CCQM-K13.1 Subsequent Key Comparison
Cadmium and Lead in Sediment

Final Report

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1. Abstract

CCQM-K13.1 is a Subsequent Key Comparison for Cadmium and Lead in Sediment conducted to provide the opportunity for two NMIs to demonstrate and document improvements in measurement capability achieved since the conduct of CCQM-K-13, Amount content of Cadmium (Cd) and Lead (Pb) in sediment. The CCQM-K13 key comparison, completed in 2001, was a successor to CCQM-P15 (Cadmium and Lead content in sediment) study, and was performed to demonstrate and document the capability of interested National Metrology Institutes to measure Cd and Pb content in a sediment sample. The P15, K13 and K13.1 comparisons were activities of the Inorganic Analysis Working Group (IAWG) of CCQM. CCQM-P15 and K13 were coordinated 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.

Satisfactory agreement of reported results was observed for most participants in CCQM-K13, however, two NMIs (CEMAN and PTB) wished to participate in a subsequent Key Comparison to demonstrate improved performance of their analytical capabilities. Since NIST was in the process of certifying a new marine sediment SRM (2702), and both Cd and Pb were going to be determined by the same methods used in CCQM-K13, it was decided to use this opportunity to perform a Subsequent Key Comparison (CCQM-K13.1). As NIST had successfully participated in both the pilot study and K13, it served as the anchor point to which the other participants in the subsequent study could be compared. CENAM signed up to determine Cd only in this study, and PTB signed up for both Pb and Cd. The NIST and PTB results for Pb exhibited good overlap. However, problems were observed for Cd. The NIST and CENAM Cd results did not overlap, and PTB could not report an official result for Cd largely due to suspected isobaric interferences.

2. Introduction

SUMMARY of CCQM-K13: 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 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 final report for this CCQM-K13 is available on the web at: http://kcdb.bipm.org/AppendixB/appbresults/ccqm-k13/ccqm-k13_final_report.pdf.

The following laboratories participated in CCQM-K13 (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 for most participants. However, two NMIs (CEMAN and PTB) wished to participate in a subsequent Key Comparison to demonstrate improved performance of their analytical capabilities. Since NIST was in the process of certifying a new marine sediment SRM (2702), and both Cd and Pb were going to be determined by the same methods used in CCQM-K13, it was decided to use this opportunity to perform a Subsequent Key Comparison (CCQM-K13.1).

3. Participation in CCQM-K13.1 Subsequent

Two NMIs registered for this study: CENAM, Mexico (for Cd only) and PTB, Germany (for both Cd and Pb). NIST ID-ICPMS measurements would anchor the results of this study to the original Key Comparison.

4. Samples

The samples for this study consisted of material that would later be certified as NIST SRM 2702 (Inorganics in Marine Sediment). The Cd amount content in this material is about 35% higher than that in the CCQM-K13 material, while the Pb amount content is about 4 times higher.

5. Instructions

A minimal set of instructions was sent to each participant by the coordinating laboratory. The NMIs were instructed to follow the same analytical protocol as for the Key Comparison (CCQM-K13) with the following additional specifications:

1) Sample size: minimum sample size is 0.15 g.
2) Basis mass: a correction factor for drying should be applied. Drying should be conducted on a separate sample for 18 hours at 90 ^{o}C in a conventional oven.
3) Appropriate analytical procedures should be applied to completely dissolve the sample. A full uncertainty budget should be submitted.

6. Methods

All NMIs used ID-ICPMS. Dissolution and instrumental methods as reported by participants are summarized in Table 1.

Table 1. Analytical Methods used for CCQM-K33

Institute	Dissolution Method	Instrumental Method	Calibration Method
CENAM	Microwave dissolution with nitric and hydrofluoric acids; followed by an open digestion in order to reduce the acid concentration	HR-ICPMS	IDMS
NIST	Microwave dissolution with nitric, perchloric and hydrofluoric acids	ICPMS	IDMS
PTB	Microwave dissolution with nitric, hydrofluoric, and perchloric acids with hydrogen peroxide	ICPMS	IDMS

7. Results submitted for CCQM-K13.1

The participants' results are summarized in Tables 2 and 3. Relative values combined with the results of the original CCQM-K13 are given in Figures 1 and 2. CENAM submitted results for Cd, and PTB submitted official results for Pb only. Although PTB signed up for both Pb and Cd, PTB reported that their "… Cadmium content can only be regarded as an information value. It was obtained as the average of 2 calibration procedures using different certified sediment samples (NIST SRM 1646a, CCQM-P15, CCQM-K13) and of 3 IDMS procedures (in one of these we tried to separate Cd from the matrix). The main reasons for our doubts according to the result for Cd were the various interferences caused by several Zr species (ZrO, ZrOH, $ZrOH_2$ and $ZrOH_3$), several Mo species (MoO, MoOH, $MoOH_2$) and ClO_4N (perchloric acid!). All efforts to separate the Cd from the matrix failed. Therefore the Cd value we measured is no reliable value in terms of metrology in chemistry."

Table 2. Measurement Results Reported for Cd in CCQM-K13.1

Participant	Reported Value (µmol/kg)	Uncertainty (µmol/kg)	Uncertainty (%)	number of samples	k value
CENAM	8.32	0.51	6.1	6	2
NIST	7.29	0.09	1.2	6	2

Table 3. Measurement Results Reported for Pb in CCQM-K13.1

Participant	Reported Value (µmol/kg)	Uncertainty (µmol/kg)	Uncertainty (%)	number of samples	k value
NIST	641	5	0.8	7	2
PTB	638	19	3.0	11	2

8. Discussion

The agreement for the PTB and NIST Pb results were excellent with strong overlap of central values with expanded uncertainties. Results for Cd did not agree to the degree anticipated. PTB could not provide an official measurement value for this element, and the CENAM results (including expanded uncertainties) did not overlap the NIST results. However, the CENAM results for this study were greatly improved compared to the original CCQM-K13.

The NIST results were used to anchor the results of the CCQM-K13.1 to CCQM-K13. Since the amount contents of the materials for CCQM-K13 and CCQM-K13.1 were significantly different, especially for Pb, it was necessary to normalize for these differences. Therefore, the amount contents and absolute uncertainties determined for the CCQM-K13.1 comparison were normalized by the ratios of amount contents in the materials for CCQM-K13.1 and CCQM-K13 comparisons, as determined by NIST. The normalized amount contents and uncertainties are given in Tabless 4 and 5. A graphical representation of the data for both CCQM-K13 and K13.1, relative to the KCRVs, are given in Figures 1 and 2.

9. Equivalence Statements

Since equivalence statements are usually presented in absolute and not relative values, and since the amount contents of the materials for CCQM-K13 and CCQM-K13.1 were significantly different, especially for Pb, the normalized amount contents and uncertainties (described above) were used for the equivalence statements.

The degree of equivalence and its uncertainty between an NMI result and the KCRV is calculated according to the following equations:

$$D_i = (x_i - x_R)$$

$$U_i^2 = (k_i^2\, u_i^2 + k_R^2\, u_R^2)$$

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 of D_i calculated by both the combined standard uncertainty u_i of x_i and the standard uncertainty u_R of x_R. Note that k_i =2 and k_R = 2. Equivalence statements in both absolute and relative values (to the KCRV) are given in Tables 4 and 5. Slight differences in the values of the NIST D_i for Cd, and the NIST U_i for Pb are probably due to round off differences.

Table 4. Equivalence Statement for Cadmium

NMI	Normalized Amount Content (µmol/kg)	Normalized U k=2 (µmol/kg)	D_i (µmol/kg)	U_i (µmol/kg)	D_i (%)	U_i (%)
NIST-original*	5.397	0.058	-0.02	0.18	-	-
NIST-current	=5.397	0.065	-0.02	0.18	-0.3%	3.3%
CENAM	6.16	0.38	0.75	0.41	13.8%	7.6%
PTB	Not Reported	Not Reported				

* Original values reported in CCQM-K13 Final Report

Table 5. Equivalence Statement for Lead

NMI	Normalized Amount Content (µmol/kg)	Normalized U k=2 (µmol/kg)	D_i (µmol/kg)	U_i (µmol/kg)	D_i (%)	U_i (%)
NIST-original*	169.50	0.65	-0.4	1.7	-	-
NIST-current	=169.50	1.32	-0.4	1.5	-0.2%	0.9%
PTB	168.7	5.0	-1.2	5.1	-0.7%	2.9%

* Original values reported in CCQM-K13 Final Report

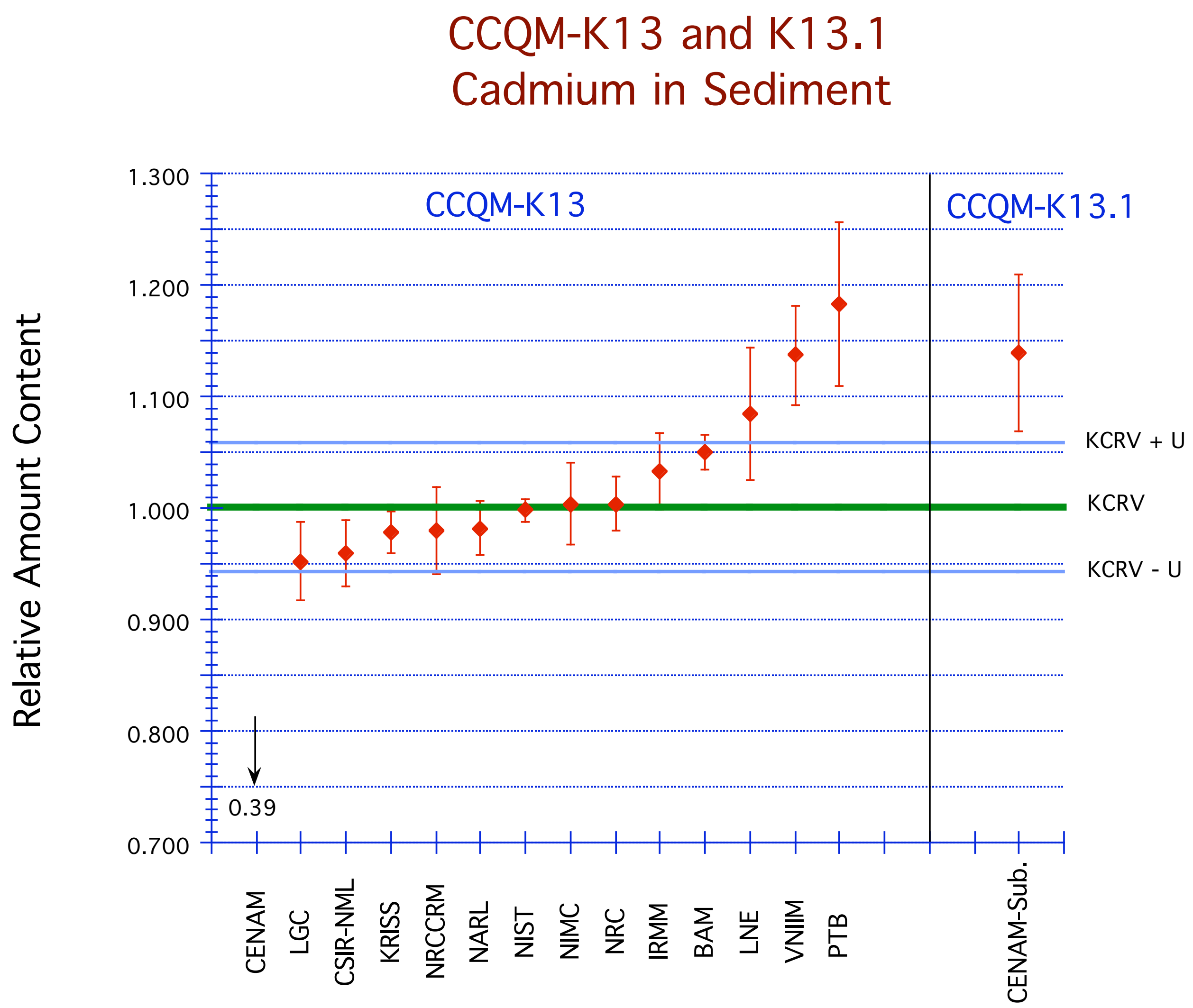

Figure 1. Normalized Cadmium results for CCQM-K13 and CCQM-K13.1

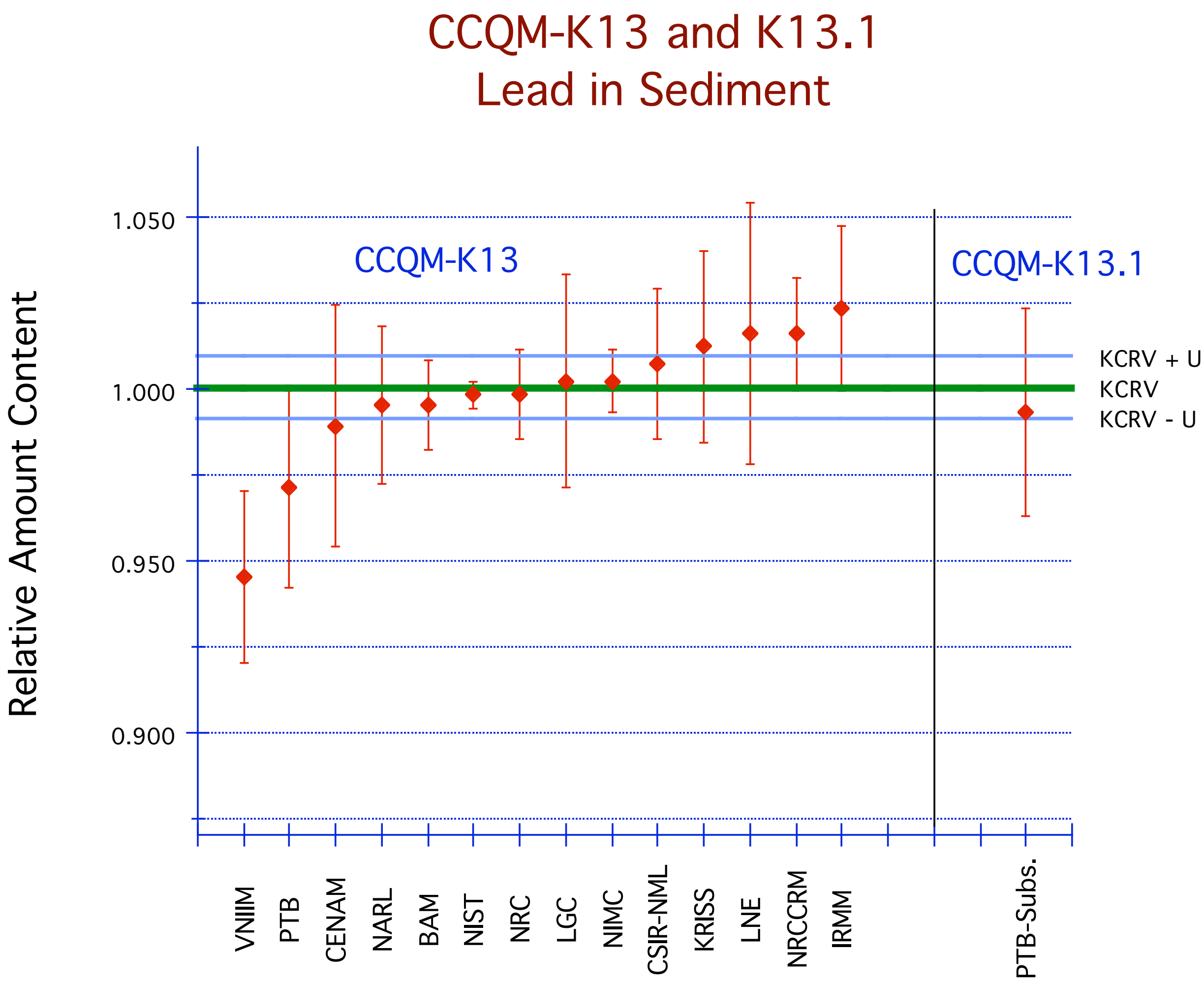

Figure 2. Normalized Lead results for CCQM-K13 and CCQM-K13.1