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CCQM-P29 pilot study
Cadmium and zinc amount content in rice

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Final Report

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Abstract

The CCQM-P29 was performed in parallel to the CCQM-K24 key comparison in order to demonstrate and document the capability of interested National Metrology Institutes to measure the Cd and Zn amount content in a rice sample. Participants to the CCQM-P29 did not have to register prior to result reporting. 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. It was decided during the IAWG meeting, April 2002, BIPM, Paris not to include the Cd measurements results from participants in CCQM-K24 in this CCQM-P29 pilot study.

The methods applied were isotope dilution mass spectrometry (IDMS) using thermal ionisation MS (TIMS), sector field or quadrupole inductively coupled plasma MS (ICP-MS), inductively coupled plasma emission spectrometry (ICP-AES) and neutron activation analysis (NAA) using instrumental neutron activation analysis (INAA) and k_0-NAA as analytical technique.
NIST reported two results for Cd and Zn measurements (IDMS and INAA). VNIIM reported two results for Zn (ICP-MS and ICP-AES).

The following laboratories participated in this pilot study (alphabetical order).

BAM, Germany
CENA, Brazil
CENAM, Mexico
IRMM, European Union
KRISS, South Korea
LGC, United Kingdom
LNE, France
NARL, Australia
NIST, United States of America
NMi, The Netherlands
NMIJ, Japan
NRC Canada
NRCCRM, China
PTB, Germany
VNIIM, Russian Federation

The reported results of all participants are displayed in this report. Good agreement of reported results was observed. To be complete the results for Cd measurements of all participants in CCQM-P29 and CCQM-K24 are also graphically displayed in this report.

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 not wanting to take part in the key comparison for Cd, had the possibility to demonstrate their measurement capabilities via participation in the pilot study. The pilot study CCQM-P29 is an activity of the "Inorganic Analysis Working Group" of the CCQM.

The same samples measured by the CCQM-P29 participants were also used for the key comparison CCQM-K24 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].

Zinc is well known as an essential trace element for humans. It is proven to be an essential factor in over 100 enzymes. Recently the European Commission has requested the Scientific Committee on Food (SCF) to review the upper level of daily intake of zinc. [3].

3. Participation in CCQM-P29

Participants in CCQM-P29 are listed in Table 1.

Table 1. CCQM-P29 participants

institution / organisation	origin
BAM Bundesanstalt für Materialforschung und –Prüfung, Berlin	**Germany**
CENA Centro de Energia Nuclear na Agricultura	**Brazil**
CENAM Centro National de Metrologia	**Mexico**
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**
LNE Laboratoire National d'Essais	**France**
NARL National Analytical Reference Laboratory	**Australia**
NIST National Institute of Standards and Technology	**United States of America**
NMi Nederlands Meetinstituut	**The Netherlands**
NMIJ National Institute of Materials and Chemical Research	**Japan**
NRC National Research Council of Canada	**Canada**
PTB Physikalisch-Technische Bundesanstalt	**Germany**
VNIIM Mendeleyief Institute of Metrology	**Russian Federation**

4. Sample

The CCQM-P29 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 and INAA by analysing 2 sub-samples of 5 bottles for each element. 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 [4, 5]. No significant difference was observed.

The samples and information/instructions documents were made available to CCQM-P29 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-P29 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 added. 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 last CCQM-IAWG meeting (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 and of CCQM-P29 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-P29 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 and Zn (2 pages)
7. results report form (1 page)
8. questionnaire (1 page)

IV. Communicated via email to all the CCQM-P29 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 and results for determination of dry-mass correction

The determination of the moisture content of the samples is to some extent "operationally defined" [6, 7]. When the study 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-P29 participants. Following the protocol, 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 and Zn 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".

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/pilot study 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 the CCQM-K24 final report.

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

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 their measurements.

In Table 2 and Table 3 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 and Zn.

Table 2. 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*
CENA	**0.928 04**	**0.1**	**2.8**	**protocol**
CENAM	**0.925 4**	**0.05**	**3.6**	**protocol**
LNE	**0.892 6**	**0.85**	**3.3**	**protocol**
NIST-IDMS	**0.896 9**	**0.87**	**1.9**	**protocol, no humidity equilibrium to 1mg attained**
NIST-INAA	**0.913**	**0.91**	**2.3**	**protocol, no humidity equilibrium to 1mg attained**
NMi-TU Delft	**0.9**	**1**	**4**	**protocol, no humidity equilibrium to 1mg attained**
PTB	**0.931 3**	**0.066**	**0.7**	**-**
VNIIM-1	**0.964 8**	**0.03**	**3.7**	**-**

Table 3. Reported results for dry-mass correction for Zn measurements with their relative uncertainties compared to the relative uncertainties of the reported measurement result for Zn

participant	*reported factor for dry-mass correction*	*relative uncertainty (%) for dry-mass correction factor*	*relative uncertainty (%) for reported Zn amount content*	*moisture content determination approach*
BAM	**0.911 185**	**0.11**	**1.9**	**protocol, no humidity equilibrium to 1mg attained**
CENA	**0.928 04**	**0.1**	**2.6**	**protocol**
CENAM	**0.918 9**	**0.28**	**5.4**	**protocol**
IRMM	**0.904 4**	**0.070**	**6.0**	**protocol**
KRISS	**0.902 95**	**0.12**	**2.6**	**protocol (without weighing to 1mg for hum. equil.)**
LGC	**0.920 81**	**0.1**	**1.6**	**protocol**
LNE	**0.892 6**	**0.85**	**2.7**	**protocol**
NARL	**0.952 4**	**0.12**	**1.6**	**protocol on non-equilibrated sample**
NIST-IDMS	**0.896 9**	**0.87**	**1.9**	**protocol, no humidity equilibrium to 1mg attained**
NIST-INAA	**0.913**	**0.91**	**2.4**	**protocol, no humidity equilibrium to 1mg attained**
NMi-TU Delft	**0.9**	**1**	**3.6**	**protocol, no humidity equilibrium to 1mg attained**
NMIJ	**0.9301 1**	**0.066**	**2.0**	**protocol, no humidity equilibrium to 1mg attained**
NRC	**0.953 72**	**0.13**	**1.8**	**protocol on sample equilibrated in the sample glass container**
PTB	**0.931 3**	**0.066**	**0.8**	**-**
VNIIM-1	**0.964 8**	**0.03**	**4.9**	**-**
VNIIM-2	**0.945 3**	**0.25**	**4.2**	**-**

5.2. 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 [8]. 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.*

5.3. 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. 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. 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*

   One participant (NARL) reported hand-written results. Another participant (LNE) filled in the questionnaire manually.

2. *State your measurement equation*

   Two participants (VNIIM-1, VNIIM-2) did not state explicitly their measurement equation or referred to an equation as given in the information package or in the open literature.

3. *State your input quantities*

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

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

   There were three participants (NMi-TU-Delft, VNIIM-1, VNIIM-2) who did not include a factor for dry mass correction in their equation. Four participants (CENA, CENAM, VNIIM-1, VNIIM-2) did not include a factor related to sample preparation in their measurement equation.

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

   Only one participant (NARL) stated the applied evaluation process and also added the assumed distribution for the evaluation of each parameter in their uncertainty budget. The majority (10 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. Three participants (CENA, IRMM, PTB) neither stated the evaluation process nor the type of assumed distribution.

6. Methods and instrumentation used

The CCQM-P29 participants applied either isotope dilution or neutron activation for the measurement of the Cd and Zn amount content in the rice. VNIIM used IDMS and external standard calibration for the Cd measurement and external standard calibration for the Zn measurement. The majority of the participants used mass spectrometry as the analytical method. One participant (BAM) used thermal ionisation MS (TIMS), three participants (CENAM, KRISS, LGC) used ICP-magnetic sector field MS and four participants (LNE, NIST, NRC and VNIIM) used ICP-QMS. NMIJ (He as collision gas) and NARL used ICP-QMS with collision cell. Three participants used INAA (CENA, NIST and NMi). IRMM used k_0-NAA for the Zn measurement. VNIIM-2 reported a result for Zn using ICP-AES.

Table 4 gives an overview of the method applied and the instrumentation used by each CCQM-P29 participant for the Cd measurements. Table 5 gives an overview of the method applied and the instrumentation used by each CCQM-P29 participant for the Zn measurements.

Table 4. Analytical methods and instrumental techniques used by CCQM-P29 participants for Cd measurements

participant	*method*	*instrumentation*
CENA	NAA	INAA
CENAM	IDMS	ICP-magnetic sector field MS
LNE	IDMS	ICP-QMS
NIST	IDMS and NAA*	ICP-QMS and INAA
* ***NMi-TU Delft**	NAA	INAA
NRC	IDMS	ICP-QMS
PTB	IDMS	ICP-magnetic sector field MS
NRCCRM	IDMS	TIMS
VNIIM-1	IDMS	ICP-QMS

* NIST reported a result for IDMS and INAA.

* * The Interfaculty Reactor Institute (IRI) was designated by NMi to report the INAA Cd result

Table 5. Analytical methods and instrumental techniques used by CCQM-P29 participants for Zn measurements

participant	*method*	*instrumentation*
BAM	IDMS	Multi collector TIMS
CENA	NAA	INAA
CENAM	IDMS	ICP-magnetic sector field MS
IRMM	NAA	k_0-NAA
KRISS	IDMS	ICP-magnetic sector field MS
LGC	IDMS	ICP-magnetic sector field MS
LNE	IDMS	ICP-QMS
NARL	IDMS	ICP-QMS, collision cell
NIST	IDMS and NAA*	ICP-QMS and INAA
****NMi-TU Delft**	NAA	INAA
NMIJ	IDMS	ICP-QMS, collision cell
NRC	IDMS	ICP-QMS
PTB	IDMS	ICP-magnetic sector field MS
VNIIM	external calibration* **	ICP-QMS and ICP-AES

* NIST reported a result for IDMS and a result for INAA.

* * The Interfaculty Reactor Institute (IRI) was designated by NMi to report the INAA Zn result

** * VNIIM reported a result for IDMS and a result for ICP-AES

In Table 6 and Table 7 all the questionnaire data are summarised for Cd and Zn measurements.

Table 6. Questionnaire data for Cd measurements

	CENA	CENAM	LNE	NIST-IDMS	NIST-INAA	NMi-TU-Delft	PTB	VNIIM-1
method	NAA	IDMS	IDMS	IDMS	NAA	NAA	IDMS	IDMS
technique	INAA	ICP-magnetic sector field MS	ICP-QMS	ICP-QMS	INAA	INAA	ICP-magnetic sector field MS	ICP-QMS
experimental design	comparator method, k_0 to check standard procedure	double-IDMS	double-IDMS	double-IDMS	comparator method	comparator method	double-IDMS	double-IDM
digestion method	N/A	microwave	microwave	pre digestion on hot plate followed by HP microwave digestion	N/A	N/A	microwave	acid digestion, open syste
mixture acids	N/A	HNO_3	4mL HNO_3,1 mL H_2O_2	HNO_3, HF, H_2O_2	N/A	N/A	6mL H_2O_2,10mL HNO_3	H_2SO_4:HNC (1:3)
correction dry mass	7.20%	7.46%	10.70%	10.31%	8.70%	10.00%	6.87%	3.52%
sqrt(n) for typeA		YES	YES	YES	YES	YES	YES	YES
ref isotopes	N/A	^{111}Cd	^{111}Cd/^{106}Cd	**^{111}Cd**/^{112}Cd	N/A	N/A	^{114}Cd	^{110}Cd/**^{111}Cd**
number of blends	N/A	6	4	4	N/A	N/A	10	4
exp reproducibility (stdev on Cx)			2.00%	0.50%		2.30%	0.16%	2.10%
reported blank correction	<0.6%	36±9 nmol/g	No blank correction	4.4±3.4 pmol/g				4±0.5 pmol/
spikes, assay standards, reference materials	SRM 1570a			SRM 746, Gallard Schlesinger high purity Cd, NIES 10c	NIES 10c	SRM 3108	SRM 746, Chemotrade 364-4	

Table 7. Questionnaire data for Zn measurements

	BAM	CENA	CENAM	IRMM	KRISS	LGC	LNE
method	IDMS	NAA	IDMS	NAA	IDMS	IDMS	IDMS
technique	Multi-collector TIMS	INAA	ICP-magnetic sector field MS	k_0-NAA	ICP-magnetic sector MS	ICP-magnetic sector MS	ICP-QMS
experimental design	double-IDMS	comparator method, k_0 to check standard procedure	double-IDMS	sample/neutron flux monitors	double-IDMS	double matching IDMS	double-IDMS
digestion method	microwave	N/A	microwave	N/A	microwave	microwave	microwave
mixture acids	HNO_3	N/A	HNO_3	N/A	HNO_3 $HClO_4$, HF	5mL HNO_3, 0.5 mL HCl	4mL HNO_3,1 mL H_2O_2
correction dry mass	8.88%	7.20%	8.11%	9.56%	9.70%	9.00%	10.70%
sqrt(n) for typeA	YES			NO	YES	YES	YES
ref isotopes	$^{67}Zn/^{66}Zn$	N/A	^{66}Zn	N/A	^{68}Zn	^{67}Zn	$^{68}Zn/^{67}Zn$
number of blends	6	N/A	6	N/A	4		4
exp reproducibility (stdev on Cx)	0.80%			0.19%	0.43%		1.00%
reported blank correction	250±140 ng	<0.6%	2.8±0.9 nmol/g	no blank correction applied, HDPE vials free of Zn	1.78±0.21 nmol/g	<0.1%	No blank correction
spikes, assay standards, reference materials		SRM 1570a				^{67}Zn spike from Oak Ridge Laboratories, Tennessee, USA;Specpure, Johnson Matthey, UK;SRM3168a,SRM1568a	

	NARL	NIST-IDMS	NIST-INAA	NMi-TU-Delft	NMIJ	NRC	PTB
method	IDMS	IDMS	NAA	NAA	IDMS	IDMS	IDMS
technique	ICP-QMS with collision cell	ICP-QMS	INAA	INAA	ICP-MS , He collision was used	ICP-QMS	ICP-magnetic sector field MS
experimental design	exact matching double IDMS	double-IDMS	comparator method	comparator method	double-IDMS	double-IDMS	double-IDMS
digestion method	microwave	pre digestion on hot plate followed by HP microwave digestion	N/A	N/A	microwave	microwave	microwave
mixture acids	5ML HNO_3	HNO_3, HF, H_2O_2	N/A	N/A	HNO_3 $HClO_4$, HF	HNO_3, HF, H_2O_2	6mL H_2O_2,10mL HNO_3
correction dry mass	5.00%	10.31%	8.70%	10.00%	6.99%	4.63%	6.87%
sqrt(n) for typeA	YES	YES	YES	YES	YES	YES	YES
ref isotopes	^{66}Zn	^{66}Zn sample, ^{67}Zn spike	N/A	N/A	$^{68}Zn/^{66}Zn$	^{66}Zn	^{64Zn}
number of blends	5	4	N/A	N/A	4	7	10
exp reproducibility (stdev on Cx)	0.71%	0.26%		0.92%	0.25%	0.47%	0.34%
reported blank correction	<1.5%	266±0.214 pmol/g			46±15 pmol/g		
spikes, assay standards, reference materials	^{66}Zn spike from Oak Ridge Laboratories, Tennessee, USA; NARL1-10099	SRM 746, Gallard Schlesinger high purity Cd, NIES 10c	NIES 10c	SRM 3168a			SRM 682,Chemotrade 42

	VNIIM-1	VNIIM-2
method	external calibration	ICP-ES
technique	ICP-QMS	ICP spectrometer "BAIRD"
experimental design	calibration using reference solution	calibration using standard solution
digestion method	acid digestion, open system	acid digestion, open system
mixture acids	H_2SO_4:HNO_3 (1:3)	H_2SO_4:HNO_3 (1:3)
correction dry mass	3.52%	5.47%
sqrt(n) for typeA	YES	YES
ref isotopes		
number of blends	number of subsamples 6	number of subsamples 6
exp reproducibility (stdev on Cx)	5.00%	3.50%
reported blank correction		
spikes, assay standards, reference materials	ref solution Zn>99.96%	assay standard PM-2, aqueous solution of Zn 0.1 g/L

7. CCQM-P29 participants' results

The CCQM-P29 participants' results, as reported to the pilot institute (IRMM), are given in Table 8 and Table 9. They are graphically displayed in Figure 1 and Figure 2. All uncertainties given are expanded uncertainties. The coverage factors given was k=2. KRISS reported a result for Zn with a coverage factor k=1.98.
To be complete the results for Cd measurements from all participants in CCQM-P29 **and** CCQM-K24 are plotted in Figure 3.

Table 8. CCQM-P29 participants' measurement results for Cadmium

participant	*reported result* $nmol \cdot g^{-1}$	*expanded uncertainty (k=2)* $nmol \cdot g^{-1}$	*relative uncertainty (%)*
CENA	**14.40**	**0.40**	**2.8**
CENAM	**13.75**	**0.49**	**3.6**
LNE	**14.00**	**0.46**	**3.3**
NIST-IDMS	**14.41**	**0.28**	**1.9**
NIST-INAA	**14.30**	**0.33**	**2.3**
NMi-TU Delft	**14.50**	**0.26**	**1.8**
PTB	**14.36**	**0.10**	**0.7**
VNIIM	**14.06**	**0.52**	**3.7**

Figure 1. CCQM-P29 and CCQM-K24 participants' measurement results for cadmium with the CCQM-K24 KCRV

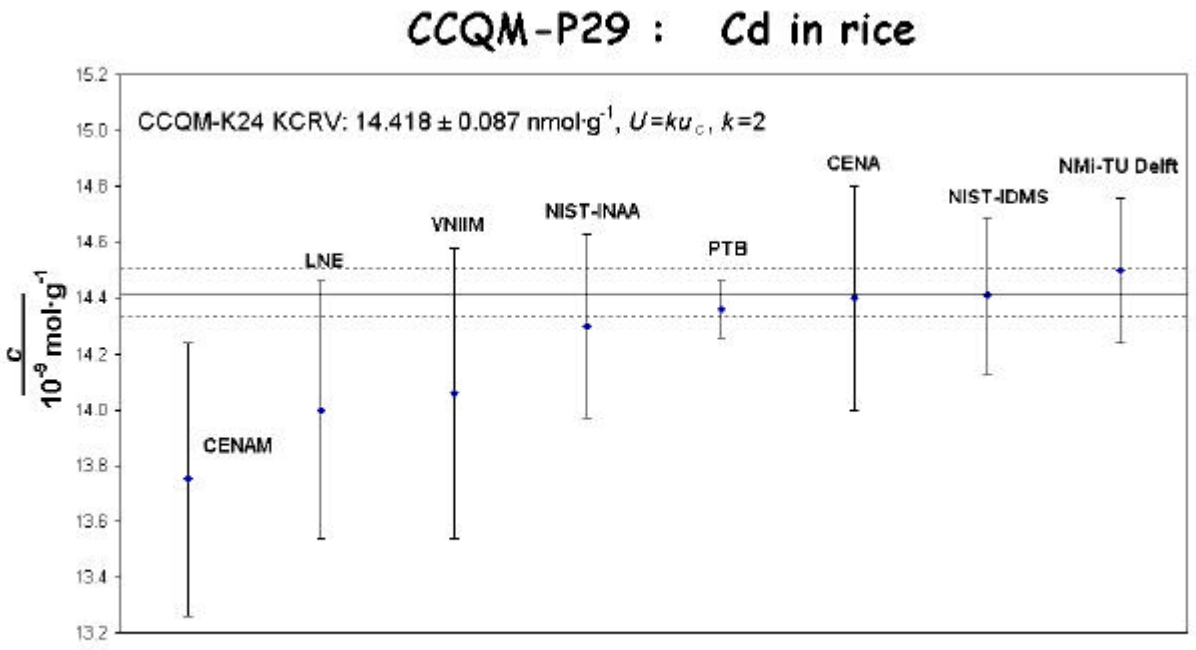


Table 9. CCQM-P29 participants' measurement results for Zinc

participant	*reported result* $\mu mol \cdot g^{-1}$	*expanded uncertainty (k=2)* $\mu mol \cdot g^{-1}$	*relative uncertainty (%)*
BAM	**0.351 5**	**0.006 8**	**1.9**
CENA	**0.349 0**	**0.009 0**	**2.6**
CENAM	**0.335 0**	**0.018 0**	**5.4**
***IRMM**	**0.357**	**0.021**	**6.0**
****KRISS**	**0.348 0**	**0.009 2**	**2.6**
LGC	**0.352 0**	**0.005 5**	**1.6**
LNE	**0.360 0**	**0.009 7**	**2.7**
NARL	**0.353 4**	**0.005 6**	**1.6**
NIST-IDMS	**0.355 4**	**0.006 7**	**1.9**
NIST-INAA	**0.355 9**	**0.008 5**	**2.4**
NMi-TU Delft	**0.350 0**	**0.007 7**	**2.2**
NMIJ	**0.350 4**	**0.006 9**	**2.0**
NRC	**0.359 3**	**0.006 4**	**1.8**
PTB	**0.357 0**	**0.003 0**	**0.8**
VNIIM-1	**0.350**	**0.017**	**4.9**
VNIIM-2	**0.356**	**0.015**	**4.2**

* Results reported in mg/kg were calculated by the author of this report into mol/g using the IUPAC-table "Atomic weights of the elements 1999", *Pure Appl. Chem.,* 73,4, (2001) 73,No. 4, 667-683
** KRISS reported a Zn result with a coverage factor k=1.98.

Figure 2. CCQM-P29 participants' measurement results for zinc with the arithmetic mean

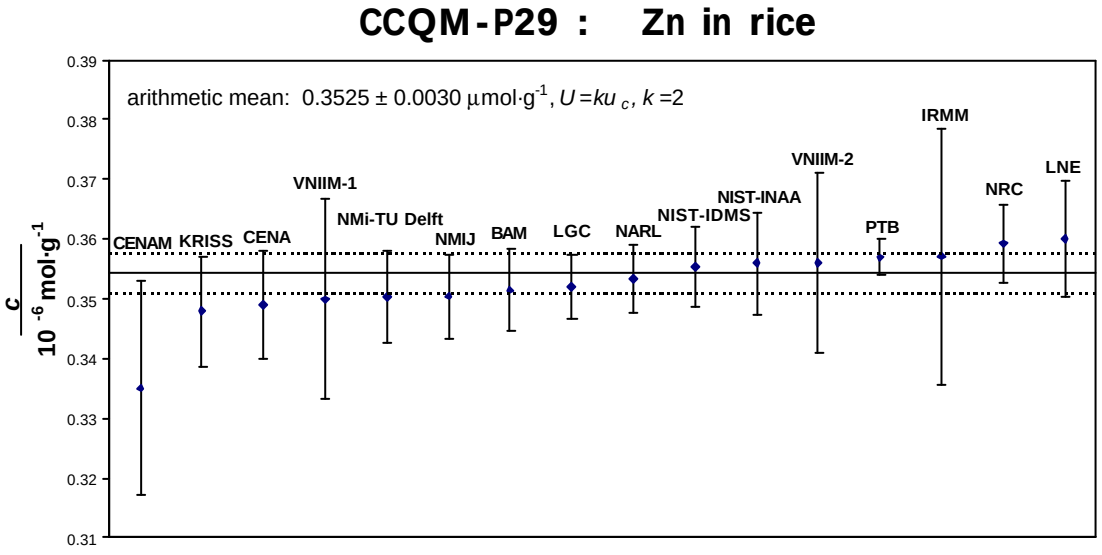
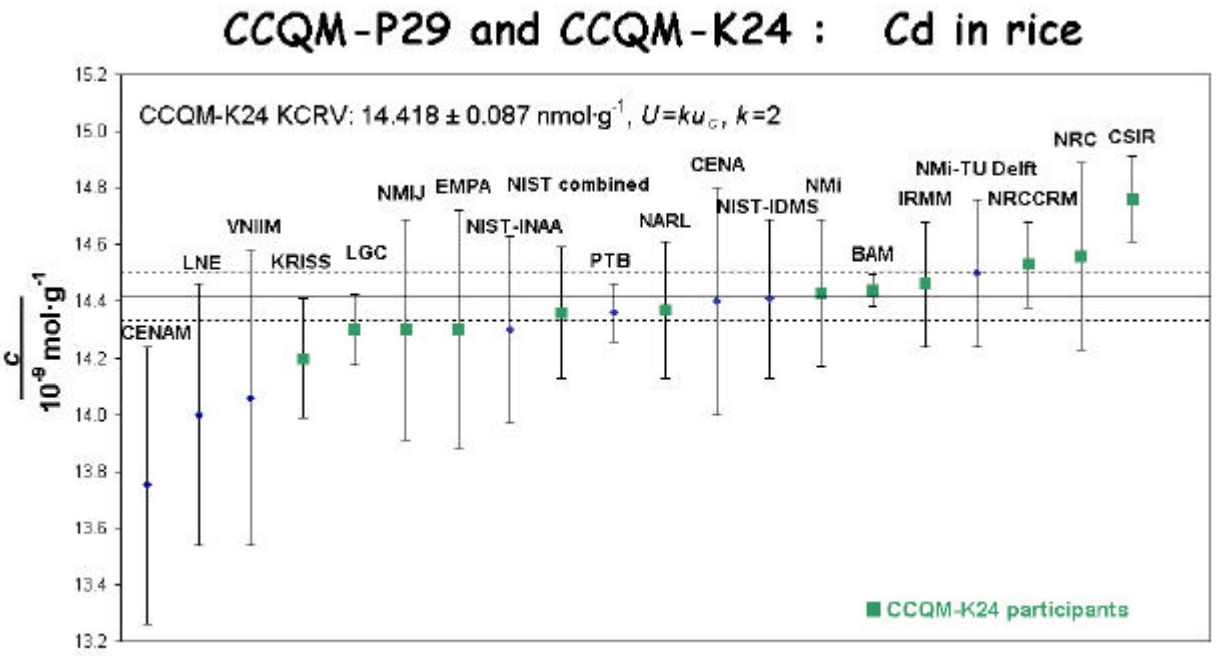


Figure 3. CCQM-P29 and CCQM-K24 participants' measurement results for cadmium with the CCQM-K24 KCRV



8. Summary statistics of this study

In Table 10 the mean, the median and the weighted mean are given for the CCQM-P29 study with a coverage factor k=2.
There were no significant differences between the three values observed for Cd and for Zn.

Table 10. Summary statistics for CCQM-P29

	CCQM-P29 Cd in rice nmol·g^{-1} uncertainty (k=2)	**CCQM-P29 Zn in rice mmol·g^{-1} uncertainty (k=2)**
Mean*	14.22 ± 0.18	0.3525 ± 0.0030
Median**	14.33 ± 0.13	0.3527 ± 0.0024
Weighted Mean***	14.33 ± 0.16	0.3540 ± 0.0034

* uncertainty of the mean estimated as stdev. of the mean
**uncertainty of the median was estimated applying "robust statistics" [9]
***uncertainty of the weighted mean estimated as stdev. of the weighted mean

Although there is no need to agree on a KCRV in a pilot study, the CCQM-K24 KCRV is included in Figure 1 and Figure 3. The arithmetic mean of participants' results for the Zn measurements is included in Figure 2 as information to the CCQM-P29 participants.

9. Discussion

The pilot study CCQM-P29 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-P29 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 and Zn amount content in CCQM-P29 are comparable, despite the slight differences in the applied methods for dry-mass correction.

The performance of participants in the CCQM-P29 was very good. Laboratories participating in CCQM-P29 and/or CCQM-K24 could prove their measurement capability to measure Cd and Zn in rice. The good agreement of results in CCQM-P29 clearly showed "how far the light of the key-comparison CCQM-K24 shines". There is no further need to organise a key-comparison on Zn in rice.

After approval by the CCQM this study will be published in the "Technical Supplement to Metrologia".

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