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**Key comparison CCQM-K96.1**  
**Determination of amount content of**  
**dichromate**  
**Final report**

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**Daejeon, 2 July 2015**

## **Abstract**

The CCQM-K96.1 key comparison was a subsequent bilateral comparison to the CCQM-K96 “Determination of amount content of dichromate.” The comparisons were organized jointly by the inorganic analysis and electrochemical analysis working groups of the CCQM to test the abilities of the metrology institutes to measure the amount content of dichromate. The NIM China has obtained unsatisfactory results from the CCQM-K96. The NIM requested a bilateral comparison to demonstrate its capability after improvement. The KRISS acted as the coordinating laboratory and served as a link to the reference value of CCQM-K96. Both participants used high-accuracy constant current coulometry. Good agreement of the results was observed.

## 1 INTRODUCTION

A subsequent bilateral key comparison “Determination of amount content of dichromate” was proposed at the EAWG meeting in April 2013 as a follow-up of the CCQM-K96[1], where the result from the National Institute of Metrology (NIM) of China was not equivalent with other participants’ results and NIM result was not used in the calculation of reference values.

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. NIM therefore requested a bilateral comparison with KRISS, one of the coordination laboratories of CCQM-K96, to confirm its measurement capability. At the 19th meeting of the CCQM in April 2013 the bilateral comparison was agreed as a subsequent comparison of the CCQM-K96 with the KC code of CCQM-K96.1.

The scope of the comparison is the same as in CCQM-K96. The comparison demonstrated the capabilities and methods to determine the amount content of oxidants expressed as potassium dichromate in a sample of pure potassium dichromate. Both participants used high-accuracy constant current coulometry.

## 2 LIST OF PARTICIPANTS

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

Table 1. List of participants

<b>Institution</b>	<b>Country</b>	<b>Contact person</b>
<b>KRISS</b> Korea Research Institute of Standards and Science	Korea	HWANG Euijin
<b>NIM</b> National Institute of Metrology of P. R. China	China	MA Liandi

## 3 SAMPLES

Sample preparation and homogeneity test have been done by NIM. 60 g of highly pure commercial material were ground into fine powders in an agate mortar and bottled in four glass bottles. Each bottle contained about 15 g of powders was sealed in a Mylar bag. The homogeneity of the sample material was measured based on assay by coulometry using sample size of about 200 mg. The between-bottle standard deviation (which includes contribution from measurement repeatability) was 0.0048 %. The result indicates that the homogeneity is adequate for the comparison.

KRISS received a bottle of sample containing about 15 g of material in July 2013. The sample was stored at laboratory temperature in the original container until used.

The deadline for reporting results was set to 28 February 2014. Both participants reported their results in time.

Table 2. Sample receipt and result report dates

<b>Institute</b>	<b>Sample receipt date</b>	<b>Date report sent</b>
<b>KRISS</b>	16 July 2013	26 February 2014
<b>NIM</b>	-	28 February 2014

## 4 INSTRUCTIONS TO PARTICIPANTS

The instructions sent to the participant 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.

## 5 METHODS OF MEASUREMENT

All participants used constant current coulometric titration. Some details on measurements as derived from the reports are given in Tables 3 and 4.

Table 3. Details on measurement methods used

<b>Institute</b>	<b>Indication</b>	<b>EP estimation</b>	<b>Major uncertainty sources</b>	<b>Their contribution</b>
<b>KRISS</b>	Amperometry, 0.85 V vs. SCE	Linear regression, x-intercept	Reproducibility	95 %
<b>NIM</b>	Amperometry, 0.85 V vs. SCE	Linear regression, x-intercept	Repeatability, end-point	91 %

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 <sup>2</sup> )	Sample added before main titration
KRISS	0.5	horizontal, 2 inter-compartment	120	102	1.1*	No
NIM	0.2	horizontal, 2 inter-compartment	150	102	6.5	No

\* without stirring

All coulometric titrations followed the same procedure and used the same electrolytes.

## 6 RESULTS AND DISCUSSION

The reported values and uncertainties are summarized in Table 5 and also displayed graphically in Figure 1. Mass fractions were derived by using the molar mass of potassium dichromate as 294.1846 g/mol.

Table 5. Measurement results with amount contents, mass fractions, relative standard deviations, relative combined standard uncertainties and numbers of measurements

NMI	Measurement date	Amount content /(mol kg <sup>-1</sup> )	Mass fraction	RSD	$u_{c,r}$	$n$
KRISS	21-28 January 2014	3.399041	99.9946 %	0.0005 %	0.0016 %	6
NIM	2 July 2013, 15-17 January 2014	3.39893	99.9912 %	0.0034 %	0.0024 %	8

## 7 DEGREE OF EQUIVALENCE

KRISS result was used as a link to KCRV from CCQM-K96. Relative difference between two KRISS results from CCQM-K96 and CCQM-K96.1 was around 0.06 %, so the degrees of equivalence are directly comparable.

The degree of equivalence (DoE) for the participant (NIM) result ( $D_{NIM}$ ) was calculated with the DoE of the coordinator (KRISS) resulted in CCQM-K96 ( $D_{KRISS(K96)}$ ) and difference between the results of both the participant ( $v_{NIM(K96.1)}$ ) and the coordinator ( $v_{KRISS(K96.1)}$ ) as expressed in the

equation below. The expanded uncertainty of DoE of the NIM ( $U_{D_{NIM}}$ ) was also calculated by combining the reported standard uncertainties of the NIM ( $u_{NIM(K96.1)}$ ) and the KRISS ( $u_{KRISS(K96.1)}$ ) with the uncertainty of the KCRV of CCQM-K96 ( $u_{KCRV(K96)}$ ).

$$D_{NIM} = D_{KRISS(K96)} + (v_{NIM(K96.1)} - v_{KRISS(K96.1)})$$

$$U_{D_{NIM}} = 2 \cdot \sqrt{u_{KRISS(K96.1)}^2 + u_{NIM(K96.1)}^2 + u_{KCRV(K96)}^2}$$

The DoE of KRISS in CCQM-K96 ( $D_{KRISS(K96)}$ ) was 0.0035 % and the standard uncertainty of KCRV in CCQM-K96 ( $u_{KCRV(K96)}$ ) was 0.0019 %.[1] The DoE relative to the KCRV of CCQM-K96 is given in Table 6 and shown graphically in Figure 2 with the DoEs from the original key comparison CCQM-K96.

Table 6. Degree of equivalence in CCQM-K96.1

NMI	$D_i$	$U_{D_i}$
NIM	0.0002 %	0.0069 %

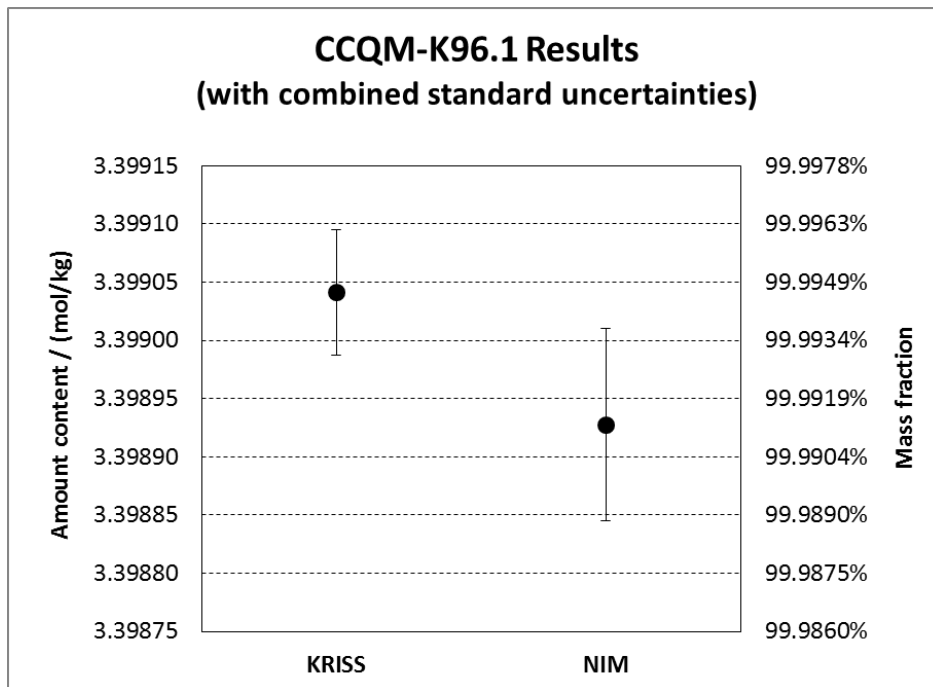


Figure 1. Results of CCQM-K96.1. Error bars denote the combined standard uncertainties.

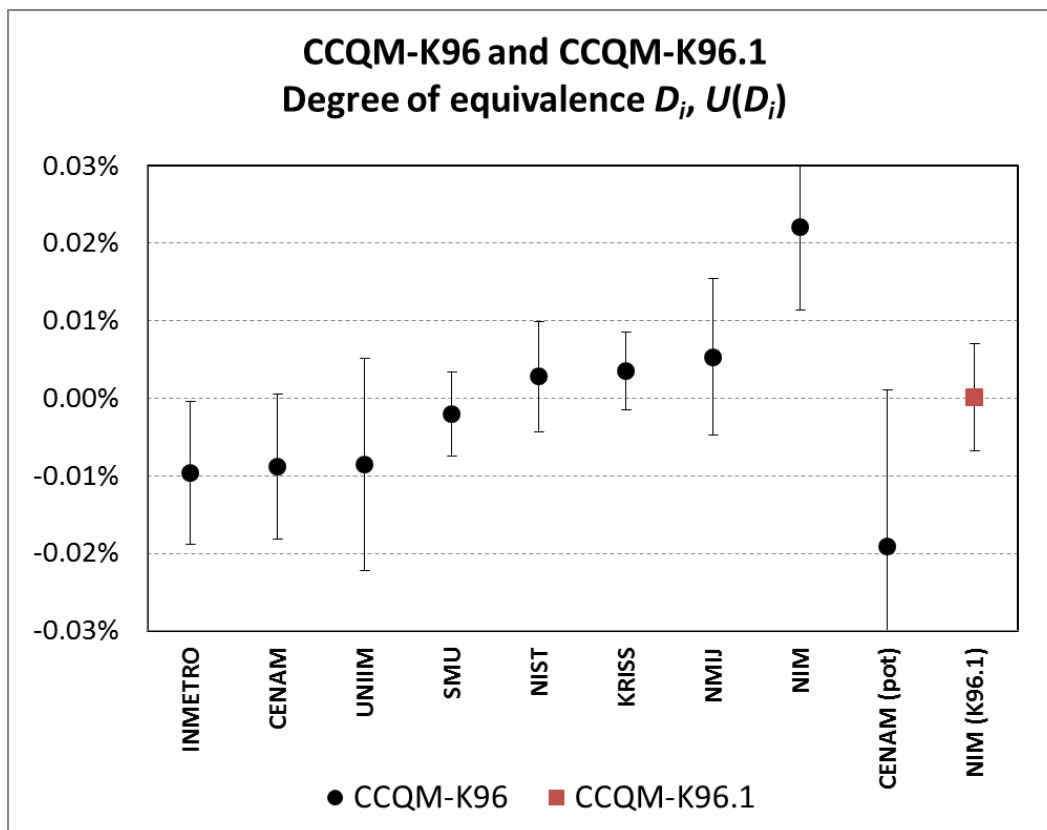


Figure 2. Degree of equivalence in CCQM-K96.1 linked to the results of CCQM-K96. Error bars denote expanded uncertainties with a coverage factor  $k=2$ .

Study on drying at higher temperature was performed as done in CCQM-K96. Relative mass loss of CCQM-K96.1 sample after drying at 350 °C for four hours was only 0.004 %. In CCQM-K96 the relative mass loss was 0.03 %. These results can support the conclusion of mass loss in CCQM-K96 in which water has been assumed as the main impurity of the sample.

## 8 SCOPE OF THE COMPARISON (HOW FAR THE LIGHT SHINES)

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

## 9 CONCLUSION

The results of the subsequent bilateral comparison, CCQM-K96.1, confirmed good performance of the NIM. The KRISS provided the necessary link to CCQM-K96 for the calculation of NIM's degree of equivalence.

## REFERENCES

- [1] Máriássy M.; Hanková Z.; Hwang E.; Lim Y.; Pratt K. W.; Hioki A.; Asakai T.; Wu B.; Ma L.; Wei C.; Sobina A.; Shimolin A.; Junior W. B. S.; Borges P. P.; Matehuala F. J.; Segoviano F.; Rivera G.; Ramírez P.; Arvizu M. R.; Ortiz-Aparicio J. L.; Final report on key comparison CCQM-K96: Determination of amount content of dichromate, *Metrologia*, **50**, Tech. Suppl., 08012 (2013). The final report is available from [http://www.bipm.org/utils/common/pdf/final\\_reports/QM/K96/CCQM-K96.pdf](http://www.bipm.org/utils/common/pdf/final_reports/QM/K96/CCQM-K96.pdf)
- [2] JCGM, Evaluation of measurement data – Guide to the expression of uncertainty in measurement. JCGM 100:2008, [http://www.bipm.org/utils/common/documents/jcgm/JCGM\\_100\\_2008\\_E.pdf](http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf)



## Appendix A – Technical Protocol



### **CCQM-K96.1 Determination of amount content of dichromate Subsequent bilateral comparison of CCQM-K96**

#### **Technical protocol**

##### **Introduction**

Key Comparison CCQM-K96 “Determination of amount content of dichromate” has been performed to evaluate the degree of equivalence of national measurement procedures for the assay of potassium dichromate. The measurand was amount content of oxidants expressed as potassium dichromate,  $\nu_{\text{K}_2\text{Cr}_2\text{O}_7}$ .

The results of CCQM-K96 showed the result from National Metrology Institute (NIM) of China was not equivalent and NIM result was not used in the calculation of reference values. 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. NIM asked a bilateral comparison with KRIS, one of the coordination laboratories of CCQM-K96. At the 19th meeting of CCQM in April 2013 the bilateral comparison was agreed as the subsequent comparison of CCQM-K96 with the KC code of CCQM-K96.1.

##### **Time schedule**

Dispatch of the samples:	July 2013
<b>Deadline for receipt of the report:</b>	<b>28 February 2014</b>
Distribution of Draft A for comments:	March 2014
Draft A discussion:	IAWG/EAWG meeting in April 2014
Draft B report:	July 2014

##### **Samples**

Sample preparation and homogeneity test have been done by NIM. KRIS received a bottle of sample containing about 15 g of material in July 2013. The homogeneity of the sample material was measured based on assay using sample size of about 200 mg and found to be adequate for the key comparison. 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

All participants will use coulometry. 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. At least five determinations should be performed (where applicable).

## Reporting

The report should be sent to the coordinating laboratory **by February 28, 2014**, preferentially by e-mail. The coordinator will confirm the receipt of the 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. A detailed description of the measurement procedure is to be given including cell description, volume of electrolyte in working chamber, endpoint evaluation procedure, example titration curves for initial and final titration and equipment used.
3. 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.
4. State all the individual results, not only the final mean value.
5. The uncertainty budget has to include instrumental sources of uncertainty (mass, time, voltage, volume, ...) as well as chemical ones (endpoint estimation, equilibria, O<sub>2</sub> interference, impurities, ...). 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.
6. In order to facilitate comparisons of your measured masses, please also provide either (1) the air density used for each buoyancy correction, or (2) the air temperature, humidity and pressure in your laboratory at the time of each mass measurement.
7. Report the details of the procedure used (a separate text file can be used).

**Link to CCQM-K96**

Degree of equivalence (DoE) of the participant ( $D_{\text{NIM}}$ ) will be calculated with the DoE of the coordinator resulted in CCQM-K96 ( $D_{\text{KRISS(K96)}}$ ) and difference between the results of both the participant ( $v_{\text{NIM(K96.1)}}$ ) and the coordinator ( $v_{\text{KRISS(K96.1)}}$ ) as expressed in the equation below. The expanded uncertainty of DoE of the participant ( $U_{\text{DNIM}}$ ) will be also calculated by combining the reported standard uncertainties of the participants ( $u_{\text{NIM(K96.1)}}^2$ ) and the coordinator ( $u_{\text{KRISS(K96.1)}}^2$ ) with the uncertainty of the KCRV of CCQM-K96.

$$D_{\text{NIM}} = D_{\text{KRISS(K96)}} + (v_{\text{NIM(K96.1)}} - v_{\text{KRISS(K96.1)}})$$
$$U_{\text{DNIM}} = 2 \cdot \sqrt{u_{\text{KRISS(K96.1)}}^2 + u_{\text{NIM(K96.1)}}^2 + u_{\text{KCRV(K96)}}^2}$$

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

### **Coordinating laboratory and contact person**

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