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CCQM-K24 key comparison Cadmium amount content in rice

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Final Report

Contains measurement contributions from:

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L. Mackay and R. Hearn from NARL
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Abstract

The CCQM-K24 was performed without a pilot study prior to the key comparison in order to demonstrate and document the capability of interested National Metrology Institutes to measure the Cd amount content in a rice sample. The comparison was an activity of the Inorganic Analysis Working Group of CCQM and was piloted by the Institute for Reference Materials and Measurements (IRMM, Geel, Belgium) of the European Commission.

All participants applied isotope dilution mass spectrometry (IDMS) using thermal ionisation MS (TIMS), sector field or quadrupole inductively coupled plasma MS (ICP-MS) as analytical technique.
NIST reported a combined result of IDMS and instrumental neutron activation analysis (INAA) for the Cd amount content in the rice.

The following laboratories participated in this key comparison (alphabetical order).

BAM (Germany)
CSIR-NML (South Africa)
EMPA (Switzerland)
IRMM (European Union)
KRISS (South Korea)
LGC (United Kingdom)
NARL (Australia)
NIST (United States of America)
NMi (The Netherlands)
NMIJ (Japan)
NRC (Canada)
NRCCRM (China)

Very good agreement of reported results was observed. The Key Comparison Reference Value (KCRV) was agreed upon during the IAWG meeting in April 2002 at BIPM in Paris as the arithmetic mean of the reported participants' results. Accordingly the equivalence statements were calculated.

1. Introduction

In April 2000 it was agreed to organise a CCQM P29 pilot study *Cd in rice* as jointly proposed by IRMM and NMIJ. At the Inorganic Analysis Working Group meeting in Paris, 2-6 April 2001, it was agreed to split the CCQM P29 into two parallel comparisons. These were a key comparison for *Cd in rice* CCQM K24 and a pilot study CCQM P29 for *Cd and Zn in rice*. Participants who were confident that their measurement capability is appropriate wanting to take part in the key comparison needed to register formally prior to reporting of results. This key comparison (CCQM-K24) is an activity of the "Inorganic Analysis Working Group" of the CCQM.

The same samples measured by the CCQM-K24 participants were also used for the CCQM-P29 pilot study and the EUROMET project 565. Field laboratories will also measure these samples in the framework of IMEP-19.

2. Rationale of this comparison

Rice seems to be the oldest cereal cultivated. It is the main foodstuff for about half of the world's population. The vast majority of the world's rice is grown and consumed in Asia. In Latin America and Africa rice is also among the major nutrients. For the last decades rice consumption has been expanding beyond the traditional rice-grown areas, particularly in Europe. In order to protect public health it is essential to keep contaminants at levels, which are toxicologically acceptable, thus surveillance measures were taken regarding the presence of contaminants in foodstuff, including rice.

Cadmium may induce dysfunctions and reproductive deficiencies in humans and is suspected to act as a human carcinogen. Therefore Cd maximum levels in foodstuff, which is the main source of human intake of Cd, are set in relevant regulation [1, 2].

3. Participation in CCQM-K24

Registered participants in CCQM-K24, as entered into the KCDB database are listed in Table 1.

Table 1. CCQM-K24 participants

institution / organisation	origin
BAM Bundesanstalt für Materialforschung und –Prüfung, Berlin	**Germany**
CSIR-NML National Metrology Laboratory	**South Africa**
***EMPA** Eidgenössische Materialprüfungs-und Forschungsanstalt	**Switzerland**
IRMM Institute for Reference Materials and Measurements	**European Union**
KRISS Korean Research Institute of Standards and Science	**South Korea**
LGC Laboratory of the Government Chemist	**United Kingdom**
NARL National Analytical Reference Laboratory	**Australia**
NIST National Institute of Standards and Technology	**United States of America**
NMi Nederlands Meetinstituut	**The Netherlands**
NMIJ National Metrology Institute of Japan	**Japan**
NRC National Research Council of Canada	**Canada**
NRCCRM National Research Centre for Certified Reference Material	**China**

* Although not registered prior to result reporting, it was decided at the CCQM meeting in April 2002, BIPM, Paris, that EMPA was admitted to participate in the CCQM-K24

4. Sample

The CCQM-K24 sample is a fine rice powder bottled in glass containers each one containing ~ 15 g of material. The rice powder originates from rice grown in Cd contaminated water. It was provided by NMIJ in glass containers, filled with 60g rice each. At IRMM the rice was reprocessed into smaller units (15g each).

Within-bottle homogeneity tests were carried out on 20 sub-samples of 8 bottles using solid sample Zeemann Atomic Absorption Spectrometry (SS-ZAAS). Between bottle homogeneity tests were performed applying IDMS by analysing 2 sub-samples from 5 bottles. Results from both measurements were evaluated accordingly and compared to procedures established in ISO 35 used for the certification of reference materials and based on analysis of variance ANOVA [3, 4]. No significant difference was observed.

The samples and information/instructions documents were made available to CCQM-K24 participants during the month of June 2001. The deadline for reporting of results and uncertainties was 30th November 2001.

5. Instructions to the participants

The CCQM-K24 samples with the information documents were sent to all participants who had expressed their interest in participating in the previously agreed CCQM-P29 *Cd in rice* study. In addition, a letter stressing the two different "natures" of the pilot study and the key comparison and a registration sheet for the key comparison CCQM-K24 was enclosed. Only participants who sent a signed "declaration for participation in the CCQM-K24, Cd in rice" to IRMM prior to result reporting were considered as participants in the CCQM-K24 key comparison. Participants who did not send this registration sheet to IRMM were considered as participants in the pilot study CCQM-P29. After the CCQM-IAWG meeting in Geel, 22-23 October 2001, a reminder was sent to participants who had not registered until that date. The final list of registered CCQM K24 participants was forwarded to R. Wielgosz from BIPM and entered into the KCDB database on 15th November 2001.
EMPA submitted a request to the pilot laboratory to participate in CCQM-K24 instead of CCQM-P29 before the results of the key comparison or the study were made public to the participants. Although not registered prior to result reporting, it was decided at the CCQM meeting in April 2002, BIPM, Paris, that EMPA was admitted to participate in the CCQM-K24 comparison.

List of documents sent to the CCQM-K24 participants (see Annex E).

I. Letter to the participants (1 page)
II. Declaration for participation in the CCQM-K24, Cd in rice (1 page)

III. Content of information package:

1. accompanying letter (1 page)
2. scope of the study (1 page)
3. general instructions (1 page)
4. instructions for determination of the dry-mass correction and the digestion of the rice (1 page)
5. instructions for uncertainty evaluation (1 page)
6. proposed uncertainty budget forms for Cd (1 page)
7. results report form (1 page)
8. questionnaire (1 page)

IV. Communicated via email to all the CCQM-K24 participants in November 2001:

a) Summary of conclusions of the Seminar on 'Reporting and Estimating Uncertainty for CCQM studies and key comparisons'. Proposal that can form a guidance document for CCQM-IAWG work
b) Check-list on reporting uncertainty

5.1. Instructions for determination of dry-mass correction

The determination of the moisture content of the samples is to some extent "operationally defined" [5, 6]. When the CCQM-K24 comparison was launched it was not clear to which extent this would be the case for the rice sample. In view of the comparability of the results a protocol for correction of the moisture was prescribed to the CCQM-K24 participants.

The moisture content determination was a challenging task for the participants, to be performed for the first time in the scope of a key comparison on a food matrix. Not all the participants could strictly follow the prescribed protocol for dry-mass correction. The different approaches of the CCQM-K24 participants to determine the moisture content in the rice were discussed at the IAWG meeting in April 2002 in Paris. This topic is summarised and discussed in more detail in Annex C of this final report.

In retrospect looking at the reported measurement results for Cd, the original concerns about the "non-comparability" of measurement results were not fully justified.

5.2. Instruction for reporting of results and uncertainty

During the IAWG meeting in October 2001 in Geel agreements for reporting and estimating uncertainty for CCQM studies and key comparisons were made. They were summarised in a memorandum that was passed on to all participants after this meeting. A check-list was sent to all CCQM-K24 and CCQM-P29 participants in order to help them to comply with the changes in reporting uncertainties compared to previous comparisons (see below). It was emphasised that the "instruction for uncertainty evaluation for CCQM-K24" as enclosed in the information package was meant to be as an example that participants can adapt to their own needs. Below there is a short summary for CCQM-K24 according to the topics on the checklist. Most of the participants responded to this request, sending back detailed result reports adapted to their measurement procedures.

1. *Do not report hand-written results and uncertainties*

   Two participants (NARL and NMi) reported hand-written results

2. *State your measurement equation*

   All participants, except one (EMPA), reported either their measurement equations or referred to the equation as given in the information package.

3. *State your input quantities*

   All participants reported input quantities. In some cases not all of the input quantities as given in the measurement equation were defined.

4. *Include factors related to sample treatment in your measurement equations*

   There was one participant (NRCCRM) who did not explicitly state a factor for dry mass correction in the equation. All except two participants (EMPA, NRCCRM) included a factor for the digestion procedure or a factor related to sample preparation.

5. *Describe the applied evaluation process and type of assumed distribution for your uncertainty estimation*

   Only 2 participants (IRMM and NARL) stated the applied evaluation process and also added the assumed distribution for the evaluation of each parameter in their uncertainty budget. The majority (8 participants) stated the applied evaluation process (type A or type B uncertainty). One participant (BAM) reported the assumed distribution for the evaluation of the uncertainty of each input quantity, but not the applied evaluation process. One participant (LGC) neither stated the evaluation process nor the type of assumed distribution.

6. Methods and instrumentation used

All CCQM-K24 participants applied isotope dilution. The instrumentation used by all participants was based on mass spectrometry (MS). Two participants (BAM and NRCCRM) used thermal ionisation MS (TIMS), five participants (CSIR-NML, KRISS, LGC, NARL and NMi) used ICP-magnetic sector field MS and three participants (IRMM, NIST and NRC) used ICP-QMS. EMPA used multi-collector ICP-MS. NMIJ applied ICP-QMS in the collision mode using He as collision gas. NIST reported a combined result of IDMS and INAA as result for the Cd amount content in the rice.

Table 2 gives an overview of the method applied and the instrumentation used by each CCQM-K24 participant.

Table 2. Analytical methods and instrumental techniques used by CCQM-K24 participants.

participant	***method***	***instrumentation***
BAM	IDMS	Multi collector TIMS
CSIR	IDMS	ICP-magnetic sector field MS
EMPA	IDMS	Multi collector ICP-MS
IRMM	IDMS	ICP-QMS
KRISS	IDMS	ICP-magnetic sector field MS
LGC	IDMS	ICP-magnetic sector field MS
NARL	IDMS	ICP-magnetic sector field MS
NIST	IDMS and NAA*	ICP-QMS and INAA
NMi	IDMS	ICP-magnetic sector field MS
NMIJ	IDMS	ICP-QMS, collision cell
NRC	IDMS	ICP-QMS
NRCCRM	IDMS	Multi-collector TIMS

* NIST reported a combined result of IDMS and INAA.

7. CCQM-K24 participants' results

The CCQM-K24 participants' results, as reported to the pilot institute (IRMM), are given in Table 3. All uncertainties given are expanded uncertainties. The coverage factors given was k=2. KRISS and NARL reported a result for Cd with a coverage factor k=1.97. EMPA reported a result for Cd with combined uncertainty u_c.

Table 3. CCQM-K24 participants' measurement results for Cadmium

participant	***reported result nmol·g⁻¹***	***expanded uncertainty (k=2) nmol·g⁻¹***	***relative uncertainty (%)***
BAM	**14.440**	**0.055**	**0.4**
CSIR	**14.76**	**0.15**	**1.0**
***EMPA**	**14.30**	**0.21**	**1.5**
IRMM	**14.46**	**0.22**	**1.5**
****KRISS**	**14.20**	**0.21**	**1.5**
LGC	**14.30**	**0.13**	**0.9**
****NARL**	**14.37**	**0.24**	**1.7**
NIST	**14.36**	**0.23**	**1.6**
NMi	**14.43**	**0.26**	**1.8**
NMIJ	**14.30**	**0.39**	**2.7**
NRC	**14.56**	**0.33**	**2.3**
NRCCRM	**14.53**	**0.15**	**1.0**

* EMPA reported a result with combined uncertainty u_c.

** KRISS and NARL reported a Cd result with a coverage factor k=1.97.

8. Agreement on the KCRV

As known from BIPM and from previous key comparisons there is no rule as to the choice of average in the calculation of the KCRV. This is left to the discretion of the CCQM working groups. The KCRV for CCQM K-24 was discussed and agreed upon during the CCQM-IAWG meeting on 15th April in Paris.

As can be seen from Table 4 there were no significant differences between the three values. In principle, each value could serve as the KCRV because the agreement of results for CCQM-K24 was very good. To use the median as KCRV would be recommended if there were results reported with significant lower or higher amount content compared to the other results of the participants, which was not the case for CCQM-K24. The weighted mean is applicable for independent normal distributed results of the same population. To apply the weighted mean, there has to be an agreement on the exact calculation of uncertainty for CCQM-K24, in other words, the participants have to agree on each reported uncertainty of

the Cd amount content. Although the participants followed "guidance instructions" for reporting uncertainties, which resulted in more transparent uncertainty budgets, this might be difficult to achieve.
Finally, the arithmetic mean as the average of all the results was agreed upon to serve as the KCRV for the CCQM-K24.

Table 4. Comparison of the approaches to calculate the KCRV for CCQM-K24

	CCQM-K24 KCRV nmol·g^{-1} uncertainty (k=2)
Mean*	**14.418 ± 0.087**
Median**	14.400 ± 0.086
Weighted Mean***	14.442 ± 0.081

*uncertainty of the mean estimated as stdev. of the mean
**uncertainty of the median was estimated applying "robust statistics" [7]
***uncertainty of the weighted mean estimated as stdev. of the weighted mean

9. Graphical display results and KCRV

The results of the participants are graphically displayed together with the KCRV and its uncertainty in the Annex A of this report.

10. Equivalence statements

The equivalence statements are calculated according to the BIPM guidelines. The degree of equivalence (and its uncertainty) between a NMI result and the KCRV is calculated according to the following equations:

$$D_i = (x_i - x_R) \qquad U_i^2 = 2^2(u_i^2 + u_R^2)$$

where D_i is the degree of equivalence between the NMI result x_i and the KCRV x_R and U_i is the expanded uncertainty (k=2) of the D_i calculated by the combined uncertainty (k=1) of the NMI result u_i and the uncertainty (k=1) of the KCRV u_R.
The equivalence statement of the CCQM-K24 and the relevant graphical display are presented in the Annex B of this report, together with the relevant graphical display.

At the CCQM meeting on 15th April in Paris it was decided that the matrix representing the degree of equivalence between two NMI results is not a part of a final key-comparison report anymore.
The degree of equivalence (and its uncertainty) between two NMI results is calculated **on request only**, according to the following equations:

$$U_{ij}^2 = 2^2(u_i^2 + u_j^2)$$

$$D_{ij} = (x_i - x_j)$$

where D_{ij} is the degree of equivalence between the NMI results x_i and x_j and U_{ij} is the expanded uncertainty (k=2) of the D_{ij} calculated by the combined uncertainty (k=1) of the NMI results u_i and u_j.

11. Discussion

The key comparison CCQM-K24 Cd in rice dealt for the first time with a food matrix. The sample treatment is complex, including acid digestion, which can result in losses and higher blank values. Furthermore the measurement of the moisture content of the rice was a "challenging task" and an additional source of uncertainty. The CCQM-K24 protocol for dry-mass correction emphasised the fact that corrections for moisture content and hygroscopic effects, if not correctly applied and implemented in the overall uncertainty budget, have a major impact on the result of an amount content measurement and it's comparability when analysing a food matrix. In case of this rice material it could be proven by means of thorough studies of the properties of the rice that the reported results for the Cd amount content in CCQM-K24 are comparable, despite the differences in the applied methods for dry-mass correction.

The performance of participants in the CCQM-K24 was extremely good. CCQM-K24 is going to be used for documentation of measurement capability in view of the CIPM MRA. The Key Comparison Reference Value (KCRV) and based on this the calculated equivalence statements will be placed in the Appendix B of the MRA after approval by CCQM.

12. Acknowledgement

The work described here contains the contributions of many scientists: J. Vogl and M. Ostermann from BAM, A. Barzev from CSIR-NML, S. Wunderli from EMPA, E. Vassileva and C. Quétel from IRMM, E. Hwang from KRISS, P. Evans and C. Wolff-Briche from LGC, L. Mackay and R. Hearn from NARL, K. Okamoto and K. Inagaki from NMIJ, R. Greenberg, K. Murphy and R. Zeisler from NIST, M. van Son from NMi, R. Sturgeon and L. Yang from NRC, W. Jun and Z. Motian from NRCCRM.
Special thanks is ought to all colleagues at IRMM who contributed to this study: K-H. Grobecker, U. Wätjen, A. Bernreuther, P. Robouch, J. Pauwels, G. Kramer, S. Kuxenko, P. Smeyers, M. De Smet, C. Harper and L. Van Nevel. The pilot laboratory acknowledges in particular the efforts of K. Okamoto (NMIJ) for supplying the samples and of M. Sargent (LGC) for his assistance as chairman of the Inorganic Analysis WG of CCQM.

13. References

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CCQM-K24
Cd in rice

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Annex A

Graphical display of CCQM-K24 results and the KCRV

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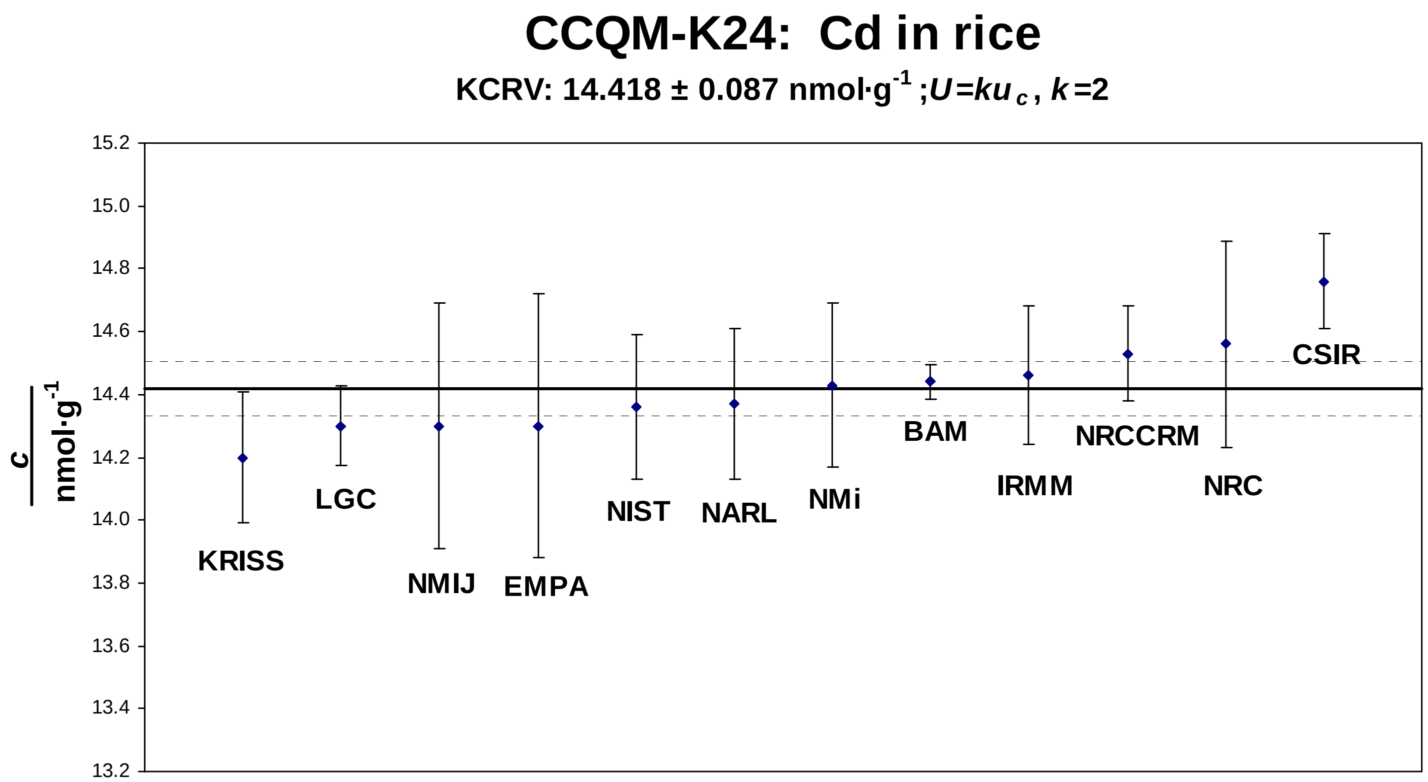
Graphical display of CCQM-K24 results



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Annex B

Equivalence Statement

- equivalence statements for Cd measurement
- graphical display of equivalence statement

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Equivalence statements for Cd measurement

MEASURAND : **amount content of Cd in rice**
NOMINAL VALUE: **~ 10 nmol·g^{-1}**

Key comparison reference value (KCRV) x_R = **14.418** **nmol·g^{-1}**

Standard uncertainty of KCRV u_R = **0.043** **nmol·g^{-1}**

The KCRV was calculated as the arithmetic mean of all results

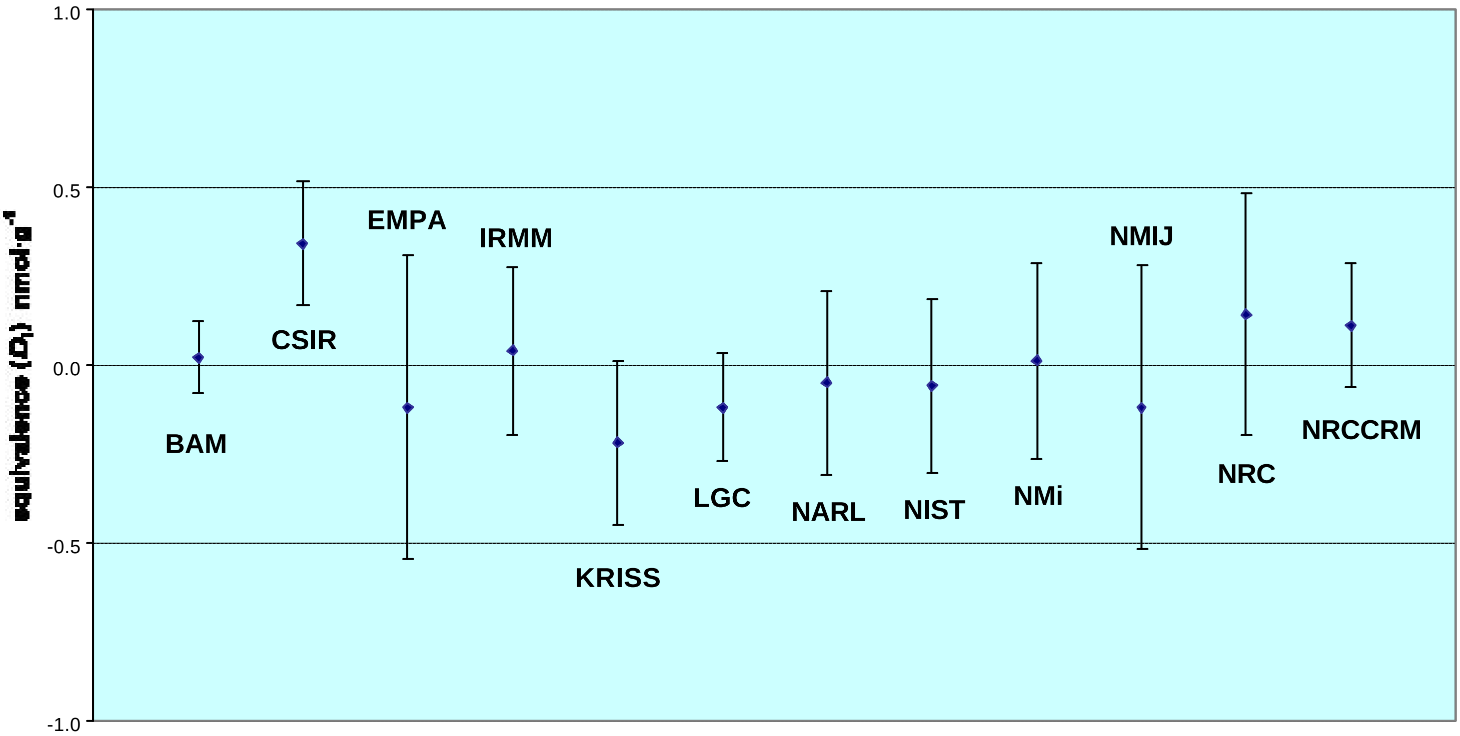
The standard uncertainty of the KCRV was calculated as the standard deviation of the mean

The degree of equivalence of each laboratory with respect to the KCRV is given by a pair of numbers:
$D_i = (x_i - x_R)$ **and** U_i**, its expanded uncertainty (*k* = 2),**
$U_i^2 = 2^2(u_i^2 + u_R^2)$**, both expressed in nmol·g^{-1}**

Lab *i*	D_i	U_i
	nmol·g^{-1}	
BAM	0.02	0.10
CSIR	0.34	0.17
EMPA	-0.12	0.43
IRMM	0.04	0.24
KRISS	-0.22	0.23
LGC	-0.12	0.15
NARL	-0.05	0.26
NIST	-0.06	0.25
NMi	0.01	0.27
NMIJ	-0.12	0.40
NRC	0.14	0.34
NRCCRM	0.11	0.17

Graphical display of equivalence statement

CCQM-K24 key comparison Cd in rice; *U=ku c, k=2*



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Annex C

Dry-mass correction

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Instructions for determination of dry-mass correction

Following the protocol for “dry-mass correction”, the rice sample should be equilibrated with ambient conditions (successive weights should not differ more than 0.001 g). Any kind of contamination during this process had to be avoided. The Cd measurements had to be performed on a sub-sample of this “equilibrated” rice material. A separate portion of this “equilibrated” material, of minimum mass of 1 g, should be used for the “dry-mass correction”.

Some CCQM-K24 participants, although they agreed that participants had to follow a common protocol, criticised mainly the equilibration of the rice sample by spreading it on a tray. Besides the higher risk of contamination, changes in rel. humidity and temperature and changes of the oven temperature could influence the result significantly. Ambient conditions in a laboratory can change rapidly depending on weather conditions and climate zones. Therefore it was a difficult, in some cases unachievable, task for the participants to attain humidity equilibrium of the rice sample as prescribed in the protocol. Some of the participants did not state in how far they could follow the protocol, particularly not if consecutive weighings to a constant mass difference of 0.001g was attained.

Four participants explicitly reported that they could not attain the requested equilibration within this limit (BAM, NIST, NMi, NMIJ). Only IRMM and LGC reported that they attained equilibrium with consecutive weighings to a constant mass difference of 0.001g. The participants reported that the time until equilibration with ambient conditions was achieved varied between one to two days. Drying of the sample in a ventilated oven at a temperature of 85 ± 2 ^{o}C to a constant mass took also from 12 hours on up to 3 days. Four participants (NARL, CSIR-NML, NRC and NRCCRM) could not follow the first part of the protocol and did not spread the sample on a tray for equilibration purpose. NRC equilibrated the rice sample in the sample bottle for 6 hours, instead, before following the drying procedure in the protocol. CSIR-NML used the moisture content as determined from the non-equilibrated sample for dry-mass correction. The rice samples for analysis were bracketed by two sample portions used for the determination of the moisture content. NARL and NRCCRM used the non-equilibrated sample.

Two participants (LGC and NIST) applied a “method validation” for their dry-mass correction using the certified rice reference material NIES 10c.

The majority of the participants reported correction for dry-mass as a minor contribution to their overall uncertainty budget (0.1%-10%). NIST reported that correction for dry-mass was the major contribution to the overall uncertainty for the Cd measurement.

In Table 1 the correction factors reported by the participants for dry-mass correction with their relative uncertainties and the method used are listed next to the relative uncertainties of the reported measurement results for Cd

Table 1. Reported results for dry-mass correction for Cd measurements with their relative uncertainties compared to the relative uncertainties of the reported measurement result for Cd

participant	*reported factor for dry-mass correction*	*relative uncertainty (%) for dry-mass correction factor*	*relative uncertainty (%) for reported Cd amount content*	*moisture content determination approach*
BAM	**0.911 185**	**0.11**	**0.4**	**protocol, no humidity equilibrium to 1mg attained**
CSIR-NML	**0.956 13**	**0.023**	**1.0**	**protocol on non-equilibrated sample, bracketing**
EMPA	**0.937 9**	**0.11**	**1.5**	**Protocol, but not stated if equilibration following protocol**
IRMM	**0.888 3**	**0.53**	**1.5**	**protocol**
KRISS	**0.902 95**	**0.12**	**1.5**	**Protocol (without weighing to 1mg for hum. equil.)**
LGC	**0.920 81**	**0.1**	**0.9**	**protocol**
NARL	**0.957 4**	**0.11**	**1.7**	**protocol on non-equilibrated sample**
NIST	**0.896 9**	**0.87**	**1.6**	**protocol, no humidity equilibrium to 1mg attained**
NMi	**0.910 4**	**0.055**	**1.8**	**protocol, no humidity equilibrium to 1mg attained**
NMIJ	**0.930 11**	**0.066**	**2.7**	**protocol, no humidity equilibrium to 1mg attained**
NRC	**0.953 72**	**0.13**	**2.3**	**protocol on sample equilibrated in the sample glass container**
NRCCRM	**0.953 1**	**0.094**	**1.0**	**protocol on non-equilibrated sample**

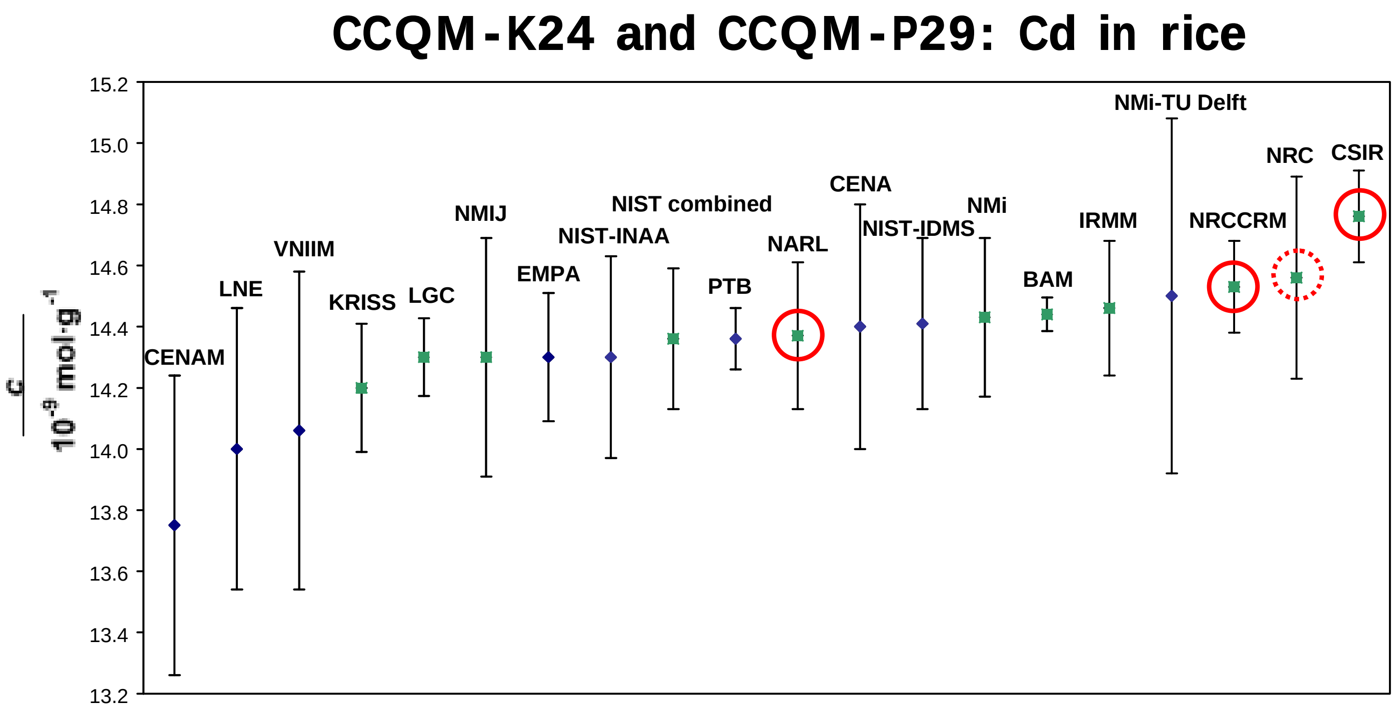
Further investigations of the moisture content in the rice

The ICP-MS group at IRMM carried out a thorough study on the determination of the water content and the hygroscopic behaviour of the rice sample [1].Three independent methods (K.F. Titration, oven method and thermogravimetry) were compared to determine the moisture content of the non-equilibrated rice sample and two independent methods to determine the moisture content of the humidity equilibrated rice sample. Furthermore, the measurement results for the Cd amount content were compared in view of the various corrections for moisture content and moisture uptake on the equilibrated and non-equilibrated sample. *As a result of this study it was shown that there was no significant difference in the result of the Cd amount content for this rice material using the different approaches for moisture content determination.*

Figure 1 shows the results for Cd in rice measurements of all participants in CCQM-K24 **and** CCQM-P29. It was confirmed that there is no significant difference in the measured Cd amount content applying humidity equilibration of the sample or using the non-equilibrated rice sample for “dry-mass correction”.

In view of the use of this rice material for an IMEP comparison four of the CCQM-K24 participants “volunteered” to perform additional measurements of the moisture content of the non-equilibrated rice sample using oven methods and K.F.-Titration. These measurements were not requested in the CCQM-K24 comparison protocol. The results will be published elsewhere with the agreement of the laboratories.

Figure 1. Results from CCQM-K24 (green squares) and results from CCQM-P29 (blue triangles) for Cd in rice measurements. Results corrected for dry-mass using the non-equilibrated sample are in red circles.



1 E. Vassileva and C. Quétel, Determination of the water content in rice sample, GE/R/IM/19/01

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CCQM-K24
Cd in rice

Final Report

Annex D

Questionnaire data

- experimental design
- digestion method and acid mixture
- use of sqrt(n) for type A uncertainty contributions
- reference isotope pair for IDMS
- number of blends prepared/measured
- experimental reproducibility
- reported blank correction; spikes and assay standards

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experimental design

CCQM-K24 participant	*experimental design*
BAM	double IDMS
CSIR	double IDMS
EMPA	direct IDMS
IRMM	direct IDMS
KRISS	double IDMS
LGC	double matching IDMS[1]
NARL	exact matching double IDMS
NIST[2]	direct IDMS, INAA comparator method
NMi	double IDMS
NMIJ	double IDMS
NRC	double-IDMS
NRCCRM	double-IDMS

[1] double IDMS sample/spike ratio matched to a mass bias blend prepared from a gravimetric standard and the spike

[2] NIST reported a combined result of IDMS and INAA

digestion method and acid mixture

CCQM-K24 participant	*digestion method*	*acid mixture*
BAM	microwave	**HNO_3,**
CSIR	microwave	**HNO_3 , H_2O H_2O_2 (4:5:1)**
EMPA	microwave	**HNO_3**
IRMM	microwave	**HF, HNO_3, (1:2.3)**
KRISS	microwave	**HF, HNO_3, $HClO_4$ (1:6:1)**
LGC	microwave	**HNO_3, HCl (10:1)**
NARL	microwave	**HNO_3**
NIST	microwave	**HF, HNO_3, H_2O_2**
NMi	microwave	**HF, HNO_3**
NMIJ	microwave	**HF, HNO_3, $HClO_4$**
NRC	microwave	**HF, HNO_3 , H_2O_2**
NRCCRM	wet digestion	**HF, HNO_3 , H_2O_2 (5:25:1)**

use of sqrt(n) for type A uncertainty contributions

CCQM-K24 participant	**use of sqrt(n) for type A uncertainty contributions**
BAM	yes
CSIR	yes
EMPA	no
IRMM	yes
KRISS	yes
LGC	yes
NARL	yes
NIST	yes
NMi	yes
NMIJ	yes
NRC	yes
NRCCRM	yes

reference isotope pair for IDMS

CCQM-K24 participant	*reference isotope pair for Cd measurement*
BAM	^{112}Cd/$\mathbf{^{113}Cd}$
CSIR	$\mathbf{^{111}Cd}$/^{112}Cd
EMPA	$\mathbf{^{111}Cd}$*****
IRMM	^{110}Cd/$\mathbf{^{111}Cd}$
KRISS	^{112}Cd *
LGC	$\mathbf{^{106}Cd}$/^{111}Cd
NARL	^{114}Cd/$\mathbf{^{111}Cd}$
NIST	$\mathbf{^{111}Cd}$/^{112}Cd
NMi	$\mathbf{^{111}Cd}$/^{114}Cd
NMIJ	^{112}Cd/$\mathbf{^{111}Cd}$
NRC	$\mathbf{^{114}Cd}$/^{111}Cd
NRCCRM	^{112}Cd/$\mathbf{^{111}Cd}$

*only reference isotope specified

number of blends prepared/measured for IDMS

CCQM-K24 participant	*number of blends for Cd measurement*
BAM	6
CSIR	3
EMPA	9
IRMM	10
KRISS	4
LGC	7
NARL	6
NIST	4
NMi	4
NMIJ	4
NRC	14
NRCCRM	6

experimental reproducibility (stdev on c_x)

CCQM-K24 participant	*standard deviation on c_x (in %) for Cd measurement*
BAM	0.3
CSIR	0.81
EMPA	0.71
IRMM	0.19
KRISS	0.4
LGC	0.25
NARL	0.55
NIST	0.5
NMi	0.42
NMIJ	0.43
NRC	0.69
NRCCRM	0.45

reported blank measurement; spikes and assay standards

CCQM-K24 participant	*blank for Cd measurement*	*Spike, assay standard, reference material*
BAM	**0.49±0.12 ng**	**-**
CSIR	**4.4±1.7 pmol/g**	**-**
EMPA	**-**	**^{111}Cd_IRMM-621**
IRMM	**0.058±0.052 ng**	**^{111}Cd_IRMM-622, Specpure Cd, Johnson Matthey, UK**
KRISS	**40±13 pmol/g**	
LGC	**<0.1%**	**^{106}Cd Teknolab (Norway), Specpure, Johnson Matthey, UK, SRM3108, NIES 10c**
NARL	**3.96%**	**^{111}Cd_IRMM-621, SRM3108**
NIST	**4.4±3.4 pmol/g**	**SRM 746, Gallard Schlesinger high purity Cd, NIES 10c**
NMi	**111±26 pmol/g**	**-**
NMIJ	**3.6±1.1pmol/g**	**-**
NRC	**-**	**-**
NRCCRM	**9.78±1.1pmol/g**	**-**

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CCQM-K24, Cd in Rice

Final Report

Annex E

- Letter to the participants
- Declaration for participation in the CCQM-K24, Cd in rice

Information Package

- cover page including participants list
- accompanying letter
- scope of the study
- general instructions
- instructions for determination of the dry-mass correction and the digestion of the rice
- instructions for uncertainty evaluation
- proposed uncertainty budget form for Cd
- results report form
- questionnaire

Distributed to participants via email:

- Summary of conclusions of the Seminar on 'Reporting and Estimating Uncertainty for CCQM studies and key comparisons'.
- Check-list on reporting uncertainty

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Geel, 20th June 2001
L/IM/39/01

To: **Registered participants for the rice comparisons of CCQM**
From: **Dr Ioannis Papadakis**
Subject: **Rice comparisons of CCQM (CCQM-K24 and CCQM-P29)**

Dear colleague,

During the last Inorganic Analysis Working Group and CCQM meetings (Paris, 2-6 April 2001) it was agreed that the CCQM-P29 pilot study would be separated into two different comparisons using the same rice sample. One pilot study with the same number and subject, CCQM-P29 *"Cd and Zn in rice"* and a new key comparison with limited subject, CCQM-K24 *"Cd in rice"*.

The reason for the above decision was the fact that most of the registered CCQM-P29 participants expressed the opinion that it is better to participate directly to a key comparison for the Cd in rice measurement and avoid the participation in the pilot study. No similar opinions were expressed for the Zn measurement. Thus it was agreed that the two activities would be organised. The CCQM-K24 key comparison for the participants who are confident that their measurement capability for *"Cd in rice"* measurement is appropriate and the CCQM-P29 pilot study for both *"Cd and Zn in rice"* measurement. Evidently the participants, who believe that they do not possess appropriate capability in order to participate at this stage at a key comparison for the Cd measurement, it is more appropriate to participate first to the pilot study.

The clear difference is that participation to the key comparison would result to equivalence statements in the Appendix B of the CIPM MRA, which can support CMCs in the Appendix C of the CIPM MRA. This is not the case for the participants in the pilot study.

Together with this letter you will find, the rice sample, a declaration for participation in CCQM-K24 and the information packages of both CCQM-K24 and CCQM-P29.

If you would like to participate in the CCQM-K24 please return the relevant declaration by 30th July 2001. If you do not return the declaration, you are only registered as CCQM-P29 participant. This cannot be changed at a later stage of the comparisons.

If you require any further information please do not hesitate to contact us.

Dr I. Papadakis
CCQM-K24 & CCQM-P29 Co-ordinator
IM Unit

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CCQM-K24
Cd in rice

Declaration for participation in the CCQM-K24, Cd in rice

(please return the latest by 30th July 2001)

NMI Identification: **(or designated laboratory)**	*name*	:
	institute	:
	address	:
	country	:
	e-mail	:
	tel. number	:
	fax number	:

I would like to confirm that the above NMI (or designated laboratory) which I represent is going to participate in the CCQM-K24 Key Comparison, “Cd in rice”.
It is clear to my organisation that the reported results and the equivalence statements of our measurements would be included in the Appendix B of the CIPM MRA and there is no possibility for their withdrawal.

Date :

Signature :

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20th June 2001

CCQM-K24
Cd in rice

Information Package

For further information, please contact:

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Dr E. Hwang	KRISS
Dr G. Labarraque	LNE
Dr B. Fairman	LGC
Dr L. Mackay	NARL
Dr J. Fassett	NIST
Dr M. Van Son	NMi
Dr K. Okamoto	NMIJ
Dr R. Sturgeon	NRC
Prof. Z. Mo-tian	NRCCRM
Dr D. Schiel	PTB
Dr L. Konopelko	VNIIM

CCQM and RMO delegates for info:

Dr R. Kaarls	president CCQM
Dr R. Wielgosz	CCQM exec. Secretary
Dr M. Sargent	Inorg. Anal. WG chair
Dr H. Semerjian	KC WG chair
Dr E. de Leer	Gas Anal. WG chair
Dr W. May	Org. Anal. WG chair/SIM
Dr W. Richter	pH WG chair
Mrs É. Deák	EUROMET METCHEM
Dr L. Mackay	APMP
Dr F. Hengstberger	SADCMET
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Dr C. Thomas	BIPM
Prof. M. Grasserbauer	IRMM
Prof. P. De Bièvre	IRMM
Dr P. Taylor	IRMM

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Geel, 20h June 2001
L/IM/40/01

To: **CCQM-K24 potential participants**
From: **Dr Ioannis Papadakis**
Subject: **CCQM-K24 "*Cd in Rice*"**

Dear colleague,

As proposed, discussed and decided in the last Inorganic Analysis Working Group and CCQM meetings (Paris 2-6 April 2001), IRMM in collaboration with NMIJ (Tsukuba, Japan) will be the pilot laboratory of the CCQM-K24 Key Comparison, "*Cd in Rice*".

The CCQM-K24 sample is a fine rice powder bottled in glass containers each one containing ~ 15 g of material. The rice powder was provided by NMIJ and originates from rice grown in contaminated water. The material is tested for stability and homogeneity and found appropriate for the needs of the comparison.

The deadline for report of the CCQM-K24 results is **30th November 2001**. This will allow us to prepare the draft report early in 2002 and consequently discuss it in the April 2002 working group meeting in Paris.

IRMM prepared an information package for the CCQM-K24, which is similar with the package distributed for other comparisons organised by IRMM and includes:

- This letter
- Scope of the CCQM-K24 Key Comparison
- General instructions
- Instructions for the dry mass correction and digestion of the sediment
- Instructions for uncertainty evaluation (for IDMS)
- Uncertainty budget form (for IDMS)
- Results report form
- Questionnaire for better interpretation of the data

The CCQM-K24 key comparison reference values will be established in the next working group meeting immediately after the deadline for the reporting of the results. The equivalence statements will then prepared accordingly and will appear to the appendix B of the MRA after approval by CCQM.

If any further information is required, please do not hesitate to contact us.

Yours sincerely

Dr I. Papadakis
CCQM-K24 Co-ordinator
IM Unit

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Geel, 20th June 2001
L/IM/41/01

Scope of CCQM-K24 key comparison
"Cd in rice"

This document describes the scope of the CCQM-K24 key comparison "*Cd in rice*". The CCQM-K24 was decided during the 7th CCQM meeting as an activity of the inorganic working group of CCQM and IRMM was designated as the pilot laboratory in collaboration with NMIJ.

Rice seems to be the oldest cereal cultivated. It is the main foodstuff for about half of the world's population. The vast majority of the world's rice is grown and consumed in Asia. In Latin America and Africa rice is also among the major nutrients. For the last decades rice consumption has been expanding beyond the traditional rice-grown areas, particularly in Europe. In order to protect public health it is essential to keep contaminants at levels, which are toxicologically acceptable, thus surveillance measures were taken regarding the presence of contaminants in foodstuff, including rice.

Cadmium may induce dysfunctions and reproductive deficiencies in humans and is suspected to act as a human carcinogen. Therefore Cd maximum levels in foodstuff, which is the main source of human intake of Cd, are set in relevant regulation [1, 2].

Laboratories who demonstrate their capability of measuring Cd amount content in the CCQM-K24 rice samples, are likely to have the capability, knowledge and skills to measure the amount content of other elements at similar levels in other food matrices which require similar sample preparation.

Dr I. Papadakis
CCQM-K24 Co-ordinator
IM Unit

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1 Commission Regulation (EC) No 466/2001 of 8 March 2001 setting maximum levels for certain contaminants in foodstuff, Official Journal of the European Communities L077, 16/03/2001, 0001-0013

2. K. Okamoto, Preparation and certification of rice flour – unpolished reference material, The Science of the Total Environment, 107 (1991) 29-44

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Geel, 20th June 2001

General Instructions for CCQM-K24 key comparison

This document gives general guidelines for participation in the CCQM-K24 key comparison "*Cd in rice*".

- ♦ store the sample (provided to you in a glass bottle) at room temperature.
- ♦ It is open to the participant to use the analytical procedure of his/her choice. However, this document will give instructions for the use of a measurement procedure using isotope dilution mass spectrometry similar to the one used in the previous inorganic key comparisons and pilot studies [1]. A few specific points are highlighted, hereafter, realising that most of the participants have considerable experience in isotope dilution measurements:
  - minimise contamination (work in closed systems or class 100 clean bench, check reagents and labware used)
  - prepare the blends and all dilutions gravimetrically
  - correct sample weighing for dry mass (see special instructions)
  - spike the rice material prior to the digestion
  - make sure that the rice digestion is complete (see specific instructions)
  - avoid weighing of small aliquots of solids or liquids in order to minimise the weighing uncertainty
  - possible isobaric interferences for the Cd isotopes should be investigated and treated accordingly
  - the correction factors for mass discrimination in the ratio measurements should be measured repeatedly using materials of known isotopic composition and ratios similar to those in the blends or samples
- ♦ the uncertainty statement should be evaluated according to ISO/GUM [2]. Use the attached "Instructions for uncertainty evaluation" document, to summarise the major uncertainty contributions.

If you require further information or assistance, please do not hesitate contact us.

Dr I. Papadakis
CCQM-K24 Co-ordinator
IM Unit - IRMM

---

1. R. L. Watters, Jr., K. R. Eberhardt, E. S. Beary and J. D. Fassett, Protocol for isotope dilution using inductively coupled plasma-mass spectrometry (ICP-MS) for the determination of inorganic elements, Metrologia, Vol. 34, No 1 (1997) 87-96

2 International Organisation for Standardisation, "Guide to the Expression of Uncertainty in Measurement", © ISO, ISBN 92-67-10188-9, Geneva, Switzerland,1993.

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Instructions for determination of the dry-mass correction and the digestion of the rice sample in the CCQM-K24 key comparison

The subject of CCQM-K24 key comparison is the measurement of Cd amount content in a fine rice powder. There are two potential problems in such measurement.
Firstly, and most important, the water content of the rice powder will affect the rice mass, and a correction for that is needed. From recent work in that area [1, 2] it seems that this correction is very important because depending on the method used a different results can be obtained. This means that the "measurand" is to some extent "operationally defined". If the instructions, given below, are not followed it would be practically impossible to achieve "comparable" results.
Secondly, the digestion of a rice material (if needed for the procedure which you are following) is never a trivial exercise.
This document intents to give guidance on the above matters.

1. Dry-mass correction

There are two potential problems concerning the "dry-mass correction". The first is the moisture content already present in the sample, the second is the humidity that the sample will pick-up from the environment since it is highly hygroscopic. The method prescribed below tackles both problems.
The bottled rice sample that is provided to your laboratory should be spread on a tray and be exposed to ambient conditions for at least 6 hours until humidity equilibrium is attained (successive weights should not differ more than 0.001 g). Any kind of contamination has to be avoided during this procedure.
The Cd measurements have to be performed on a sub-sample of this "equilibrated" rice material.
A separate portion of this "equilibrated" material, of minimum mass of 1 g, should be used for the "dry-mass correction". The material should be dried for a minimum of 8 hours in a ventilated oven at a temperature of 85 ± 2 ^{o}C. Then weigh and repeat drying until constant mass is attained. Each weighing has to be carried out after the sample reached thermal equilibrium at room temperature in a desiccator (successive weights should not differ more than 0.001 g). The loss of mass corresponds to the "dry-mass correction" that should be applied to the mass of the sample that is used for the Cd measurement.

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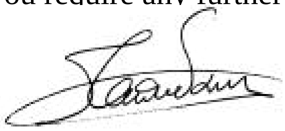
2. Digestion of the rice (only in case the method used requires digestion)

There is a variety of digestion methods, employing various combinations of acids and for which different instruments are used.

- use minimum sample mass of 250 mg.
- aim is to digest the rice material completely.
- should this fail, Cd content in the residue should be measured in order to estimate the correction needed and its uncertainty contribution.

If you require any further assistance or information, please do not hesitate to contact us.



Dr I. Papadakis
CCQM-K24 Co-ordinator
IM Unit - IRMM

1. S. Rückold et. al. Water as a source of errors in reference materials, Fresenius J Anal Chem (2001) 370: 189 - 193
2. S. Rückold et. al. Determination of the contents of water and moisture in milk powder, Fresenius J Anal Chem (2000) 368: 522 - 527

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Geel, 20h June 2001

Instructions for uncertainty evaluation in the CCQM-K24 key comparison

In the CCQM-K24 key comparison no measurement method is prescribed. The organisers do not want to prescribe a method for uncertainty evaluation, this document just gives an example for uncertainty evaluation when Isotope Dilution Mass Spectrometry (IDMS) is the method used.
According to the ISO/BIPM Guide to the Expression of Uncertainty in Measurement, an equation must be written down which describes the measurement procedure. IDMS, when applied for a measurement in a rice matrix, can be described by the following equation:

$$c_x = \left[D \cdot c_z \cdot \frac{m_y}{w \cdot m_x} \cdot \frac{m_z}{m'_y} \cdot \frac{K_y \cdot R_y - K_b \cdot R_b}{K_b \cdot R_b - K_x \cdot R_x} \cdot \frac{K_{b'} \cdot R_{b'} - K_z \cdot R_z}{K_y \cdot R_y - K_{b'} \cdot R_{b'}} \cdot \frac{\sum (K_{ix} \cdot R_{ix})}{\sum (K_{iz} \cdot R_{iz})} \right] - B$$

The indexes refer to different materials: *x* to the sample, *y* to the spike, *z* to the primary assay standard, *b* to the blend of fractions of sample and spike and *b'* to the blend of fractions of spike and the primary assay standard. The parameter *c* refers to the amount content (this symbol is used instead of *k*[1] to avoid confusion with *K*-factors) in the materials denoted by the indexes, *m* to the mass fractions of each material used for the blends (m_y used to the blend of fractions of *x* and *y* and m'_y to the blend of fractions of *y* and *z*), *R* to the measured isotope amount ratio in different materials denoted by the indexes and *K* to the correction factor for mass bias in a measured ratio. The two sum factors (Σ) at the end of the equation are the sums of all corrected isotope amount ratios of the specific element (measured isotope amount ratios multiplied by the corresponding correction factor for mass discrimination) in materials *x* and *z*. Finally the parameters *D*, *w* and *B* are variables introduced to the measurement procedure by the digestion procedure, the dry mass correction and the subtraction of the procedure blank respectively.
You are requested to evaluate the uncertainty for each parameter of the equation and calculate the combined and expanded uncertainty. Complete the attached uncertainty budget and forward it to IRMM together with your results' report. In this basic uncertainty budget we have divided the parameters into two groups, major and secondary contributions. This division is only indicative and may vary upon the experimental conditions in each laboratory.

Dr I. Papadakis
CCQM-K24 Co-ordinator
IM Unit - IRMM

[1] T. Cvitaš, *Metrologia*, 1996, **33**, 35-39

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CCQM-K24

Uncertainty Budget[2]

for Cd amount content measurement

Parameter	typical value[3]	standard uncertainty	type A/B[4]	n[5]	description
major contributions to uncertainty					
R_b					measured isotope amount ratio of blend *b*
$R_{b'}$					measured isotope amount ratio of blend *b'*
R_x					measured isotope amount ratio in the sample
R_z					measured isotope amount ratio in the primary assay standard
K_b					mass bias correction factor of R_b
$K_{b'}$					mass bias correction factor of $R_{b'}$
K_x					mass bias correction factor of R_x
K_z					mass bias correction factor of R_z
D					digestion procedure
B					procedure blank subtraction
secondary contributions to uncertainty					
c_z					amount content of the primary assay standard
R_y					measured isotope amount ratio in the spike
K_y					mass bias correction factor of R_y
m_x					mass fraction of sample in blend *b*
m_y					mass fraction of spike in blend *b*
m'_y					mass fraction of spike in blend *b'*
m_z					mass fraction of primary assay standard in blend *b'*
w					dry mass correction
$\sum(K_{ix} \cdot R_{ix})$					sum of all the corrected isotope amount ratios in the sample (measured isotope amount ratios multiplied by the corresponding mass bias correction factor)
$\sum(K_{iz} \cdot R_{iz})$					as above but in the primary assay standard
					any additional parameter of importance
results					
c_x			**amount content in the sample** (end result)		
u_c			**combined uncertainty**		
$U\ (= k \cdot u_c)$			**expanded uncertainty (k=2)**		

---

2. Please return together with the results' report sheet.
3. Please indicate the unit used for each parameter where appropriate.
4. According to ISO/BIPM Guide to the Expression of Uncertainty in Measurement
5. Number of measurements performed for the calculation of type A uncertainty contributions

CCQM-K24

Cd in Rice

RESULTS REPORT

(please return together with questionnaire by 30th November 2001)

Lab Identification :

name :
institute :
address :

country :
e-mail :
tel. number :
fax number :

Report all your results and uncertainties in the unit **mol·g^{-1}**. Measurement uncertainty should be evaluated according to ISO/GUM[1] and have a coverage factor *k*=2.

element	*content (mol·g^{-1})*	*uncertainty (mol·g^{-1})*
Cd		

Date :

Signature :

1 International Organisation for Standardisation, "Guide to the Expression of Uncertainty in Measurement", ©ISO, ISBN 92-67-10188-9, Geneva, Switzerland,1993.

CCQM-K24

Cd in Rice

Questionnaire

(please return together with the results report form)

Lab Identification : *name* :
institute :

This information is needed for better recording and interpretation of the reported results and uncertainty statements:

1. Analytical method used:…………………………………………………………….
2. Instrumental technique used:………………………………………………………….
3. Experimental design (please use additional sheet):..……………………………….
4. Digestion method used:……………………………………………………………….
5. If mixture of acids was used, please specify:……………………………………….
6. Correction for dry mass (% of the weighted):………………………………………
7. Use of square root of n for type A uncertainty contributions: YES/NO..………….
8. Reference Isotope (for IDMS):.……………………………………………………….
9. Number of blends (for IDMS):………..……………………………………………….
10. Experimental reproducibility (as standard deviation and not standard deviation of the mean) of c_x from different blends in % (for IDMS):……………………………

(if more space is needed for your answers please use additional pages)

Date :

Signature :

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MEMORANDUM

Geel, 23 Oct 2001

**Summary of conclusions of the Seminar on 'Reporting and Estimating Uncertainty for CCQM studies and key comparisons'.
Proposal that can form a guidance document for CCQM-IAWG work.**

1. As for reporting: participants agreed that it should be possible to do an a posteriori calculation of the result and its uncertainty, based on the data supplied in the uncertainty budget and the report documenting that result. Also, participants should not return data in hand written way.

2. As for reporting: participants agreed that it is needed to state the measurement equation for their measurement. Even though a similar measurement method might be used, the measurement equation will differ depending on the design of experiment.

3. As for reporting: there is a need for new, ,more general instructions and example of budget form in the technical protocol for the study/key comparison. These instructions should clearly state which ingredients are needed: the equation, the input quantities, uncertainty estimates (type of evaluation process and type of distribution assumed). It When and if the protocol includes an example of equation and explanation of input quantities, it should clearly state that the this is an just an example and participants should adapt it to their own experimental design. A checklist should be made of what parts are needed for a complete uncertainty statement. The pilot laboratory should build in a formal 'compliance check' to see that participants deliver what is needed.

4. As for estimating uncertainty: participants agreed that on the one hand the magnitude of uncertainty estimates will obviously differ depending on the technical experience of people, the equipment used, the design of experiment. But on the other hand, having a different estimation process or practice should be avoided.

5. As for estimating uncertainty: participants agreed that estimating uncertainty in the context of a key comparison or pilot study will be slightly different from what one does in a CRM value assignment (e.g. in case of a 'one-off' exercise, less data will be available to base the estimation on)

6. As for estimating uncertainty: participants agreed that type A evaluation calls for standard deviation of the mean, but it was noted that in some cases participants still used the standard deviation of a single result. It was noted that type A evaluation can

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only be done for unbiased observations/results, and that bias factors should isolated (e.g. as a factor)

7. As for estimating uncertainty: participants agreed that type B estimation is complicated, and often, limited time or resources are available to do this estimate. But the objective is to describe reality by a model and document this (the model used might not be the exact description, but that one was used).

8. As for estimating uncertainty: participants agreed that metrology laboratories will do type B estimation often based on experimental data, on clever experiments (and therefore caution to be exerted when deducing conclusions from comparing your value to a value of an existing CRM)

9. As for estimating uncertainty: participants agreed that sample preparation is an integral part of the measurement and often a decisive one. As a consequence, participants agree that this must be modelled in the measurement equation (e.g. have a factor in the equation linked to digestion, and even if assumed to be unity, it will carry an uncertainty)

10. As for estimating uncertainty: participants agreed that when effects are studied experimentally and found to have no measurable effect, ignoring this type B uncertainty will lead to uncertainty statements which are smaller compared to people who do not ignore these. This should be avoided. According to ISO-GUM philosophy, the idea is to use the experimental knowledge available and not to ignore this, though this will lead to larger uncertainty statements.

Drafted by P. Taylor, chair of this seminar

CCQM-K24

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Check-list on reporting uncertainty

During the last IWG meeting in October 2001 in Geel agreements for reporting and estimating uncertainty for CCQM studies and key comparisons were made. They are summarised in a memorandum that was passed on to all participants. Although at this stage this document is not yet finalised and participants are invited to comment on it, IRMM as one of the pilot institutes for CCQM K24 and CCQM P29 would like to implement the major topics already to these key comparison/pilot study.

The document *"Instructions for uncertainty evaluation in the CCQM-K24 key comparison"* as included in the distributed information package is only meant to be as an example that participants can adapt to their own needs according to their own experimental design.

This check-list is sent to all CCQM K24 and CCQM P29 participants in order to help them to comply with the changes in reporting uncertainties compared to previous comparisons:

1. Do not report hand-written results and uncertainties
2. State your measurement equation
3. State your input quantities
4. Include factors related to sample treatment in your measurement equations
5. Describe the applied evaluation process and type of assumed distribution for your uncertainty estimation