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**IRMM** **GE/R/IM/13/01**
**Isotope Measurements Unit** **July 2001**

# CCQM-K13 key comparison Cadmium and Lead amount content in sediment

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## *Final Report*

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## Abstract

The CCQM-K13 key comparison was performed as a successor of CCQM-P15 study in order to demonstrate and document the capability of interested National Metrology Institutes to measure Cd and Pb content in a sediment sample. The comparison is an activity of the Inorganic Analysis Working Group (IAWG) of CCQM and was piloted by the Institute for Reference Materials and Measurements (IRMM, Geel, Belgium) of the Joint Research Centre (JRC) of the European Commission. The majority of the participants applied isotope dilution mass spectrometry (IDMS) using various mass spectrometry techniques. External standard calibration was used by two participants for the Cd measurement and by one participant for the Pb measurement.

The following laboratories participated in key comparison (alphabetical order).
BAM, Germany
CENAM, Mexico
CSIR-NML, South-Africa
IRMM, European Commission
KRISS, Korea
LGC, United Kingdom
LNE, France
NARL, Australia
NIMC, Japan
NIST, United States of America
NRC, Canada
NRCCRM, China
PTB, Germany
VNIIM, Russian Federation

Satisfactory agreement of reported results was observed and displayed. The Key Comparison Reference Value (KCRV) was agreed upon (in a meeting of the participants prior to the IAWG meeting of April 2001) as the "median" of the reported participants' results excluding only the results of two participants (CENAM and PTB) for the Cd measurement. Accordingly the equivalence statements were produced.

# 1. Introduction

Taking into account the acceptable performance of the Comité Consultatif pour la Quantité de Matière (CCQM) member NMIs in the CCQM-P15 pilot study (Cd and Pb in sediment) [1], it was agreed that a key comparison should be organised in order to document the existing measurement capability in view of the CIPM Mutual Recognition Arrangement (MRA). The K13 key comparison of CCQM was agreed upon during the 6th CCQM meeting (April 2000). This key comparison (CCQM-K13) is an activity of the "Inorganic Analysis Working Group" (IAWG) of the CCQM and is titled "Cadmium and lead amount content in sediment".

# 2. Participation in CCQM-K13

Table 1 presents the NMIs that participated in CCQM-K13. Another NMI (NMi, The Netherlands) registered for the comparison, received a sample but did not submit any results due to measurement equipment problems.

**Table 1. CCQM-K13 participants**

| institution / organisation | origin |
|---|---|
| **BAM** Bundesanstalt für Materialforschung und –Prüfung, Berlin | **Germany** |
| **CENAM** Centro Nacional de Metrologia | **Mexico** |
| **CSIR-NML** National Metrology Laboratory | **South Africa** |
| **IRMM** Institute for Reference Materials and Measurements | **European Commission** |
| **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** |
| **NIMC** National Institute of Materials and Chemical Research | **Japan** |
| **NIST** National Institute for Standards and Technology | **United States of America** |
| **NRC** National Research Council of Canada | **Canada** |
| **NRCCRM** National Research Centre for Certified Reference Materials | **China** |
| **PTB** Physikalisch-Technische Bundesanstalt | **Germany** |
| **VNIIM** Mendeleyief Institute of Metrology | **Russian Federation** |

## 3. Sample

The CCQM-K13 sample was an estuarine sediment prepared and made available by the Management of Reference Materials (MRM) Unit of IRMM. Each bottle of the sample contained ~ 40 g of fine sediment powder. The samples were tested for stability and homogeneity. The minimum sample mass in order to achieve 1% precision was calculated to be 76 mg for Cd and 58 mg for Pb [2].

## 4. Time schedule

The samples, together with the information/instructions documents, were made available to CCQM-K13 participants during the month of July 2000. The deadline for reporting of results and uncertainties was 31$^{st}$ October 2000 and preliminary results were presented in the IAWG meeting in Teddington (November 2000). The "draft A" report of CCQM-K13 was distributed during March 2001 and presented to the IAWG meeting at the BIPM (April 2001), at which time the Key Comparison Reference Values were agreed upon. Then the "draft A" was presented to the 7$^{th}$ CCQM meeting at BIPM (April 2001) and provisionally accepted for equivalence after approval of this report by the CCQM WG chairmen.

## 5. Instructions to the participants

An information package similar to the one distributed for the CCQM-P15 was prepared. The CCQM-K13 samples were sent to the participants together with this information package, which included:

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

The complete information package is given in the Annex C of this report.

## 6. Methods and instrumentation used

In the instruction documents, the choice of protocol for the measurements was left to the participants. Nevertheless apart from some general suggestions, some additional suggestions were given for the participants who chose isotope dilution mass spectrometry (IDMS), which was recognised as a potential primary method of measurement (PMM).

Only two CCQM-K13 participants did not apply isotope dilution mass spectrometry for the determination of both elements. CENAM applied external standard calibration for both elements (using In and Tl as internal standards for Cd and Pb measurement respectively), whilst CSIR-NML applied external calibration for Cd measurement, but IDMS for the Pb

determination. The instrumentation used by all participants was based on mass spectrometry (MS). Two participants (BAM and NRCCRM) used thermal ionisation MS (TIMS), one participant (NARL) used both high resolution (HR) and quadrupole (Q) inductively coupled plasma MS (ICP-MS), while seven (IRMM, LNE, NIMC, NIST, NRC, PTB and VNIIM) participants used Q-ICP-MS and four (CENAM, CSIR-NML, KRISS and LGC) HR-ICP-MS. Table 2 gives an overview of the method applied and the instrumentation used by each CCQM-K13 participant.

**Table 2. Analytical methods and instrumental techniques used by CCQM-K13 participants.**

| *participant* | *method* | *instrumentation* |
|---|---|---|
| **BAM** | IDMS | TIMS |
| **CENAM** | external calibration | HR-ICP-MS |
| **CSIR-NML** | ext. calibration /IDMS* | HR-ICP-MS |
| **IRMM** | IDMS | Q-ICP-MS |
| **KRISS** | IDMS | HR-ICP-MS |
| **LGC** | IDMS | HR-ICP-MS |
| **LNE** | IDMS | Q-ICP-MS |
| **NARL** | IDMS | HR & Q ICP-MS |
| **NIMC** | IDMS | Q-ICP-MS |
| **NIST** | IDMS | Q-ICP-MS |
| **NRC** | IDMS | Q-ICP-MS |
| **NRCCRM** | IDMS | TIMS |
| **PTB** | IDMS | Q-ICP-MS |
| **VNIIM** | IDMS | Q-ICP-MS |

* External calibration applied for Cd measurement and IDMS for Pb measurement.

Several other data concerning the measurements of participating NMIs (e.g. acid mixture for the digestion, isotope pair used for IDMS) were made available via the questionnaire which was distributed and they are presented in Annex D of this report.

## 7. CCQM-K13 participants' results

The CCQM-K13 participants' results, as reported to the pilot institute (IRMM), are given in Table 4 and Table 5. All the numbers are rounded to two digit of uncertainty. All participants provided uncertainty budgets and the majority based their budget on the proposed format (given in Annex C of this report). The coverage factors given for the expanded uncertainties was $k$=2, with the exception of the coverage factors given in Table 3.

**Table 3. Measurement uncertainty coverage factors ($k$) given (other than $k$=2)**

| *participant* | *for Cd measurement* | *for Pb measurement* |
|---|---|---|
| **BAM** | **3** | **2** |
| **NIST** | **2.09** | **1.98** |
| **PTB** | **2.1** | **2.2** |

It must be noted that two of the participants (NRCCRM and CSIR-NML) originally reported results with mistakes in the decimal points, which were corrected after careful calculations by the participants themselves.

**Table 4. CCQM-K13 participants' measurement results for cadmium.**

| *participant* | *report date* | *reported value* $nmol \cdot g^{-1}$ | *uncertainty* $nmol \cdot g^{-1}$ | *relative uncertainty (%)* |
|---|---|---|---|---|
| **CENAM** | **22-12-00** | **2.13** | **0.22** | **10.3** |
| **LGC** | **1-11-00** | **5.15** | **0.19** | **3.7** |
| **CSIR-NML** | **31-10-00** | **5.19** | **0.16** | **3.1** |
| **KRISS** | **6-11-00** | **5.29** | **0.10** | **1.9** |
| **NRCCRM** | **20-11-00** | **5.30** | **0.21** | **4.0** |
| **NARL** | **6-11-00** | **5.31** | **0.13** | **2.4** |
| **NIST** | **1-11-00** | **5.397** | **0.058** | **1.1** |
| **NIMC** | **1-11-00** | **5.43** | **0.20** | **3.7** |
| **NRC** | **13-11-00** | **5.43** | **0.13** | **2.4** |
| **IRMM** | **31-10-00** | **5.59** | **0.19** | **3.4** |
| **BAM** | **30-10-00** | **5.681** | **0.087** | **1.5** |
| **LNE** | **2-11-00** | **5.87** | **0.32** | **5.5** |
| **VNIIM** | **3-11-00** | **6.15** | **0.24** | **3.9** |
| **PTB** | **7-11-00** | **6.40** | **0.40** | **6.3** |

**Table 5. CCQM- K13 participants' measurement results for lead.**

| *participant* | *report date* | *reported value* $nmol \cdot g^{-1}$ | *uncertainty* $nmol \cdot g^{-1}$ | *relative uncertainty (%)* |
|---|---|---|---|---|
| **VNIIM** | **3-11-00** | **160.6** | **4.3** | **2.7** |
| **PTB** | **7-11-00** | **165.0** | **5.0** | **3.0** |
| **CENAM** | **1-11-00** | **168.0** | **5.9** | **3.5** |
| **NARL** | **6-11-00** | **169.0** | **3.9** | **2.3** |
| **BAM** | **30-10-00** | **169.1** | **2.2** | **1.3** |
| **NIST** | **1-11-00** | **169.50** | **0.65** | **0.4** |
| **NRC** | **13-11-00** | **169.5** | **2.2** | **1.3** |
| **LGC** | **1-11-00** | **170.2** | **5.2** | **3.1** |
| **NIMC** | **1-11-00** | **170.2** | **1.5** | **0.9** |
| **CSIR-NML** | **31-10-00** | **171.1** | **3.8** | **2.2** |
| **KRISS** | **6-11-00** | **172.0** | **4.8** | **2.8** |
| **LNE** | **2-11-00** | **172.7** | **6.4** | **3.7** |
| **NRCCRM** | **31-10-00** | **172.7** | **2.8** | **1.6** |
| **IRMM** | **31-10-00** | **173.8** | **4.0** | **2.3** |

# 8. KCRV and its uncertainties

A meeting of the CCQM-K13 participants (all present except for CSIR-NML) was dedicated to the calculation of the CCQM-K13 KCRV and its uncertainties. Two important aspects were discussed. The first was whether the exclusion of some outlying results from the calculation of the KCRV and its uncertainty was permissible; the second was the exact method by which the KCRV would be calculated.

## *8.1. Results accepted for the KCRV calculation*

Concerning the data to be included, it was agreed that all data are acceptable independently of the method used. The debate focused on use of results obtained by means of primary methods of measurements and results obtained by laboratories which participated in the pilot study (CCQM-P15). The majority of the participants were of the opinion that no real differentiation should be made.
In two cases for the Cd measurement, however, the relevant participants withdrew their data from the KCRV calculation.

- PTB (voluntarily) withdrew its results from inclusion in the KCRV for Cd because of a measurement bias that was undetected prior to submission of results. Lack of experience in the method and not having participated in the pilot study were cited as reasons for this failure. The bias was attributed to undetected interference by polyatomic oxide and hydroxides of Mo and Zr that have the same nominal mass as the Cd isotopes chosen for the analysis.

- CENAM withdrew its results of Cd measurements for similar reasons. The bias observed, was mainly caused by the lack of corrections due to several sources of interference, which were produced due to the fact that internal standard method (using $^{115}In$ as internal standard) with mass spectrometry was used. Principal interference on $^{115}In$, which was not taken into account in the correction, was the $^{75}As^{40}Ar$.

### *8.2. KCRV calculation*

According to BIPM, there is no rule as to the choice of calculation of the KCRV (i.e., the KCRV can be the mean, median or weighted mean of the accepted results). This is left to the discretion of the relevant CCQM working groups and to the participants of each key comparison.
Calculations were made to compare the three possibilities for both elements.

**Table 6. KCRV (and its uncertainty) calculations**

| calculation as: | Cd measurement KCRV ± uncertainty (k=2) in mmol/kg | Pb measurement KCRV ± uncertainty (k=2) in mmol/kg |
|---|---|---|
| **Mean** | 5.48 ± 0.17 | 169.5 ± 1.8 |
| **Median** | **5.41 ± 0.17** | **169.9 ± 1.6** |
| **Weighted Mean** | 5.434 ± 0.035 | 169.63 ± 0.51 |

Table 6 presents the values of the KCRV and the relevant uncertainty (k=2) for both Cd and Pb measurements, calculated according the three different approaches available. For both type of measurement all three approaches results "overlapping" values within uncertainties.
Mean and median values give very similar uncertainty ranges while the weighted mean gives considerably lower uncertainties (a factor of 5 and 3 for Cd and Pb measurement respectively).
The weighted mean approach was rejected because the KCRV uncertainty statement would be dominated by a minority of laboratories that reported very small measurement uncertainties. This would not be appropriate for this comparison, since the difference in the measurement uncertainties of the laboratories (factor of 9 for both Cd and Pb measurements) does not reflect the difference in measurement capability but the lack of common approach for calculation of measurement uncertainties.
It was decided that the choice of the median was the most appropriate for both Cd and Pb measurement, since in this way the KCRV would be less affected by low or high values.

## 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 degree of equivalence (and its uncertainty) between two NMI results is calculated according to the following equations:

$$D_{ij} = (x_i - x_j) \qquad U_{ij}^2 = 2^2(u_i^2 + u_j^2)$$

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 $u_j$.

The equivalence statements of the CCQM-K13 are presented in the Annex B of this report, together with the relevant graphical display.

## 11. Discussion

The previous work of the IAWG of CCQM on IDMS dealt with simple matrices. CCQM-P1 [3] study involved determination of Pb in dilute aqueous acid and CCQM-K2 [4] involved determination of Pb and Cd in natural (river) water. The CCQM-P15 pilot study Cd and Pb in sediment [1] dealt for the first time with a more complicated "sediment" matrix. The sediment sample treatment is complex, including acid digestion, which can result in sample losses and higher blank values. Moreover the measurement of the water content of the sediment is an additional source of uncertainty. In addition, the determination of Cd by IDMS is complicated by the possibility of bias introduced by the overlap of the Cd isotopes selected for the analysis by oxide and/or hydroxide polyatomic species of Mo and, in particular, Zr .

The "acceptable" performance of participants in CCQM-P15 led to the organisation of the CCQM-K13 key comparison. The majority of the participants agreed that the CCQM-K13 sample was more difficult to handle in comparison with the CCQM-P15 sample, primarily because of a higher content of tin, several isotopes of which overlap the Cd isotopes. Nevertheless the performance of participants in the CCQM-K13 is of the same level as in CCQM-P15.

## 12. Acknowledgement

Special thanks is ought to Mrs L. Van Nevel and Mrs E. Poulsen (IRMM) for providing exquisite logistic and secretarial support, to Dr J. Pauwels (IRMM) and Dr A. Lamberty (IRMM) for supplying the samples and to Dr M. Sargent (LGC) for his assistance as chairman of the Inorganic Analysis WG of CCQM.

## 13. References

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3. CCQM-P1 data, contact R. Watters, NIST, Gaithersburg
4. I. Papadakis et. al. CCQM-K2 key comparison: Cadmium and Lead content in natural water, METROLOGIA, 2001, in press

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# *Annex A*

# *Graphical display of CCQM-K13 results and the KCRV(s)*

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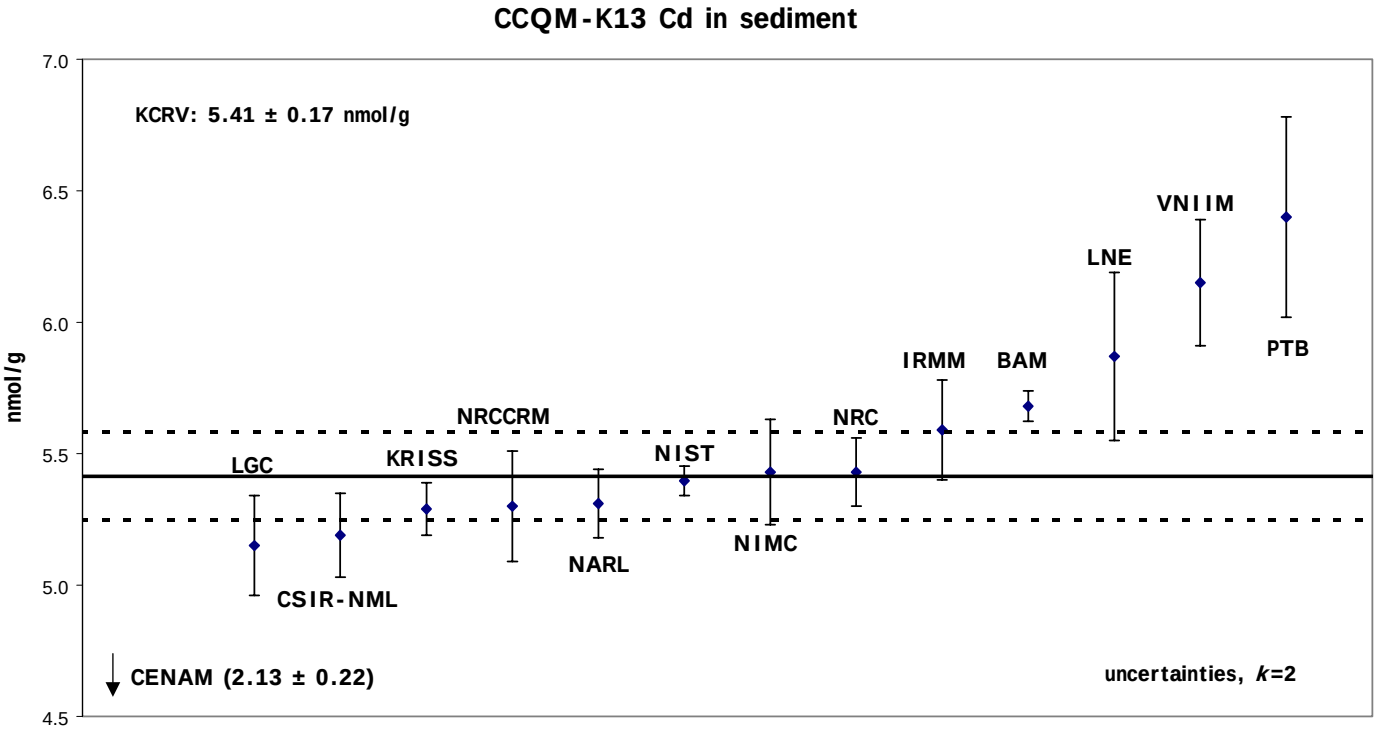
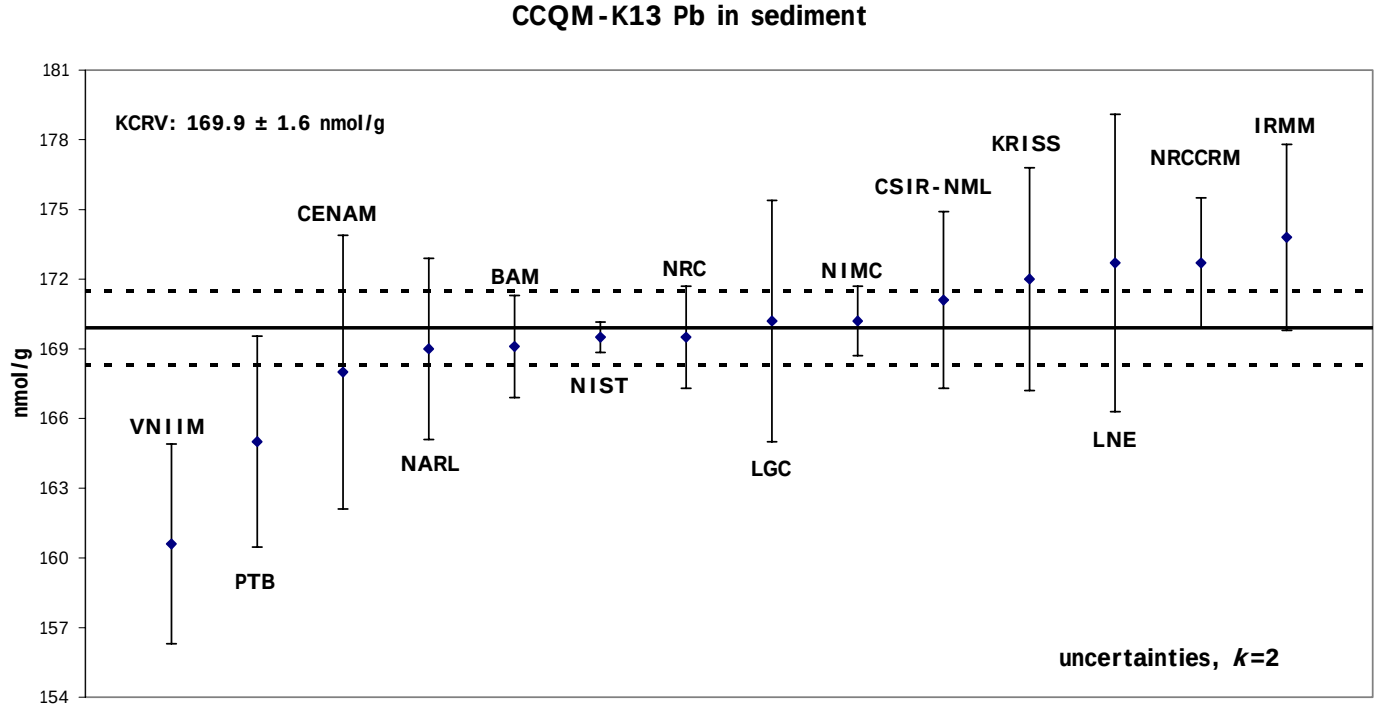
# Graphical display of CCQM-K13 results

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# *Annex B*

# *Equivalence Statements*

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

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# Equivalence statements for Cd measurement

**MEASURAND :** amount concentration of Cd in sediment
**NOMINAL VALUE:** ~ 5.5 µmol/kg

**Key comparison reference value (KCRV)** $x_{R=}$ 5.414 µmol/kg
**Uncertainty of KCRV** $u_R$= 0.084 µmol/kg ($k$=1)

**The KCRV was calculated as the median of all results excluding CENAM and PTB results**
**The uncertainty of the KCRV was calculated as the median uncertainty of the results used**

**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 µmol/kg

**The degree of equivalence between two laboratories is given by a pair of numbers:**
$D_{ii} = x_i - x_i$ and $U_{ii}$, its expanded uncertainty ($k$ = 2),
$U_{ii}^2 = 2^2(u_i^2 + u_i^2)$, both expressed in µmol/kg

Lab *j* ⇨

Lab *i* ⇩

| | $D_i$ µmol/kg | $U_i$ µmol/kg |
|---|---|---|
| BAM | 0.27 | 0.18 |
| CENAM | -3.28 | 0.28 |
| CSIR-NML | -0.22 | 0.23 |
| IRMM | 0.18 | 0.26 |
| KRISS | -0.12 | 0.20 |
| LGC | -0.26 | 0.26 |
| LNE | 0.46 | 0.36 |
| NARL | -0.10 | 0.21 |
| NIMC | 0.02 | 0.26 |
| NIST | -0.02 | 0.18 |
| NRC | 0.02 | 0.21 |
| NRCCRM | -0.11 | 0.28 |
| PTB | 0.99 | 0.42 |
| VNIIM | 0.74 | 0.29 |

| BAM | | CENAM | | CSIR-NML | | IRMM | | KRISS | | LGC | | LNE | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $D_{ij}$ µmol/kg | $U_{ij}$ µmol/kg | $D_{ij}$ µmol/kg | $U_{ij}$ µmol/kg | $D_{ij}$ µmol/kg | $U_{ij}$ µmol/kg | $D_{ij}$ µmol/kg | $U_{ij}$ µmol/kg | $D_{ij}$ µmol/kg | $U_{ij}$ µmol/kg | $D_{ij}$ µmol/kg | $U_{ij}$ µmol/kg | $D_{ij}$ µmol/kg | $U_{ij}$ µmol/kg |
| | | 3.55 | 0.23 | 0.49 | 0.17 | 0.09 | 0.21 | 0.39 | 0.12 | 0.53 | 0.21 | -0.19 | 0.33 |
| -3.55 | 0.23 | | | -3.06 | 0.27 | -3.46 | 0.30 | -3.16 | 0.24 | -3.02 | 0.30 | -3.74 | 0.39 |
| -0.49 | 0.17 | 3.06 | 0.27 | | | -0.40 | 0.26 | -0.10 | 0.19 | 0.04 | 0.26 | -0.68 | 0.36 |
| -0.09 | 0.21 | 3.46 | 0.30 | 0.40 | 0.26 | | | 0.30 | 0.22 | 0.44 | 0.28 | -0.28 | 0.38 |
| -0.39 | 0.12 | 3.16 | 0.24 | 0.10 | 0.19 | -0.30 | 0.22 | | | 0.14 | 0.22 | -0.58 | 0.34 |
| -0.53 | 0.21 | 3.02 | 0.30 | -0.04 | 0.26 | -0.44 | 0.28 | -0.14 | 0.22 | | | -0.72 | 0.38 |
| 0.19 | 0.33 | 3.74 | 0.39 | 0.68 | 0.36 | 0.28 | 0.38 | 0.58 | 0.34 | 0.72 | 0.38 | | |
| -0.37 | 0.14 | 3.18 | 0.26 | 0.12 | 0.21 | -0.28 | 0.24 | 0.02 | 0.16 | 0.16 | 0.24 | -0.56 | 0.35 |
| -0.25 | 0.21 | 3.30 | 0.30 | 0.24 | 0.26 | -0.16 | 0.28 | 0.14 | 0.22 | 0.28 | 0.28 | -0.44 | 0.38 |
| -0.28 | 0.08 | 3.27 | 0.23 | 0.21 | 0.17 | -0.19 | 0.21 | 0.11 | 0.11 | 0.25 | 0.21 | -0.47 | 0.32 |
| -0.25 | 0.14 | 3.30 | 0.26 | 0.24 | 0.21 | -0.16 | 0.24 | 0.14 | 0.16 | 0.28 | 0.24 | -0.44 | 0.35 |
| -0.38 | 0.23 | 3.17 | 0.31 | 0.11 | 0.27 | -0.29 | 0.30 | 0.01 | 0.24 | 0.15 | 0.30 | -0.57 | 0.39 |
| 0.72 | 0.39 | 4.27 | 0.44 | 1.21 | 0.41 | 0.81 | 0.43 | 1.11 | 0.39 | 1.25 | 0.43 | 0.53 | 0.50 |
| 0.47 | 0.25 | 4.02 | 0.33 | 0.96 | 0.29 | 0.56 | 0.31 | 0.86 | 0.26 | 1.00 | 0.31 | 0.28 | 0.40 |

Lab *j* ⇨

Lab *i* ⇩

| | $D_i$ µmol/kg | $U_i$ µmol/kg |
|---|---|---|
| BAM | 0.27 | 0.18 |
| CENAM | -3.28 | 0.28 |
| CSIR-NML | -0.22 | 0.23 |
| IRMM | 0.18 | 0.26 |
| KRISS | -0.12 | 0.20 |
| LGC | -0.26 | 0.26 |
| LNE | 0.46 | 0.36 |
| NARL | -0.10 | 0.21 |
| NIMC | 0.02 | 0.26 |
| NIST | -0.02 | 0.18 |
| NRC | 0.02 | 0.21 |
| NRCCRM | -0.11 | 0.28 |
| PTB | 0.99 | 0.42 |
| VNIIM | 0.74 | 0.29 |

| NARL | | NIMC | | NIST | | NRC | | NRCCRM | | PTB | | VNIIM | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $D_{ij}$ µmol/kg | $U_{ij}$ µmol/kg | $D_{ij}$ µmol/kg | $U_{ij}$ µmol/kg | $D_{ij}$ µmol/kg | $U_{ij}$ µmol/kg | $D_{ij}$ µmol/kg | $U_{ij}$ µmol/kg | $D_{ij}$ µmol/kg | $U_{ij}$ µmol/kg | $D_{ij}$ µmol/kg | $U_{ij}$ µmol/kg | $D_{ij}$ µmol/kg | $U_{ij}$ µmol/kg |
| 0.37 | 0.14 | 0.25 | 0.21 | 0.28 | 0.08 | 0.25 | 0.14 | 0.38 | 0.23 | -0.72 | 0.39 | -0.47 | 0.25 |
| -3.18 | 0.26 | -3.30 | 0.30 | -3.27 | 0.23 | -3.30 | 0.26 | -3.17 | 0.31 | -4.27 | 0.44 | -4.02 | 0.33 |
| -0.12 | 0.21 | -0.24 | 0.26 | -0.21 | 0.17 | -0.24 | 0.21 | -0.11 | 0.27 | -1.21 | 0.41 | -0.96 | 0.29 |
| 0.28 | 0.24 | 0.16 | 0.28 | 0.19 | 0.21 | 0.16 | 0.24 | 0.29 | 0.30 | -0.81 | 0.43 | -0.56 | 0.31 |
| -0.02 | 0.16 | -0.14 | 0.22 | -0.11 | 0.11 | -0.14 | 0.16 | -0.01 | 0.24 | -1.11 | 0.39 | -0.86 | 0.26 |
| -0.16 | 0.24 | -0.28 | 0.28 | -0.25 | 0.21 | -0.28 | 0.24 | -0.15 | 0.30 | -1.25 | 0.43 | -1.00 | 0.31 |
| 0.56 | 0.35 | 0.44 | 0.38 | 0.47 | 0.32 | 0.44 | 0.35 | 0.57 | 0.39 | -0.53 | 0.50 | -0.28 | 0.40 |
| | | -0.12 | 0.24 | -0.09 | 0.14 | -0.12 | 0.18 | 0.01 | 0.26 | -1.09 | 0.40 | -0.84 | 0.27 |
| 0.12 | 0.24 | | | 0.03 | 0.21 | 0.00 | 0.24 | 0.13 | 0.30 | -0.97 | 0.43 | -0.72 | 0.31 |
| 0.09 | 0.14 | -0.03 | 0.21 | | | -0.03 | 0.14 | 0.10 | 0.23 | -1.00 | 0.39 | -0.75 | 0.25 |
| 0.12 | 0.18 | 0.00 | 0.24 | 0.03 | 0.14 | | | 0.13 | 0.26 | -0.97 | 0.40 | -0.72 | 0.27 |
| -0.01 | 0.26 | -0.13 | 0.30 | -0.10 | 0.23 | -0.13 | 0.26 | | | -1.10 | 0.44 | -0.85 | 0.33 |
| 1.09 | 0.40 | 0.97 | 0.43 | 1.00 | 0.39 | 0.97 | 0.40 | 1.10 | 0.44 | | | 0.25 | 0.45 |
| 0.84 | 0.27 | 0.72 | 0.31 | 0.75 | 0.25 | 0.72 | 0.27 | 0.85 | 0.33 | -0.25 | 0.45 | | |

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# Equivalence statements for Pb measurement

**MEASURAND :** amount concentration of Pb in sediment
**NOMINAL VALUE:** ~ 170 µmol/kg

**Key comparison reference value (KCRV)** $x_{R=}$ 169.90 µmol/kg
**Uncertainty of KCRV** $u_{R=}$ 0.80 µmol/kg ($k$=1)

**The KCRV was calculated as the median of all results**
**The uncertainty of the KCRV was calculated as the median uncertainty of all results**

**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 µmol/kg

**The degree of equivalence between two laboratories is given by a pair of numbers:**
$D_{ij} = x_i - x_j$ and $U_{ij}$, its expanded uncertainty ($k$ = 2),
$U_{ij}^2 = 2^2(u_i^2 + u_i^2)$, both expressed in µmol/kg

Lab *j* ⇨

Lab *i* ⇩

| | $D_i$ µmol/kg | $U_i$ µmol/kg | BAM | | CENAM | | CSIR-NML | | IRMM | | KRISS | | LGC | | LNE | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $D_{ij}$ µmol/kg | $U_{ij}$ µmol/kg | $D_{ij}$ µmol/kg | $U_{ij}$ µmol/kg | $D_{ij}$ µmol/kg | $U_{ij}$ µmol/kg | $D_{ij}$ µmol/kg | $U_{ij}$ µmol/kg | $D_{ij}$ µmol/kg | $U_{ij}$ µmol/kg | $D_{ij}$ µmol/kg | $U_{ij}$ µmol/kg | $D_{ij}$ µmol/kg | $U_{ij}$ µmol/kg |
| BAM | -0.8 | 2.7 | | | 1.1 | 6.4 | -2.0 | 4.4 | -4.7 | 4.6 | -2.9 | 5.3 | -1.1 | 5.6 | -3.6 | 6.8 |
| CENAM | -1.9 | 6.2 | -1.1 | 6.4 | | | -3.1 | 7.1 | -5.8 | 7.2 | -4.0 | 7.7 | -2.2 | 7.9 | -4.7 | 8.8 |
| CSIR-NML | 1.2 | 4.1 | 2.0 | 4.4 | 3.1 | 7.1 | | | -2.7 | 5.5 | -0.9 | 6.1 | 0.9 | 6.4 | -1.6 | 7.4 |
| IRMM | 3.9 | 4.3 | 4.7 | 4.6 | 5.8 | 7.2 | 2.7 | 5.5 | | | 1.8 | 6.2 | 3.6 | 6.6 | 1.1 | 7.5 |
| KRISS | 2.1 | 5.1 | 2.9 | 5.3 | 4.0 | 7.7 | 0.9 | 6.1 | -1.8 | 6.2 | | | 1.8 | 7.1 | -0.7 | 8.0 |
| LGC | 0.3 | 5.4 | 1.1 | 5.6 | 2.2 | 7.9 | -0.9 | 6.4 | -3.6 | 6.6 | -1.8 | 7.1 | | | -2.5 | 8.2 |
| LNE | 2.8 | 6.6 | 3.6 | 6.8 | 4.7 | 8.8 | 1.6 | 7.4 | -1.1 | 7.5 | 0.7 | 8.0 | 2.5 | 8.2 | | |
| NARL | -0.9 | 4.3 | -0.1 | 4.6 | 1.0 | 7.2 | -2.1 | 5.5 | -4.8 | 5.7 | -3.0 | 6.2 | -1.2 | 6.6 | -3.7 | 7.5 |
| NIMC | 0.3 | 2.2 | 1.1 | 2.7 | 2.2 | 6.2 | -0.9 | 4.1 | -3.6 | 4.3 | -1.8 | 5.0 | 0.0 | 5.4 | -2.5 | 6.6 |
| NIST | -0.4 | 1.7 | 0.4 | 2.3 | 1.5 | 6.0 | -1.6 | 3.9 | -4.3 | 4.1 | -2.5 | 4.8 | -0.7 | 5.2 | -3.2 | 6.4 |
| NRC | -0.4 | 2.7 | 0.4 | 3.1 | 1.5 | 6.4 | -1.6 | 4.4 | -4.3 | 4.6 | -2.5 | 5.3 | -0.7 | 5.6 | -3.2 | 6.8 |
| NRCCRM | 2.8 | 3.2 | 3.6 | 3.6 | 4.7 | 6.6 | 1.6 | 4.7 | -1.1 | 4.9 | 0.7 | 5.6 | 2.5 | 5.9 | 0.0 | 7.0 |
| PTB | -4.9 | 4.8 | -4.1 | 5.0 | -3.0 | 7.5 | -6.1 | 5.9 | -8.8 | 6.1 | -7.0 | 6.6 | -5.2 | 6.9 | -7.7 | 7.8 |
| VNIIM | -9.3 | 4.7 | -8.5 | 4.9 | -7.4 | 7.4 | -10.5 | 5.8 | -13.2 | 5.9 | -11.4 | 6.5 | -9.6 | 6.8 | -12.1 | 7.8 |

Lab *j* ⇨

Lab *i* ⇩

| | $D_i$ µmol/kg | $U_i$ µmol/kg | NARL | | NIMC | | NIST | | NRC | | NRCCRM | | PTB | | VNIIM | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $D_{ij}$ µmol/kg | $U_{ij}$ µmol/kg | $D_{ij}$ µmol/kg | $U_{ij}$ µmol/kg | $D_{ij}$ µmol/kg | $U_{ij}$ µmol/kg | $D_{ij}$ µmol/kg | $U_{ij}$ µmol/kg | $D_{ij}$ µmol/kg | $U_{ij}$ µmol/kg | $D_{ij}$ µmol/kg | $U_{ij}$ µmol/kg | $D_{ij}$ µmol/kg | $U_{ij}$ µmol/kg |
| BAM | -0.8 | 2.7 | 0.1 | 4.6 | -1.1 | 2.7 | -0.4 | 2.3 | -0.4 | 3.1 | -3.6 | 3.6 | 4.1 | 5.0 | 8.5 | 4.9 |
| CENAM | -1.9 | 6.2 | -1.0 | 7.2 | -2.2 | 6.2 | -1.5 | 6.0 | -1.5 | 6.4 | -4.7 | 6.6 | 3.0 | 7.5 | 7.4 | 7.4 |
| CSIR-NML | 1.2 | 4.1 | 2.1 | 5.5 | 0.9 | 4.1 | 1.6 | 3.9 | 1.6 | 4.4 | -1.6 | 4.7 | 6.1 | 5.9 | 10.5 | 5.8 |
| IRMM | 3.9 | 4.3 | 4.8 | 5.7 | 3.6 | 4.3 | 4.3 | 4.1 | 4.3 | 4.6 | 1.1 | 4.9 | 8.8 | 6.1 | 13.2 | 5.9 |
| KRISS | 2.1 | 5.1 | 3.0 | 6.2 | 1.8 | 5.0 | 2.5 | 4.8 | 2.5 | 5.3 | -0.7 | 5.6 | 7.0 | 6.6 | 11.4 | 6.5 |
| LGC | 0.3 | 5.4 | 1.2 | 6.6 | 0.0 | 5.4 | 0.7 | 5.2 | 0.7 | 5.6 | -2.5 | 5.9 | 5.2 | 6.9 | 9.6 | 6.8 |
| LNE | 2.8 | 6.6 | 3.7 | 7.5 | 2.5 | 6.6 | 3.2 | 6.4 | 3.2 | 6.8 | 0.0 | 7.0 | 7.7 | 7.8 | 12.1 | 7.8 |
| NARL | -0.9 | 4.3 | | | -1.2 | 4.3 | -0.5 | 4.1 | -0.5 | 4.6 | -3.7 | 4.9 | 4.0 | 6.1 | 8.4 | 5.9 |
| NIMC | 0.3 | 2.2 | 1.2 | 4.3 | | | 0.7 | 1.6 | 0.7 | 2.7 | -2.5 | 3.2 | 5.2 | 4.8 | 9.6 | 4.6 |
| NIST | -0.4 | 1.7 | 0.5 | 4.1 | -0.7 | 1.6 | | | 0.0 | 2.3 | -3.2 | 2.9 | 4.5 | 4.6 | 8.9 | 4.4 |
| NRC | -0.4 | 2.7 | 0.5 | 4.6 | -0.7 | 2.7 | 0.0 | 2.3 | | | -3.2 | 3.6 | 4.5 | 5.0 | 8.9 | 4.9 |
| NRCCRM | 2.8 | 3.2 | 3.7 | 4.9 | 2.5 | 3.2 | 3.2 | 2.9 | 3.2 | 3.6 | | | 7.7 | 5.3 | 12.1 | 5.2 |
| PTB | -4.9 | 4.8 | -4.0 | 6.1 | -5.2 | 4.8 | -4.5 | 4.6 | -4.5 | 5.0 | -7.7 | 5.3 | | | 4.4 | 6.3 |
| VNIIM | -9.3 | 4.7 | -8.4 | 5.9 | -9.6 | 4.6 | -8.9 | 4.4 | -8.9 | 4.9 | -12.1 | 5.2 | -4.4 | 6.3 | | |

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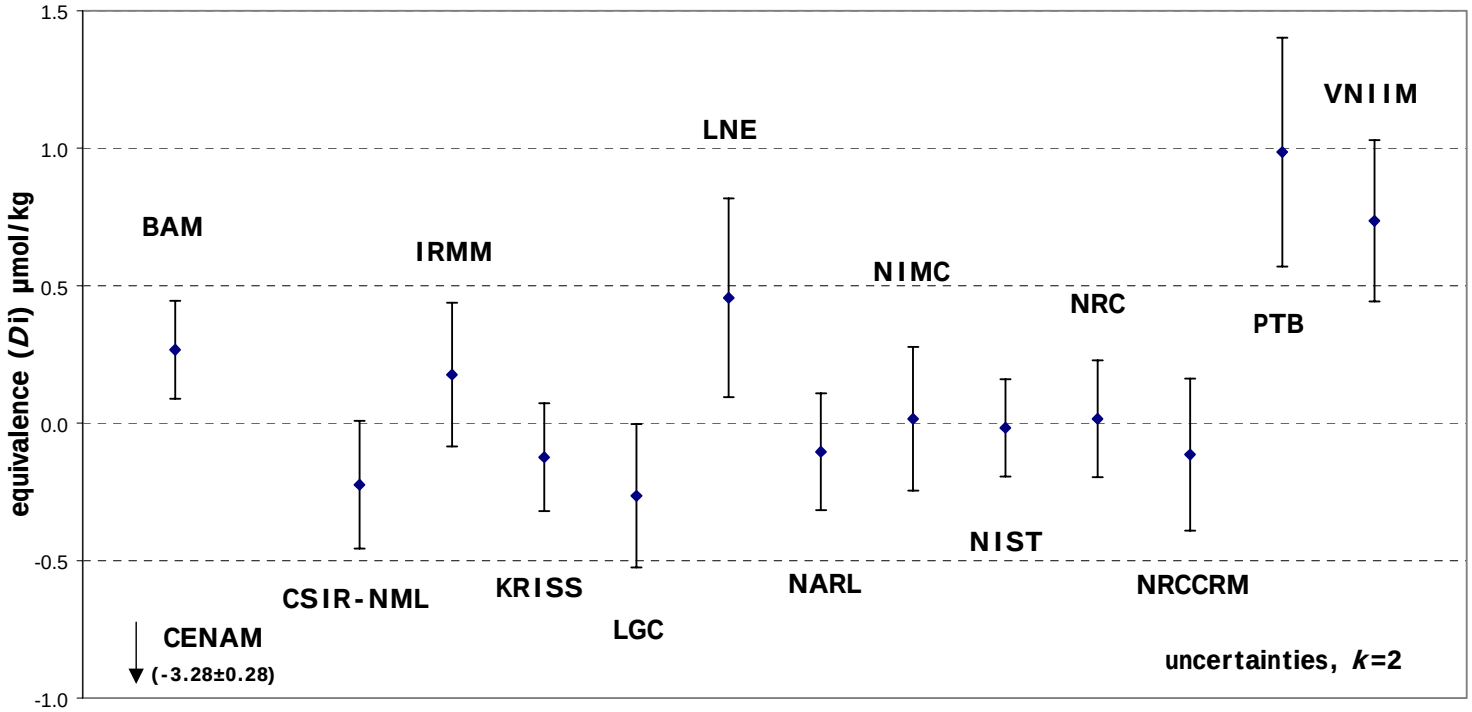
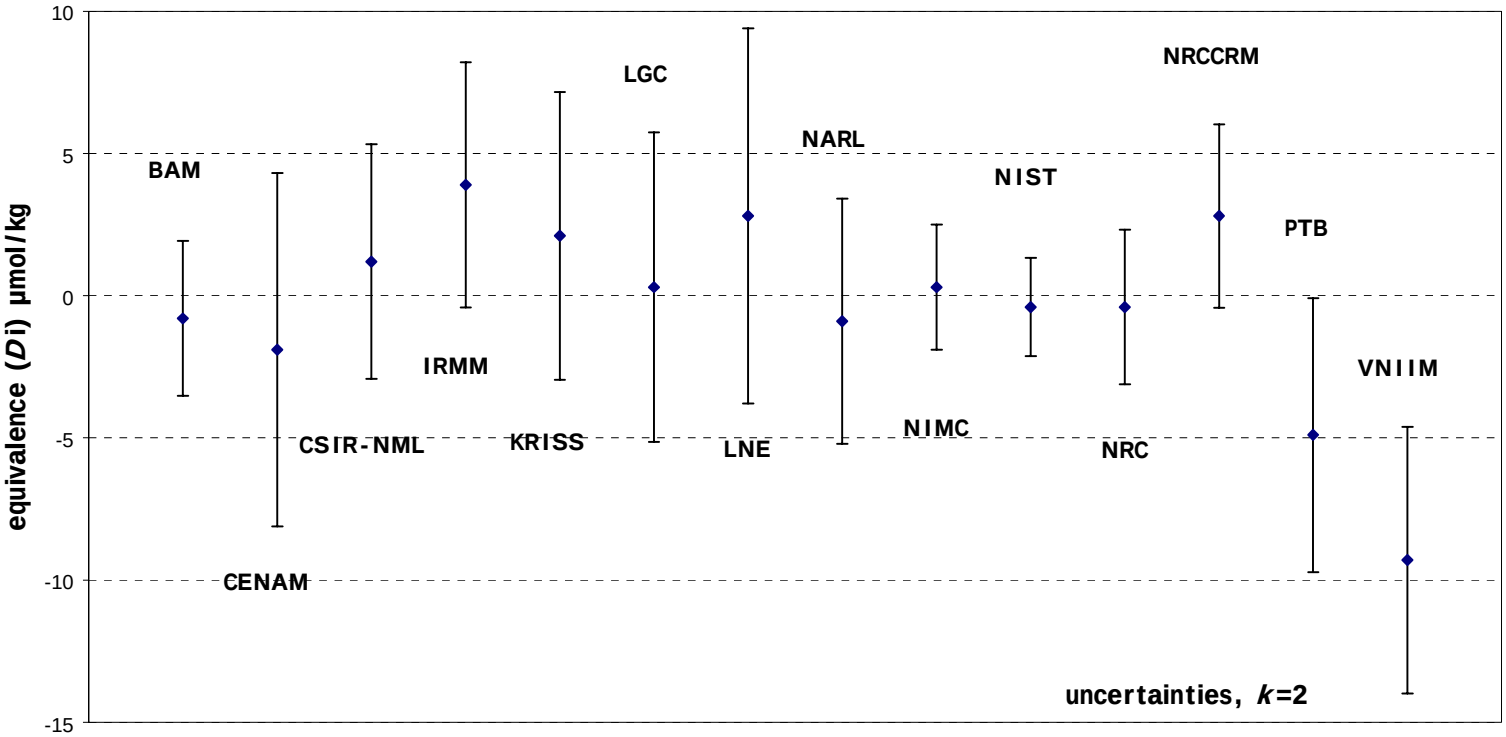
# Graphical display of equivalence statements

## *CCQM-K13 key comparison Cd in sediment*




## *CCQM-K13 key comparison Pb in sediment*

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*CCQM-K13*
*Cd and Pb in Sediment*

*Final Report*

# *Annex C*

# *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 sediment
- instructions for uncertainty evaluation
- proposed uncertainty budget forms for Cd
- proposed uncertainty budget forms for Pb
- results report form
- questionnaire

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*10th July 2000*

# *CCQM-K13*
# *Cd and Pb in Sediment*

# *Information Package*

*For further information, please contact:*

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# *Distribution list*

## CCQM-K13 registered participants:

| | |
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| **Ma. R. A. Torres** | **CENAM** |
| **Mrs M. Archer** | **CSIR-NML** |
| **Dr C. Quétel** | **IRMM** |
| **Dr E. Hwang** | **KRISS** |
| **Dr G. Labarraque** | **LNE** |
| **Dr B. Fairman** | **LGC** |
| **Dr L. Mackay** | **NARL** |
| **Dr J. Fassett** | **NIST** |
| **Dr K. Okamoto** | **NIMC** |
| **Dr M. Van Son** | **NMi** |
| **Dr J. McLaren** | **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 A. Nomura** | **APMP** |
| **Dr F. Hengstberger** | **SADCMET** |
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| **Dr P. Taylor** | **IRMM** |

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Geel, 10th July 2000
L/IM/36/00

**To:** **CCQM-K13 registered participants**
**From:** **Dr Ioannis Papadakis**
**Subject:** **CCQM-K13 *"Cd and Pb in Sediments"***

Dear colleague,

As proposed, discussed and decided in the last Inorganic Analysis Working Group and CCQM meetings (Paris 3-7 April 2000), IRMM will be the pilot laboratory of the CCQM-K13 Key Comparison, *"Cd and Pb in Sediment"*.

The CCQM-K13 is the successor of the CCQM-P15 study, which was successfully concluded in 1999. Report of the CCQM-P15 can be obtained upon request by IRMM [1]. The CCQM-K13 sample is an estuarine sediment, which is in powder form and bottled in glass containers each one containing ~ 40 g of material. The material is tested for stability and homogeneity. The minimum sample mass in order to achieve 1% precision was calculated to be 76 mg for Cd and 58 mg for Pb [2].

The deadline for report of the CCQM-K13 results is **31st October 2000**. This will allow us to discuss preliminary results in the working group meeting in November 2000 in Teddington.

IRMM prepared an information package for the CCQM-K13, which is similar with the package distributed for the CCQM-P15 and includes:

- This letter
- Scope of the CCQM-K13 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-K13 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.

Yours sincerely

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IM Unit

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1. I. Papadakis et. al. CCQM-P15 study, cadmium and lead content in sediment, GE/R/IM/9/00, IRMM, Geel, March 2000
2. K.H. Grobecker and P. Conneely, private communication, March 2000

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L/IM/37/00

# Scope of CCQM-K13 key comparison "*Cd and Pb in Sediment*"

This document describes the scope of the CCQM-K13 key comparison "*Cd and Pb in sediment*". The CCQM-K13 was decided during the 6th CCQM meeting as an activity of the inorganic working group of CCQM and it is organised as succesor of the CCQM-P15 pilot study [1], which run under the same subject. IRMM was designated as the pilot laboratory.

The analysis of sediment and soils is of key importance today. This conclusion is drawn on the basis of the following facts:

- sediments and soils influence vegetation and the water cycle, thus affecting the main food resources for man and animals.
- the increasing deterioration of soils and sediments in many parts of the world and especially those used for agriculture and forestry which each year suffer the damaging effects of pollution.
- sediments and soils are complex and dynamic matrices characterised by given flora and fauna, deteriorating under the effect of adverse mineral and organic compounds.
- sediments and soils are significant for landscape and vegetation, which are of scientific, aesthetic and cultural interest to mankind.

That importance is reflected in the international [2] and national legislation on chemical composition of sediments and soils. Moreover the large majority of CRM producers provide sediment and soil CRMs and most of the PT scheme organisers include sediment and soil measurement schemes in their programmes.

Laboratories who demonstrate their capability of measuring Cd and Pb amount content in the CCQM-K13 sediment samples, are likely to have the capability, knowledge and skills to measure the amount content of other elements at similar levels in soil and sediment matrices.

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1. I. Papadakis et. al. CCQM-P15 study, cadmium and lead content in sediment, GE/R/IM/9/00, IRMM, Geel, March 2000

2. Council Directive 86/278/EEC, on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture, 1986, OJ L 181/6

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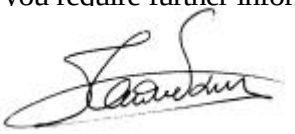
# *General Instructions for CCQM-K13 key comparison*

This document gives general guidelines for participation in the CCQM-K13 key comparison *"Cd and Pb in sediment"*.

- 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 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 sediment prior to the digestion
  - make sure that the sediment digestion is complete (see specific instructions)
  - avoid weighing of small aliquots of solids or liquids in order to minimise the weighing uncertainty
  - the isotopic composition of Pb in the sample should be determined.
  - possible isobaric interferences for the Cd and Pb 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.



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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 sediment in the CCQM-K13 key comparison*

The subject of CCQM-K13 key comparison is the measurement of Cd and Pb amount content in a fine sediment powder. There are two potential problems in such measurement. Firstly, moisture will affect the mass of the sediment powder, and a correction for that is needed. Secondly, the digestion of a sediment material (if needed for the procedure which you are following) is never a trivial exercise due to the complexity and the variety of the minerals to be digested.
This document intents to give some guidance on these matters.

## *1. Dry-mass correction*

Correction for dry-mass should be obtained from a separate portion of the material of minimum mass of 1 g. The material should be dried in a ventilated oven at a temperature of 105 ± 2 $^{o}$C. Dry the sediment for minimum 3 hours. Then weight and repeat drying until constant mass is attained (successive weights should not different more that 0.001 g). The loss of mass corresponds to the correction that should be applied. It is advisable to perform this procedure at the same time when weighing the aliquots for the Cd and Pb measurements.

## *2. Digestion of the sediment (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 100 mg.
- aim is to digest the sediment completely.
- should this fail, Cd and Pb 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.

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Institute for Reference Materials and Measurements

Geel, 10th July 2000

# *Instructions for uncertainty evaluation in the CCQM-K13 key comparison*

In the CCQM-K13 key comparison there is no prescribed method for participation. The organisers do not want to perscribe 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 sediment 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 ($\Sigma$) 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 pameters $D$, $w$ 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.

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

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# *CCQM-K13*

## *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

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# *CCQM-K13*

## *Uncertainty Budget*[6]

## *for Pb amount content measurement*

| Parameter | typical value[7] | standard uncertainty | type A/B[8] | *n*[9] | 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)** | | | |

[6]. Please return together with the results' report sheet.

[7]. Please indicate the unit used for each parameter where appropriate.

[8]. According to ISO/BIPM Guide to the Expression of Uncertainty in Measurement

[9]. Number of measurements performed for the calculation of type A uncertainty contributions

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# CCQM-K13

## *Cd and Pb in Sediment*

# RESULTS REPORT

**(please return together with questionnaire by 31st October 2000)**

**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*** | | |
| ***Pb*** | | |

Date :

Signature :

[1] 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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# CCQM-K13

## *Cd and Pb in Sediment*

# Questionnaire

**(please return together with the results report form)**

**Lab Identification** : *name* :
*institute* :

These 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 <u>not</u> 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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*CCQM-K13*
*Cd and Pb in Sediment*

*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

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# experimental design

| *CCQM-K13 participant* | *experimental design* |
|---|---|
| **BAM** | double IDMS [1] |
| **CENAM** | external calibration [2] |
| **CSIR-NML** | ext. calibration /double IDMS [3] |
| **IRMM** | single IDMS [4] |
| **KRISS** | IDMS [5] |
| **LGC** | exact matching [6] |
| **LNE** | double IDMS |
| **NARL** | exact matching |
| **NIMC** | double IDMS |
| **NIST** | double IDMS |
| **NRC** | double-IDMS |
| **NRCCRM** | double-IDMS |
| **PTB** | double-IDMS |
| **VNIIM** | double IDMS |

1. the spike material is measured against a natural material
2. external calibration with In and Tl internal standard for Cd and Pb measurement respectively.
3. external calibration was used for Cd measurement and double isotope dilution for Pb measurement
4. a certified spike material is used
5. no further specification is given
6. double IDMS with optimum sample/spike ratio

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# digestion method and acid mixture

| *CCQM-K13 participant* | *digestion method* | *acid mixture* |
|---|---|---|
| **BAM** | microwave | **HF, $HNO_3$, HCl, $HClO_4$** |
| **CENAM** | microwave | **HF, $HNO_3$ (1:1)** [1] |
| **CSIR-NML** | microwave | **HF, $HNO_3$, HCl** |
| **IRMM** | berghof | **HF, $HNO_3$** |
| **KRISS** | microwave | **HF, $HNO_3$, $HClO_4$** |
| **LGC** | microwave | **HF, $HNO_3$, HCl (1:3:1)** |
| **LNE** | microwave | **HF, $HNO_3$, $H_2O_2$ (2:2:1)** |
| **NARL** | microwave | **HF, $HNO_3$, HCl (1:5:1)** |
| **NIMC** | microwave | **HF, $HNO_3$, $HClO_4$** |
| **NIST** | wet ashing | **HF, $HNO_3$, $HClO_4$** |
| **NRC** | microwave | **HF, $HNO_3$** |
| **NRCCRM** | not specified | **HF, $HNO_3$** |
| **PTB** | microwave | **HF, $HNO_3$, then $HNO_3$, $H_2O_2$** |
| **VNIIM** | open system | **HF, $HNO_3$ (1:2)** |

1. This mixture was used for Cd measurement. For Pb measurement the HF, $HNO_3$, $HClO_4$ (3:3:1) mixture was used.

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# use of sqrt(n) for type A uncertainty contributions

| *CCQM-K13 participant* | use of sqrt(n) for type A uncertainty contributions |
|---|---|
| **BAM** | yes |
| **CENAM** | yes |
| **CSIR-NML** | yes |
| **IRMM** | no |
| **KRISS** | no |
| **LGC** | yes |
| **LNE** | yes |
| **NARL** | no |
| **NIMC** | yes |
| **NIST** | yes |
| **NRC** | yes |
| **NRCCRM** | yes |
| **PTB** | yes |
| **VNIIM** | yes |

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# reference isotope pair for IDMS

| *CCQM-K13 participant* | *reference isotope pair for Cd measurement* | *reference isotope pair for Pb measurement* |
|---|---|---|
| **BAM** | $^{113}Cd/^{112}Cd$ | $^{207}Pb/^{208}Pb$ |
| **CENAM** | - | - |
| **CSIR-NML** | - | $^{208}Pb/^{206}Pb$ |
| **IRMM** | $^{113}Cd/^{111}Cd$ | $^{208}Pb/^{206}Pb$ |
| **KRISS** | $^{111}Cd/^{112}Cd$ | $^{206}Pb/^{208}Pb$ |
| **LGC** | $^{111}Cd$ [1] | $^{206}Pb$ [1] |
| **LNE** | $^{111}Cd/^{106}Cd$ | $^{208}Pb/^{206}Pb$ |
| **NARL** | $^{114}Cd/^{111}Cd$ | $^{208}Pb/^{206}Pb$ |
| **NIMC** | $^{112}Cd$ [1] | $^{206}Pb$ [1] |
| **NIST** | $^{111}Cd/^{114}Cd$ | $^{206}Pb/^{208}Pb$ |
| **NRC** | $^{114}Cd/^{113}Cd$ | $^{208}Pb/^{207}Pb$ |
| **NRCCRM** | $^{112}Cd/^{111}Cd$ | $^{208}Pb/^{207}Pb$ |
| **PTB** | $^{111}Cd/^{114}Cd$ | $^{206}Pb/^{208}Pb$ |
| **VNIIM** | $^{113}Cd/^{111}Cd$ | $^{208}Pb/^{206}Pb$ |

1. only reference isotope specified

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# number of blends prepared/measured for IDMS

| *CCQM-K13 participant* | *number of blends for Cd measurement* | *number of blends for Pb measurement* |
|---|---|---|
| **BAM** | 6 | 6 |
| **CENAM** | - | - |
| **CSIR-NML** | - | 4 |
| **IRMM** | 6 | 6 |
| **KRISS** | 4 | |
| **LGC** | 3 | 3 |
| **LNE** | 3 | 3 |
| **NARL** | 4 : 3 : 3[1] | 6 : 4 : 3[3] |
| **NIMC** | 5 | 5 |
| **NIST** | 4 | 4 |
| **NRC** | 5 | 5 |
| **NRCCRM** | 6 | 6 |
| **PTB** | 10 | 8 |
| **VNIIM** | 6 (from 3)[2] | 6 |

1. 4 blends measured by HR-ICP-MS, 3 blends measured by Q-ICP-MS and 3 blends using as reference isotope $^{108}$Cd
2. 6 blends from 3 sub-samples
3. 6 blends measured by HR-ICP-MS, 4 blends measured by Q-ICP-MS and 3 blends using as reference isotope $^{207}$Pb

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# experimental reproducibility (stdev on $c_x$)

| *CCQM-K13 participant* | *standard deviation on $c_x$ (in %) for Cd measurement* | *standard deviation on $c_x$ (in %) for Pb measurement* |
|---|---|---|
| **BAM** | 0.50 | 0.60 |
| **CENAM** | 5.41 | 3.22 |
| **CSIR-NML** | 1.34 | 0.29 |
| **IRMM** | 3.37 | 0.61 |
| **KRISS** | 1.40 | 0.10 |
| **LGC** | 1.05 | 1.14 |
| **LNE** | 1.40 | 0.36 |
| **NARL** | 0.96 | 0.58 |
| **NIMC** | 2.00 | 0.40 |
| **NIST** | 0.64 | 0.15 |
| **NRC** | 0.55 | 0.20 |
| **NRCCRM** | 2.00 | 0.80 |
| **PTB** | 2.80 | 1.40 |
| **VNIIM** | 1.90 | 1.30 |

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# reported blank measurement

| *CCQM-K13 participant* | *blank for Cd measurement* | *blank for Pb measurement* |
|---|---|---|
| **BAM** | **5 ng** | **1.04 mg** |
| **CENAM** | **43 pmol/g** | **16.3 pmol/g** |
| **CSIR-NML** | **-** | **8 pmol/g** |
| **IRMM** | **16 pmol (153 pmol/g)** | **20.6 pmol (21 pmol/g)** |
| **KRISS** | **47.8 pmol/g** | **346 pmol/g** |
| **LGC** | **-** | **-** |
| **LNE** | **n.d.** | **n.d.** |
| **NARL** | **-** | **-** |
| **NIMC** | **800 pmol/g** | **21.5 pmol/g** |
| **NIST** | **7 pmol** | **2.15 pmol** |
| **NRC** | **2.9 pmol/g** | **10 pmol/g** |
| **NRCCRM** | **-** | **-** |
| **PTB** | **-** | **-** |
| **VNIIM** | **7 pmol/g** | **9.7 pmol/g** |

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