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**Key comparison CCQM-K96
Determination of amount content of
dichromate
Final report**

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Abstract

The CCQM-K96 key comparison was organised jointly by the inorganic and electrochemistry working groups of CCQM to test the abilities of the metrology institutes to measure the amount content of dichromate. Slovak Institute of Metrology with help of KRISS acted as the coordinating laboratories. Eight NMIs took part in the comparison. All participants used high accuracy constant current coulometry. Good agreement of the results was observed.

1 INTRODUCTION

The CCQM-K96 key comparison “Determination of amount content of dichromate” has been proposed and discussed at the April 2011 CCQM Inorganic and Electrochemical Analysis Working Group meetings at BIPM. The aim of the comparison is to demonstrate and document the capability of interested National Metrology Institutes to measure the amount content of oxidant (dichromate) in a pure potassium dichromate sample. Dichromate “purity” was already measured in the framework of the CCQM-P7 study in 1998, together with NaCl and KCl [1].

Potassium dichromate is an often used reference material in oxidation-reduction titration methods. The reliability of its assay is therefore of prime importance for chemical producers and analytical chemistry in general. It is also of interest regarding its use in nuclear material inventory, where accurate results are indispensable. There are several producers, who offer this material as a certified reference material.

The objective of CCQM-K96 was to determine the amount content of oxidants expressed as potassium dichromate in a sample of potassium dichromate. The participants were free to choose the analytical procedure.

2 LIST OF PARTICIPANTS

Five institutes originally indicated interest in participating in the comparison. At last, eight institutes took part. Table 1 contains the full names of all participating NMIs and contact persons.

Table 1 List of participants

Institution	Country	Contact person
CENAM Centro Nacional de Metrologia	Mexico	Judith Velina Lara Manzano
INMETRO National Institute of Metrology, Quality and Technology	Brasil	Paulo P. Borges
KRISS Korea Research Institute of Standards and Science	Korea	Euijin Hwang
NIST National Institute for Standards and Technology	USA	Kenneth W. Pratt
NMIJ National Metrology Institute of Japan	Japan	Toshiaki Asakai
NIM National Institute of Metrology of P. R. China	China	Wu Bing
SMU Slovak Institute of Metrology	Slovakia	Michal Máriássy
UNIIM Ural Scientific Research Institute of Metrology	Russia	Gennady I. Terentiev

3 SAMPLES

A batch of commercial material was selected for comparison. The material was ground in a mortar, homogenised 10 h by rotation (30 min^{-1}) in a large bottle and filled into glass bottles closed with silicone lined plastic caps. Homogeneity was tested by analysing one 0.5 g sample from each of 10 selected bottles by coulometry. The standard deviation of results (which includes contribution from measurement repeatability) was 0.0019%. The result indicates that the homogeneity is adequate for the comparison.

KRISS distributed the samples to the participants by DG WorldNet Service (through Fedex) in December 2011 (except UNIIM, where the sample was sent on January 21 by DG WorldNet Service due to transport problems for hazardous material). All samples arrived to their destination without damage. The receipt dates and the responsible persons are given in Table 2: The deadline for reporting results was set to 29 February 2012 or three months after receipt of samples, whichever was later. All participants reported their results in time.

Table 2 Sample receipt dates and report dates

<i>Institute</i>	<i>Sample dispatch date</i>	<i>Sample receipt date</i>	<i>Date report sent</i>
CENAM	7 December 2011	20 January 2012	19 April 2012
INMETRO	15 December 2011	2 February 2012	27 April 2012
KRISS	–	–	29 February 2012
NIST	6 December 2011	14 December 2011	29 February 2012
NMIJ (AIST)	6 December 2011	28 December 2011	23 March 2012
NIM	20 December 2011	13 February 2012	12 April 2012
SMU	6 December 2011	9 December 2011	26 January 2012
UNIIM	21 January 2012	2 March 2012	30 May 2012

4 INSTRUCTIONS TO PARTICIPANTS

The instructions sent to the participants by e-mail consisted of technical protocol and results report template.

The technical protocol (appendix A) contained background information, timing of the comparison, and information on the participating institutes. Information on sample homogeneity and sample preparation for measurements was given. The participants were free to choose the measurement procedure. Participants were requested to express the results as amount content of dichromate and to provide uncertainty evaluation according to the Guide to the expression of Uncertainty in Measurement [2].

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

After receiving all the results, NIM was asked to check its results for numerical errors. No numerical errors were reported and thus the values are given as originally reported.

5 METHODS OF MEASUREMENT

The methods of measurement were left free to be selected by the participating institutes. Indirect methods had to take into account the dependence of the assay on the Cr/K (or other metals) ratio and the water content. Probably in view of the difficulties associated with the indirect assay via impurities, no one of the institutes used this approach; but four institutes provided information on impurities found in addition to the result obtained by coulometry.

All participants used coulometric titration for dichromate determination and reported more or less details on their procedure in their reports or additional information. Some details on measurements as derived from the reports are given in Tables 3 and 4.

All coulometric titrations follow roughly the same procedure and use the same electrolyte (except CENAM, where lower concentration of Fe(III) and acid was used). In INMETRO, a special step was added: the indicator electrode was taken out of the cathodic compartment before the end of the main titration, immersed during 10 min in a solution of 2 mol L⁻¹ ammonium iron(II) sulfate and after rinse with deionized water it was put again inside the catholyte.

As an additional technique CENAM used potentiometric weight titration with iron(II) solution to link the result to the assay of SRM136f.

Table 3 *Details on measurement methods used*

<i>Institute</i>	Indication	EP estimation*	Major unc. sources	their contribution
CENAM	amperometry, 0.35 V vs. Hg/Hg ₂ SO ₄	LR – 2 lines intercept	EP, mass, voltage	92%
INMETRO	biamperometry, 55 mV	LR, x-intercept	current, O ₂ influence	87%
KRISS	amperometry, 0.85 V vs. SCE	LR, x-intercept	reproducibility	94%
NIST	biamperometry, 220 mV	LR, extrapolation to min. current	u _A , mass, O ₂	91%
NMIJ	potentiometry	3rd order polynomial regr.	mass, resistance, diffusion	94%
NIM	amperometry, 0.85 V vs. SCE	LR, x-intercept	u _A , endpoint	99%
SMU	biamp, 55 mV	LR, x-intercept	el. impurities, diffusion, voltage	87%
UNIIM	biamp, 50 mV	LR – 2 lines intercept	mass	96%
CENAM (pot)	potentiometry		titrant mass and amount content	98%

* LR – linear regression

Table 4 Details on measurement methods used (continued)

Institute	Approx. sample mass /g	Procedure details				
		Cell type	Cell volume /mL	Main current /mA	Current density /(mA/cm ²)	Sample added before main titn
CENAM	0.12	vertical, 1 intermediate chamber (IC)	200	100	5.4	Y
INMETRO	0.5	vertical, 1 IC*	250	300	5	Y
KRISS	0.5	horizontal, 2 IC	120	102	1.1†	N
NIST	0.25	horizontal, 2 IC	100	102	3.7	Y
NMIJ	0.15-0.5	horizontal, 2 IC	70	50-150	2.5-7.5	N
NIM	0.2-0.5	horizontal, 2 IC	150	102	6.5	N
SMU	0.5	vertical, 1 IC*	260-275	280-300	3-3.2	Y
UNIIM	0.31	vertical, 1 IC	200	160	1.8	N

* - continuous flow from IC into the working chamber during main titration

† - without stirring

6 RESULTS AND DISCUSSION

The reported values and uncertainties are summarised in Table 5 and also displayed graphically in Figure 1. CENAM provided two results with two different methods; result by coulometry was provided for the key comparison and the one by potentiometric titration as information result.

Table 5 Results (amount content of dichromate, relative standard deviation, relative combined standard uncertainty and number of measurements)

Institute	Measurement date	Result /mol.kg ⁻¹	RSD	$u_{C,r}$	n
CENAM	Apr 11-17, 2012	3.39672	0.0054%	0.0043%	12
INMETRO	Mar 12 –Apr 20, 2012	3.39670	0.0043%	0.0042%	7
KRISS	Feb 15-24, 2012	3.397142	0.0010%	0.0017%	6
NIM	Mar 13-29, 2012	3.39777	0.0132%	0.0050%	11
NIST	Feb 6-10, 2012	3.39712	0.0058%	0.0030%	10
NMIJ	Jan 20-Feb 10, 2012	3.39720	0.0022%	0.0047%	10
SMU	Dec 15-20, 2011	3.396953	0.0016%	0.0020%	7
UNIIM	May 2-25, 2012	3.39673	0.0039%	0.0066%	10
CENAM (potentiometry)	Apr 11-13, 2012	3,39637	0,0043%	0,0099%	6

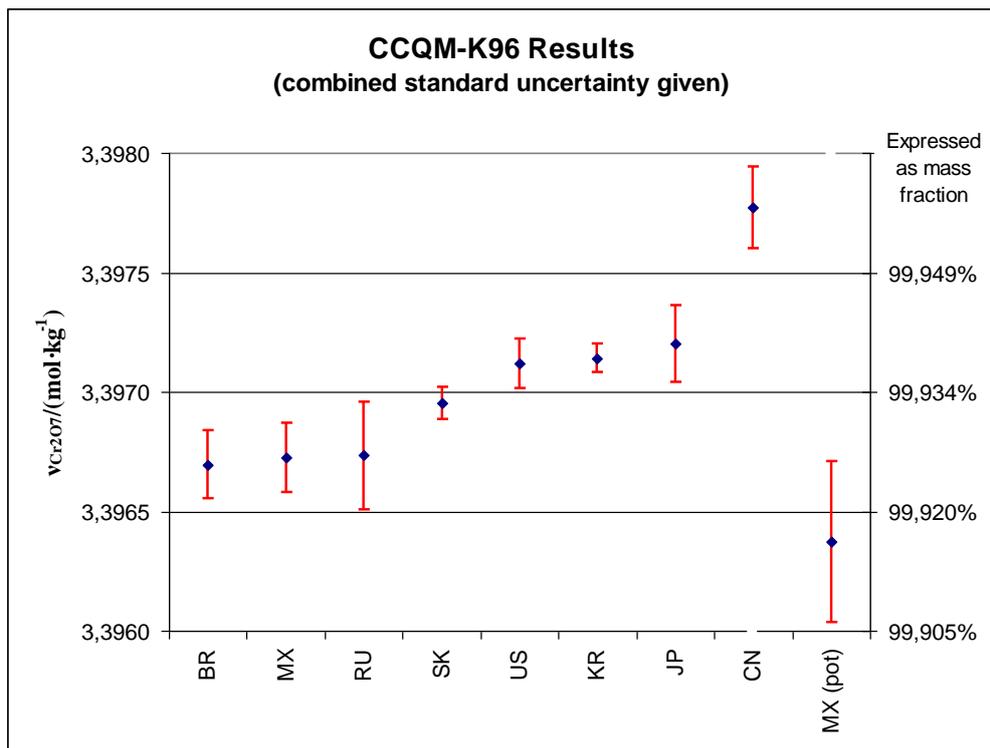


Figure 1 Results of CCQM-K96

Several approaches to estimate the key comparison reference value (KCRV) were considered. All gave values identical within the uncertainty (Table 6). Due to presence of excess variance ($\chi^2=18.5$) the use of simple weighted mean is not appropriate. NIM result was not used in the calculation of reference values (see below).

Table 6 Some estimators of the reference value from reported CCQM-K96 results

Possible KCRV	Value / mol kg^{-1}	Standard uncertainty / mol kg^{-1}	Rel. stand. uncertainty
Arithmetic mean	3.396938	0.000083	0.0024%
Variance weighted mean	3.397022	0.000036	0.0011%
Variance weighted mean, Birge treatment for uncertainty	3.397022	0.000063	0.0019%
Median	3.396953	0.000154	0.0045%
Der Simonian-Laird mean	3.396971	0.000076	0.0022%

Variance weighted mean with Birge treatment for uncertainty was agreed as the reference value:

KCRV: 3.397022 mol kg⁻¹
U(KCRV): 0.00013 mol kg⁻¹

Relative degrees of equivalence are given in Table 7 and Figure 2.

Table 7 Results of CCQM-K96 – degrees of equivalence

Institute	D_i	$U(D_i)$
INMETRO	-0,0096%	0,0092%
CENAM	-0,0088%	0,0093%
UNIIM	-0,0085%	0,0137%
SMU	-0,0020%	0,0054%
NIST	0,0028%	0,0071%
KRISS	0,0035%	0,0050%
NMIJ	0,0053%	0,0101%
NIM	0,0221%	0,0107%
CENAM (pot)	-0,0191%	0,0202%

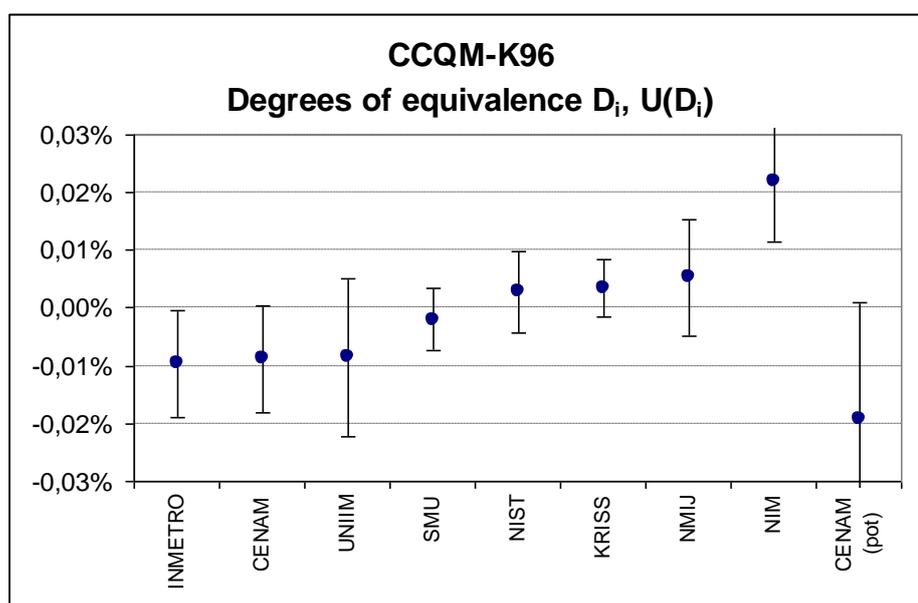


Figure 2 Results of CCQM-K96 – degrees of equivalence

Seven of the eight results are in close agreement, NIM result is by about 0.015% higher. NIM used the material from CCQM-P7 as a control, the result obtained agreed well with NRCCRM result obtained in 1998 (but this result was also about 0.015% higher than the other coulometric results in CCQM-P7). To be noted is also the highest relative standard deviation, which could indicate some influence not taken into account in calculation. NIM used relatively high current density, however NMIJ used a range of current densities that encompasses the NIM value and did not observe a significant effect. In a follow-up investigation NIM changed the cell used (silica cell with Teflon cover instead of glass with rubber cover) and obtained results with good agreement to those of other participants ($3.39699 \text{ mol kg}^{-1}$), with RSD improved to 0.0088%.

The influence of oxygen impurity present in the cell will be different depending on whether the sample is introduced before or after main titration. In the latter case the influence is expected to be higher as in the cell high concentration of Fe(II) will be present. Fe(II) oxidation leads to positive errors. Also any Fe(II) losses by diffusion would lead to positive errors.

If sample is introduced before main titration, losses of dichromate ions by diffusion (+ electromigration) would lead to negative errors.

It has been observed that slowly reacting reducing substances in the supporting electrolyte cause low results if they are not removed prior to measurements [3]. Such electrolyte treatment is routinely done at several institutes.

An interesting feature is that four laboratories using vertical cell obtained lower results than those using horizontal (NIST type) cells, however there is no scientific explanation for that.

Differences can still be observed in the uncertainty evaluations, as summarised in Table 8. The chemical sources of uncertainty were not always taken into account, thus leading to smaller uncertainty estimates. In the weight titration the design of the experiment leads to cancellation of most systematic errors (also from chemical sources).

Table 8 *Summary of uncertainty evaluation*

<i>Institute</i>	<i>Major uncertainty sources considered</i>	<i>their contribution</i>	<i>chem. uncertainties considered</i>
CENAM	EP, mass, voltage	92%	No
INMETRO	current, O ₂ influence	87%	Yes
KRISS	reproducibility	94%	No
NIST	u _A , mass, O ₂	91%	Yes
NMIJ	mass, resistance, diffusion	94%	Yes
NIM	u _A , endpoint	99%	No
SMU	electrolyte impurities, diffusion, voltage	87%	Yes
UNIIM	mass	96%	Yes
CENAM (pot. titn.)	titrant mass and amount content	98%	No

Four institutes provided also information values on impurities in the sample (some in separate reports sent later). Determined mass fractions of the main two impurities (Table 9) detected, Pb and Rb are in fair agreement. The rubidium presence was expected, high lead content is surprising. If all cation impurities are assumed to be present as dichromates, the observed assay should be about 99.995% of the theoretical one, much higher than 99.93% observed. The impurity determination does not explain the lower assay compared to the theoretical value. The lower assay therefore could be due to the presence of water, dipotassium chromate (0.25%) or reduction products, i.e. Cr(III) present in the sample (0.06% dichromate decomposed). Another option (noted by NIST) would be the presence of K₂SO₄, as ICP-MS is insensitive to sulphur due to oxygen interference. These possibilities will be addressed by separate tests. Mass change on recommended drying was about 0.001%, mass change on further drying was smaller than 0.003%. At SMU, drying 2 h at temperature 350°C, 50°C below the melting point, yielded a mass loss of about 0.04%, unexpected due to the fact that the sample was ground before homogenisation. The assay of the sample dried at 350°C increased compared to the sample dried at 110°C, so the decomposition of dichromate was not the reason for mass change.

Further study on drying the material done at KRISS revealed a mass change about 0.03% on drying at 350 °C (Figure 3). It can be concluded that water accounts for at least one half of the decrease of the dichromate content.

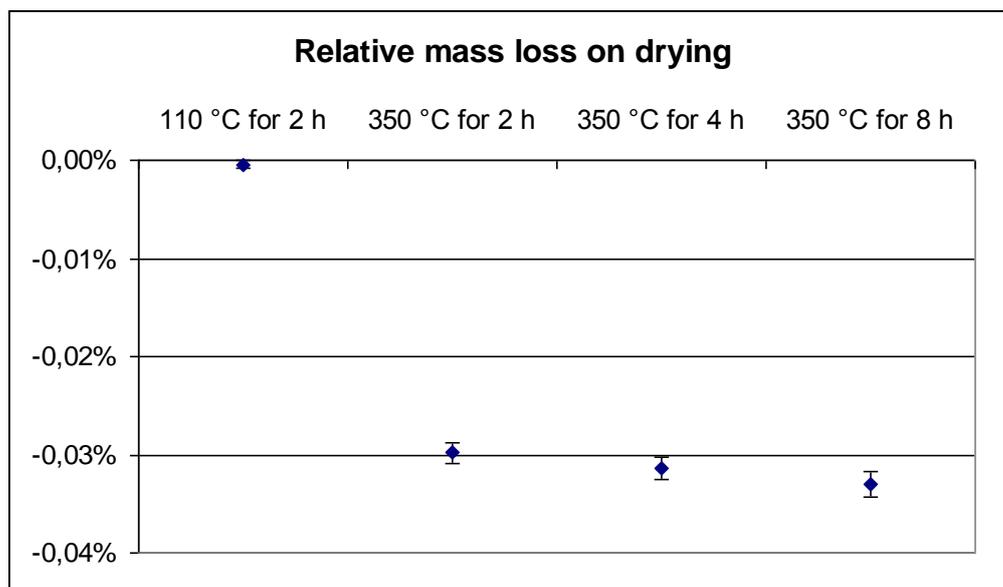


Figure 3 Mass changes of K96 samples when dried in alumina crucibles at different conditions. Standard deviations are also shown (three parallel samples).

Table 9 Impurities determined (in mg/kg)

Institute (method) Impurity	UNIIM (ICP-MS)	NIST (ICP-MS)	NIM (ICP-MS)	CENAM (ICP-SFMS)	Producer
Pb	46	65	23		60.8
Rb	25	24	40		32
Br	16				
Na	6.6		5.6		4.8
Al	2.1				0.4
Fe	2.08				
Sb	0.83	0.98	1		
V	0.72	6.2		0.511	
Nb	0.7				
Ba	0.42				0.3
Ca	0.1				3.2
Zn	0.1				0.3
Mn	0.037	0.67		0.046	0.2
Bi		0.071			
Mg					0.2
Ni					1.3
Sn					3.3
Ti					0.2
Cs					<4.2
Li					<1.6

7 SCOPE OF THE COMPARISON (HOW FAR THE LIGHT SHINES)

The comparison tested the capabilities and methods used for assay of high purity materials. For coulometric methods, good results will indicate good performance in assaying dichromate samples.

8 CONCLUSIONS

Good agreement between most participating laboratories for measurement of potassium dichromate was observed. Uncertainty weighted mean (with Birge treatment for uncertainty) of the results was agreed as the reference value (amount content of dichromate 3.397022 mol/kg, associated expanded uncertainty 0.00013 mol/kg). The spread of results (as relative standard deviation) is comparable to that in previous comparisons on solid materials – potassium hydrogen phthalate in CCQM-K34 [4] and potassium chloride in CCQM-K48 [5], much better than for hydrochloric acid solution in CCQM-K73 [6].

The comparison demonstrated again that the assay of compounds based only on “100% – impurities” concept must be used with caution.

9 REFERENCES

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CCQM-K96 Determination of amount content of dichromate

Technical protocol

Introduction

Key Comparison CCQM-K96 was launched to evaluate the degree of equivalence of national measurement procedures for the assay of potassium dichromate. The measurand is amount content of oxidants expressed as potassium dichromate, $\nu_{\text{K}_2\text{Cr}_2\text{O}_7}$. The nominal value of $\nu_{\text{K}_2\text{Cr}_2\text{O}_7}$ is $3.4 \text{ mol} \cdot \text{kg}^{-1}$.

The measurement procedure is left to the participant. Any method or combination of methods is acceptable. It is anticipated that the majority of participants will use coulometry or titrimetry.

Information on impurities, particularly vanadium and manganese, is also of interest. This information will be provided as an annex to the Key Comparison results.

Time schedule

Dispatch of the samples:	November 2011
Deadline for receipt of the report:	29 February 2012 or 3 months after receipt of samples, whichever is later
Distribution of Draft A for comments:	March 2012
Draft A discussion:	IAWG meeting in April 2012
Draft B report	June 2012

Samples

Each participant will receive one numbered bottle containing about 25 g of material. Shipment to all participants will be performed at the same time. The bottles are shipped in a cardboard box by courier and the airwaybill/consignment number¹ is reported by email to the contact person of the receiving laboratory for tracking purposes. The contents will be marked “potassium dichromate” for research purposes and value 1 USD; please be attentive of possible customs delays, etc. The measurement protocol is sent by e-mail.

The homogeneity of the sample material was measured based on assay using sample size of about 500 mg and found to be adequate for the key comparison.

Actions at receipt of samples

¹ airwaybill/consignment number, the carrier identification of the shipment allowing detailed tracking of the shipment. If you have not received the shipment within 3 days of our notice, please use the tracking facility to monitor whether your shipment is being held up in customs or similar.

Please inspect the received bottles for damage. Please inform the contact person of receipt and report any mishaps to the coordinating laboratory. The sample should be stored at laboratory temperature in the original container until used.

Sample preparation for measurement

The material should be dried at 110°C for 2 h without crushing or grinding the material.

Measurement method

Any method or method combination can be used for this comparison, but it is assumed that most participants will use coulometry or titrimetry. The results will be reported as amount content [mol/kg] of potassium dichromate and its standard uncertainty, to be accompanied by a full uncertainty budget. Information on the assay dependence on sample mass is also welcome. At least five determinations should be performed (where applicable).

Indirect methods must take into account the dependence of the assay on the Cr/K (or other metals) ratio and the water content.

Reporting

The report should be sent to the coordinating laboratory **before February 29, 2012**, preferentially by e-mail. **This deadline will however be extended on individual basis so that all participants are granted a measurement and reporting period of three months from sample receipt.** The coordinator will confirm the receipt of each report. If the confirmation does not arrive within one week, contact the coordinator to identify the problem.

A template for the report will be enclosed (Excel sheet). If possible the requested data should be entered into the corresponding boxes, if not the format can be modified or the data can be reported in another form.

Information requested:

1. Report the results as amount content [mol/kg] of potassium dichromate, accompanied by a full uncertainty budget. Information on impurities is welcome also from participants not using (100% - impurities) approach.
2. If the assay is determined from impurity analysis, results for all the elements/compounds sought must be included.
3. A detailed description of the measurement procedure is to be given (for coulometry this should include also: cell description, volume of electrolyte in working chamber, endpoint evaluation procedure, example titration curve for initial and final titration), and of the equipment used.
4. The complete measurement equation has to be given, as well as the values of the constants used and variables (raw data) for at least one measurement. The data should enable the recalculation of the result of this measurement.
5. State all the individual results, not only the final mean value.
6. The uncertainty budget has to include instrumental sources of uncertainty (mass, time, voltage, volume, ...) as well as chemical ones (endpoint estimation, equilibria, O₂ interference, impurities, purity of calibration standards, ...). The uncertainty calculations should conform to the ISO document: Guide to the expression of Uncertainty in Measurement (1995) 1st ed., ISO, Geneva. Both Type A and Type B uncertainty components and a summary of how they are calculated have to be included.

7. In order to facilitate comparisons of your measured masses (for assay measurements), please also provide either (1) the air density used for each buoyancy correction, or (2) the air temperature, humidity and pressure in your laboratory at the time of each mass measurement.
8. Report the details of the procedure used (a separate text file can be used).

Reference value

The reference value will be agreed upon on the next joint meeting of the EAWG and IAWG.

Participation

Participation is open to all institutes eligible for a key comparison in this field.

The Draft A Report, based on the reported results will be prepared and sent to the participants for comments and will be discussed at the meetings of CCQM Working Groups on Electrochemical Analysis and on Inorganic Analysis. The individual reports will also be distributed among the participants.

Coordinating laboratory and contact person

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