^2(\text{med}(x)) = \frac{\pi}{2m}\hat{\sigma}^2$$ 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$_E$.)

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

<u>DoE uncertainty (for median)</u>

The degrees of equivalence (DoE$_i$) for the median as the key comparison reference value (KCRV) can be calculated based on the following equations:

$$\text{DoE}_i = x_i - x_{\text{ref}}$$

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 best estimate for the KCRV, the 'special cases' formula from section 2.3 of the CCQM/2013-22 guidance note (page26) is applied to calculate u(DoE$_i$), as shown below. In these instances, the $u(x_i)$ values are assumed to be accurately determined, and an additional random effect contributes to the increased dispersion of the results.

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

where m is the number of results contributing to the KCRV.

Appendix

Technical protocol
Key comparison CCQM-K96.2023
Assay of potassium dichromate

23 May 2023

Purpose

This key comparison is a repeat of CCQM-K96 and CCQM-K96.1 key comparisons on potassium dichromate. The comparison is performed to evaluate the degree of equivalence of national standard measurement procedures for the measurement of the amount content of oxidants. The institutes can use a method of their choice, but it is anticipated that coulometry or titrimetry will be used in most cases. Only independent results obtained by the primary method will be used to calculate the Key Comparison Reference Value (KCRV). The results of the key comparison will underpin the calibration and measurement capability (CMC) claims of participating institutes.

Proposed schedule

Invitation:	May 2023
Registration deadline:	30 June 2023
Dispatch of samples:	September 2023
Reporting deadline:	December 2023
Draft A report:	March 2024
Discussion:	EAWG spring meeting 2024
Draft B report:	October 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 'COMPARISON SAMPLE CCQM-K96.2023, Potassium dichromate, CAS 7778-50-9' 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 31 December 2023**. **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 KCRV will be agreed upon at the EAWG spring meeting, which is tentatively scheduled for April 2024.

How far the light shines statement

Participants who successfully take part in the CCQM-K96.2023 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

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