CCQM-K2 Key Comparison
Cadmium and Lead content in natural water

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Abstract

The CCQM-K2 Key Comparison allows comparison of the capability of nine National Metrology Institutes (NMIs) for Cd and Pb content measurement in natural river water. The study was co-ordinated by the Institute for Reference Materials and Measurements (IRMM, Geel, Belgium) of the Joint Research Centre of the European Commission. The comparison was run in parallel and using the same sample with the interlaboratory comparison IMEP-9 “trace elements in water”. All participants used isotope Dilution Mass Spectrometry (IDMS) as measurement method. Good agreement of results (especially for Cd measurements) was evident and this is in agreement with conclusions from previous studies on simpler matrices and higher amount concentrations.

1. Introduction

The 2nd Key Comparison of the Comité Consultatif pour la Quantité de Matière (CCQM) was initiated during the 4th CCQM meeting (19-20 February 1998). This key comparison (CCQM-K2) was co-ordinated through the "inorganic analysis working group" of CCQM and it can be considered as a continuation of CCQM-1 study, "Lead in Water". CCQM-K2 focused on the measurement of cadmium and lead in natural water using the Primary Method of Measurement (PMM) Isotope Dilution Mass Spectrometry (IDMS).

During the CCQM meeting, it was decided to use samples from IRMM's (Institute for Reference Materials and Measurements, Joint Research Centre, European Commission, Geel, Belgium) IMEP-9 (International Measurement Evaluation Programme, round 9, trace elements in water) and IRMM was designated to co-ordinate CCQM-K2. Using the IMEP-9 samples for the needs of CCQM-K2 have two advantages. It would allow a fast response (IMEP-9 was already running by that time and samples were available) and in addition it would enable to compare the performance of high-level metrology laboratories (National Metrology Institutes which participate in CCQM-K2) against the performance of a number of "field laboratories" (IMEP participants [1]). Additionally IMEP offers links to Proficiency Testing (PT) schemes and it supports European and other regional accreditation co-operations.

2. Participation in CCQM-K2

Table 1 presents the CCQM member laboratories (NMIs), which signed on to participate in CCQM-K2. VNIIM (D.I. Mendeleyev Institute for Metrology, St. Petersburg, Russia) participated in the comparison but withdrew its results (because the sample was opened by

customs, potentially causing contamination), whereas BAM (Bundesanstalt für Materialforschung und –Prüfung, Berlin, Germany) signed on for participation, but did not participate due to technical problems.

Table 1. CCQM-K2 key comparison participants

3. Certified Test Samples

At the time of the 4th CCQM meeting, IRMM had already launched the IMEP-9 measurement round on trace elements in water. Certified Test Samples (CTS), with undisclosed values bottled in polyethylene containers, had been made available to IMEP-9 participants world wide. These CTS contained 60 mL of river water. The content of elements B, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Ni, Pb, Rb, Sr, U and Zn were offered for measurement to IMEP-9 participants. The intention was to establish IMEP reference ranges for amount content, were possible, using PMM.

For the needs of CCQM-K2, IRMM distributed CTS of 100 mL to each participant and the CCQM-K2 participants measured only cadmium and lead content. Only one CCQM-K2 participant (LNE) requested more sample.

The CTS, which were the subject of the IMEP-9 round (and CCQM-K2 accordingly), were sampled from the Clear Creek river (Colorado, USA) by United States Geological Survey (USGS, Colorado, USA) and further treated by Dr J. Moody at NIST (Gaithersburg, USA). The water was submitted to ultra filtration, sterilisation and stabilisation with nitric acid to pH<1.2. It was then bottled into pre-cleaned polyethylene bottles. The storage temperature of the samples was 5°C (normal refrigerator).

The CTS were available to CCQM-K2 participants from the end of April 1998 onwards. The initial deadline for reporting of results was 1st September 1998. This was extended to 1st October 1998. The CTS were sent to the CCQM-K2 participants via express mailing.

4. Instructions for the participants

Participants were left the choice of their own protocol (measurement method) and spike materials. The CTS were sent to the participants together with an information/instructions package including:

1. accompanying letter (1 page)
2. general instructions (1 page)
3. results report form (1 page)
4. instructions for uncertainty calculation (1 page)
5. proposed uncertainty budget forms for Cd and Pb (1 page each)
6. the announcement of IMEP-9(1 page)

4.1. Accompanying letter

The accompanying letter introduced the participants to the key comparison. The initial deadline of 1st September to report the results was highlighted as well as the fact that isotopically enriched materials needed for the measurements could be chosen freely by the participants or could, upon request, be provided by IRMM.

Only two participants requested isotopically enriched materials, NIMC for cadmium and VNIIM for both cadmium and lead.

4.2. General Instructions

General instructions were prepared in order to make up for the absence of an imposed protocol, as agreed during the CCQM meeting. Information concerning the CTS conditions was provided and the participants were advised to consult the protocol of CCQM-1 [2]. General instructions were given in relation to the minimisation of the possible contamination, to the preparation dilutions and blends gravimetrically, to avoidance of weighings of small aliquots, to the measurement of isotopic composition, to the correction for isotopic interferences and to the measurement of mass discrimination effects.

4.3. Results report form

This form was prepared in order to obtain consistency in the reporting of results. The unit of the reported results was requested to be $mol \cdot kg^{-1}$ (amount content). Uncertainty had to be calculated according to ISO/GUM [3].

4.4. Instructions for uncertainty calculation

The instructions document was prepared to facilitate consistent reporting of uncertainties (according to ISO/GUM [3]). The document included the recommended IDMS equation [4, 5] with explanations for each parameter. Participants were asked to evaluate the uncertainty for the measurement of each parameter of the IDMS equation and accordingly fill in the uncertainty budgets for the measurement of each element.

4.5. Proposed uncertainty budget form

A proposed uncertainty budget form was sent to each participant. In this uncertainty budget form, all the parameters of the IDMS equation (which was given in the uncertainty instruction document) were listed. They were divided into two categories depending on the

(expected) size of the contribution to the final uncertainty: major and secondary. The reported uncertainty had to be an expanded uncertainty with coverage factor k=2.

4.6. Announcement of IMEP-9

The announcement letter of IMEP-9 was added to the package purely for informative reasons and offering participation in the measurement of all 15 elements of IMEP-9. Only one CCQM-K2 participant (VNIIM) reported measurement results (and uncertainties) for all 15 elements.

5. CCQM-K2 participants' results

The CCQM-K2 participants' results together with the associated uncertainties (expanded uncertainties k=2), as reported to IRMM, are given in Table 2 and Table 3 and additionally they are graphically displayed in Figure 1 and Figure 2.

Table 2. CCQM-K2 participants' measurement results for cadmium.

Figure 1. CCQM-K2 participants' measurement results for cadmium.

Table 3. CCQM-K2 participants' measurement results for lead.

Figure 2. CCQM-K2 participants' measurement results for lead.

6. Conclusions and considerations

Contrary to the original fear of the organisers of the study, with respect to the ~1000 fold decrease in amount content (compared to CCQM-1) and the more complex composition of the sample (natural water sample instead of high purity water), the CCQM-K2 was very successful in terms of demonstrating the degree of equivalence of participants' measurement results. Another improvement was that participants supplied full uncertainty budgets.

Table 4. Instrumental techniques used by CCQM-K2 participants.

All participants used double isotope dilution (i.e. using a primary assay standard in order to characterise their spike) as measurement method, except IRMM, who used direct isotope dilution (i.e. using a previously certified spike reference material). The instrumental techniques used by the participants for the measurement of the isotope amount ratios are given in Table 4.

The following conclusions can be drawn from the CCQM-K2 key comparison:

- The NMIs that participated in the comparison demonstrated their capability to supply equivalent measurement results for measurement of Cd and Pb in water to an adequate (fit for purpose) degree. The degree of equivalence statements can be found in the BIPM Mutual Recognition Arrangement (MRA) [6] Key Comparison database [7]. The above should be seen in light of the comparison with the IMEP-9 results [1], where field laboratories report a spread of results which is significantly larger (i.e. 90% of IMEP-9 participants reported measurement results within an interval of ± 40% of the reference value).
- It is also confirmed that the absence of uncertainty budget (as observed in previous studies, e.g. CCQM-1) makes the comparison between different "measurement results" (including their uncertainties) – and hence the establishment of their "degree of equivalence" – difficult. In this comparison the submission of uncertainty budgets by the participants simplified the above.

Taking into account the outcome of the CCQM-K2, some considerations for the future can be made:

- Similar key comparisons will be continued investigating measurement performance in more complicated matrices, especially after the launch of the BIPM MRA [6] which is partially based on demonstrated performance in Key Comparisons.

- The differences on the magnitude of the uncertainty statement are very large (in same cases a factor of 10). Taking into account that the participants used the same measurement method and similar analytical instrumentation, this might not be true. More work should be spent towards a harmonised approach of calculating and reporting uncertainties.
- An important challenge for the future metrological infrastructure in chemical measurement is to ensure a proper link between demonstrated measurement capability at the NMI level and the measurement capability of the field laboratories.

7. Acknowledgement

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8. References

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7. The BIPM key comparison database http://www.bipm.fr/enus/8_Key_Comparisons/database.html

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Table 1. CCQM-K2 key comparison participants

institution / organisation	origin
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**
NIMC National Institute of Materials and Chemical Research	**Japan**
NIST National Institute for Standards and Technology	**USA**
NMi Nederlands Meetinstituut	**The Netherlands**
NRC National Research Council of Canada	**Canada**
PTB Physikalisch-Technische Bundesanstalt	**Germany**

Table 2. CCQM-K2 participants' measurement results for cadmium.

participant	report date	reported result amount content/($nmol \cdot kg^{-1}$)	expanded uncertainty (k=2) amount content/($nmol \cdot kg^{-1}$)
NIST	98-12-07	82.38	0.22
PTB	98-09-04	82.7	2.2
KRISS	98-08-25	82.9	1.25
LGC	98-09-03	83.07	0.60
IRMM	98-08-28	83.4	2.5
NRC	98-09-14	83.7	2.2
NMi	98-08-26	83.9	1.8
NIMC	98-09-18	84.6	2.0
LNE	98-09-03	84.8	3.9

Table 3. CCQM-K2 participants' measurement results for lead.

participant	report date	reported result amount content/($nmol \cdot kg^{-1}$)	expanded uncertainty (k=2) amount content/($nmol \cdot kg^{-1}$)
PTB	98-09-04	61.0	0.9
NMi	98-12-03	61.4	2.2
NIMC	98-09-18	62.21	0.60
KRISS	98-08-25	62.3	0.89
LGC	98-09-03	62.34	1.24
NRC	98-09-14	62.6	1.5
IRMM	98-08-28	62.73	0.52
NIST	98-12-07	62.84	0.29
LNE	98-09-03	65.9	2.7

Table 4. Instrumental techniques used by CCQM-K2 participants.
(ICP-MS: Inductively Coupled Plasma Mass Spectrometry. HR-ICP-MS: High Resolution ICP-MS)

participant	technique
PTB	ICP-MS
NMi	sector ICP-MS
NIMC	ICP-MS
KRISS	HR-ICP-MS
LGC	HR-ICP-MS *
NRC	ICP-MS
IRMM	ICP-MS
NIST	ICP-MS
LNE	ICP-MS

* LGC used a HR-ICP-MS in low-resolution mode.

Figure 1. CCQM-K2 participants' measurement results for cadmium.

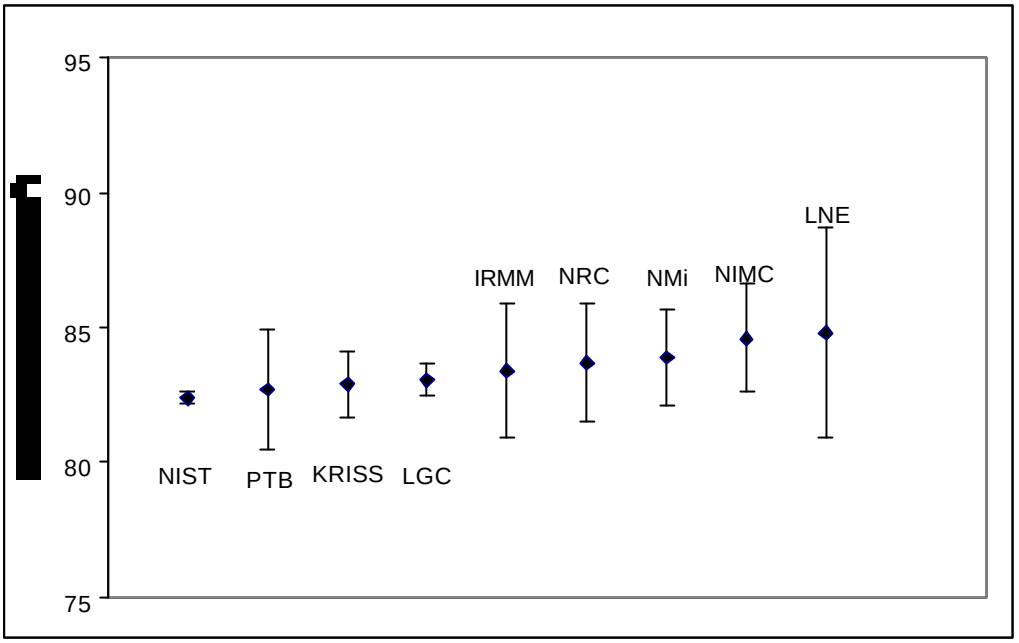

Figure 2. CCQM-K2 participants' measurement results for lead.