

CCQM-P43: Tributyltin and dibutyltin in sediment

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Abstract

The pilot study CCQM P43 was undertaken to allow the assessment of the current capabilities of interested National Metrology Institutes (those which are members of the CCQM) and selected outside 'expert' laboratories for quantification of $(C_4H_9)_2Sn^+$ (DBT) and $(C_4H_9)_3Sn^+$ (TBT) in a prepared marine sediment. It was organised in parallel to the key comparison CCQM-K28, in which only NMIs determined TBT.

This exercise was sanctioned by the 8th CCQM meeting, April 18-19, 2002, as an activity of the Inorganic Analysis Working Group and was jointly co-ordinated by the Institute for National Measurement Standards of the National Research Council of Canada (NRC) and LGC, UK.

A total of 13 laboratories initially indicated interest (9 NMIs, and 4 external laboratories). Only one external laboratory utilised a standard calibration approach based on natural abundance TBT and DBT standards, whereas all NMIs relied on isotope dilution mass spectrometry for quantitation (one NMI used ID-MS and an internal standard approach for the analysis of DBT). For this purpose, species specific ¹¹⁷Sn-enriched TBT and DBT standards were supplied by LGC. No sample preparation methodology was prescribed by the co-ordinating laboratories and, as a consequence, a variety of approaches was adopted by the participants, including mechanical shaking, sonication, accelerated solvent extraction, microwave assisted extraction and heating in combination with Grignard derivatization, ethylation and direct sampling. Detection techniques included ICP-MS (coupled to GC or HPLC), GC-MS and GC-AED.

1. Introduction

Organotin compounds are ubiquitous contaminants in the environment, and some exhibit deleterious effects in aquatic ecosystems. In particular, the use of tributyltin (TBT) as a marine antifouling agent has led to its near global dispersal and it is now detected in the coastal sediments and waters of most developed nations. Tributyltin, as well as its degradation products such as dibutyltin (DBT), persists in sediments, despite international efforts to curtail its usage in TBT-based paints since 1982 in France and subsequently in other countries. Organotin levels in water and in marine sediment samples continue to pose an ecotoxicological threat in the aquatic environment.

Quantification of organotin species is a difficult task due to their instability, low concentration levels and questions concerning extraction efficiency.

Following the success of the pilot study CCQM P-18 of the Comité Consultatif pour la Quantité de Matière (CCQM) for the analysis of TBT in a marine sediment, [1, 2] two other comparisons were sanctioned at the 8th CCQM meeting, on April 18-19, 2002. The Inorganic Analysis Working Group was tasked to conduct two inter-comparisons on the determination of DBT and TBT in sediment. One consisted of a key comparison, CCQM-K28, for the determination of TBT in sediment, in which only National Metrology Institutes (NMI) could participate. The second was a pilot study, CCQM-P43, for the determination of DBT and TBT, which included laboratories that were not entitled to participate in the key comparison (i.e. non NMIs). The exercise was jointly co-ordinated by the Institute for National Measurement Standards of the National Research Council of Canada (NRC), Ottawa, and LGC, Teddington, UK.

It was agreed that the NRC would make available and distribute both a control standard (PACS-2 Marine Sediment CRM certified for TBT and DBT content) as well as the test sediment material, and that LGC would make available species specific calibration standards based on synthesised ¹¹⁷Sn-enriched DBT and ¹¹⁷Sn-enriched TBT to be used by participants wishing to conduct isotope dilution mass spectrometry (ID-MS). The advantages of such calibration methodology to the enhancement of data quality have recently been demonstrated by Encinar *et al.* [3], who also noted significant degradation of tributyltin to dibutyltin (and monobutyltin), which was easily detected with use of multiple enriched isotopic species.

2. Participation in CCQM-P43

A call for participation was sent out to all NMIs in October, 2002. In January 2003, all respondents were sent one bottle of CRM PACS-2 control sediment. PACS-2 is certified for TBT at $0.98 \pm 0.13 \mu\text{g/g}$ as Sn corresponding to $8.26 \pm 1.10 \text{ nmol/g}$ and for DBT at $1.09 \pm 0.15 \mu\text{g/g}$ as Sn corresponding to $9.18 \pm 1.26 \text{ nmol/g}$ and two bottles of the sample material material (with a nominal range of 100-200 $\mu\text{g/g}$ TBT as Sn corresponding to 0.84 – 1.68 nmol/g, and a nominal range of 150-250 $\mu\text{g/g}$ DBT as Sn corresponding to 1.26 – 2.11 nmol/g) from the NRC. In December 2002, a 3 mL solution of the ¹¹⁷Sn enriched DBTCl₂ (with a nominal mass fraction of 110 $\mu\text{g/g}$ in methanol, i.e. 362 nmol/g, and a 3 mL solution of the ¹¹⁷Sn enriched TBTCl (with a nominal mass fraction of 110 $\mu\text{g/g}$ in methanol, i.e. 926 nmol/g) were sent to each participant by LGC to be used for ID-MS analysis. Instructions for handling and storage of all samples and calibration standards were provided to each participant.

Table 1 summarises the institutes, which initially agreed to participate in this pilot study, and to which materials were distributed. Results were requested to be submitted to LGC no later than April 30th, 2003.

Table 1: CCQM-P43 participants. All NMIs participated in CCQM-K28 (except KRISS) for the analysis of TBT.

INSTITUTION / ORGANIZATION	COUNTRY	CONTACT
National Metrology Institutes (NMIs)		
BAM Federal Institute for Materials Research and Testing, Berlin	Germany	T. Win
BNM-LNE Bureau National de Métrologie – Laboratoire National d’Essais	France	B. Lalère
KRISS* Korean research Institute of Standard and Science	Korea	E. Hwang
LGC Laboratory of the Government Chemist	United Kingdom	R. Wahlen
NARL National Analytical Reference Laboratory	Australia	L. Mackay
NIST National Institute for Standards and Technology	U.S.A.	M. Schantz
NMIJ National Metrology Institute of Japan	Japan	K. Inagaki
NRC National Research Council of Canada	Canada	R. Sturgeon
SP Swedish National Testing and Research Institute	Sweden	B. Magnusson
“Expert” laboratories but non NMI		
Oviedo University of Oviedo, Dept. of Physical and Analytical Chemistry	Spain	J.I. Garcia Alonso
Pau Université de Pau et des Pays de l’Adour, Lab. de Chimie	France	O. Donard
PUC Pontificia Universidade Catolica do Rio de Janeiro	Brazil	A. Wagener
Umeå** University of Umeå	Sweden	W. Frech

* Only participated in the analysis of DBT in the sediment

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For the determination of TBT, all NMIs participated in the key comparison CCQM-K28, while the “expert” laboratories participated in the pilot study CCQM-P43. For the analysis of DBT, no distinction was made between NMIs and “expert” non-NMI laboratories, as all participated in CCQM-P43.

After reception of the samples, SP notified the co-ordinating laboratories of its inability to perform the analysis within the time frame, and withdrew their participation from this exercise.

3. Samples and labelled standards for ID-MS

The CCQM-P43 sample (identical to the CCQM-K28 sample) was a marine sediment matrix prepared in-house at NRC by gravimetrically blending two NRC CRM marine

sediments: PACS-2 and HISS-1, the latter containing negligible concentrations of TBT and DBT, thus serving as a solid, inert diluent.

The material was tumbled for homogeneity at NRC and then irradiated as a single large sample, which was thereafter bottled in a clean room under sterile conditions. This route was selected, rather than first bottling and then irradiating, as it had been discovered that irradiation introduced a detectable bottle to bottle variation. The extent of photolytic degradation of the butyltins was found to be dependent on the geometry of the samples placed within the irradiation chamber.

The sample was partitioned into pre-cleaned glass bottles, each containing nominal 25 g amounts of sample, then labelled and packaged in trilaminate foil pouches. A homogeneous distribution of TBT between bottles was also verified. No significant difference was noted for the within bottle versus between bottle homogeneity.

A calibration standard was provided by LGC and distributed direct to participants as requested as a 3 mL methanolic solution containing nominally 110 µg/g DBTCl₂ in the form of ¹¹⁷Sn-enriched material for those laboratories undertaking isotope dilution mass spectrometry. Safety data sheets accompanied the standard, as did instructions for their use and storage. The material was deemed stable for at least 5-6 months at room temperature in their amber vials. For the “expert” laboratories undertaking ID-MS of TBT, LGC distributed a 3 mL methanolic solution containing nominally 110 µg/g TBTCl in the form of ¹¹⁷Sn-enriched material, an identical solution to that distributed to the NMIs participating in CCQM-K28.

4. Instructions to the participants

The CCQM-P43 sample, with the information documents, was sent to all participants in January 2003.

The participants were free to choose one or more suitable methods of measurement for DBT and TBT.

The information packages distributed to the participants from both the NRC and LGC (independently) included:

- accompanying letter;
- scope of the study;
- general instructions for handling samples and calibration standards;
- target value for the analyte in the pilot material;
- instructions for determination of the dry mass correction;
- request for results for a minimum of 6 replicate determinations;
- request for full, itemised uncertainty budget in accordance with the GUM;
- request for details of procedures and instrumentation;
- request for example chromatograms of blank, sample and spiked sample;
- an estimate of the achievable detection limit;
- all uncorrected raw data for samples and blanks;
- an estimate of the extraction efficiency.

5. Methods and instrumentation used

No method was recommended in the protocol, and the choice was left to the participant. All participants but one used isotope dilution mass spectrometry, but their extraction methods varied. There are a number of extraction techniques currently in use for determination of organotin species, including mechanical shaking, sonication, microwave assisted extraction, heating and accelerated solvent extraction coupled with solvents such as KOH, HCl, acetic acid and methanol. Further, extracts may be analysed directly or immediately derivatised with alkylating (ethylation) or Grignard reagents (pentylation) prior to detection. Detection is achieved following separation with either gas chromatography (GC) coupled to mass spectrometry (MS), inductively coupled plasma mass spectrometry (ICP-MS) or by high performance liquid chromatography (HPLC) coupled to ICP-MS.

Table 2: Analytical methods and instrumental techniques used by CCQM-P43 participants for the analysis of TBT and DBT

Participant	Method	Instrumentation
National Metrology Institutes (NMI)		
BAM	HOAc/MeOH/sonicate/ethylation	(1) GC-MS (2) GC-AED
BNM-LNE	12 h HOAc/shaking; ethylation	GC-MS
KRISS	MeOH/HOAc/Tropolone/ microwave	HPLC-ICP-MS
LGC	HOAc/MeOH; ASE extraction	HPLC-ICP-MS
NARL	HOAc/microwave	HPLC-ICP-MS
NIST	HOAc/microwave/ ethylation	GC-MS
NMIJ	HOAc/MeOH/tropolone; microwave; ethylation	GC-ICP-MS
NRC	HOAc/microwave	GC-SF-ICP-MS
“Expert” non NMI laboratories		
Oviedo	HOAc/MeOH/ microwave /ethylation (1) ^{119}Sn and (2) ^{118}Sn (for DBT) and ^{117}Sn (for TBT)spikes	GC-ICP-MS
Pau	HOAc/microwave/ ethylation	GC-ICP-MS
PUC	HOAc/toluene sonicate/ APDC complexation / Derivatisation / clean-up	GC-pulsed flame photometric detection
Umeå	HBr sonicate/Tropolone- Cl_2CH_2 extraction/Derivatisation	GC-ICP-MS

It must be noted that, for CCQM-P43, BAM determined DBT using two methods: one was isotope dilution using GC-MS (1), the other one was the quantitation of DBT by GC-AED using TPrT (tripropyltin) as the internal standard (2). The University of Oviedo also did the determination twice. For the method indexed (1), the in-house produced triple spike ^{119}Sn (1) (which contained enriched TBT, DBT and MBT) was used. For the method indexed (2), the ^{117}Sn spike provided by LGC was used for the analysis of TBT and a ^{118}Sn spike for the analysis of DBT.

When several data sets were provided by one participant, the participant was asked to explicitly mention which result should be taken as their official result, i.e., the value to be used to calculate the reference value. The other values provided would be displayed in tables and graphs as information only. Both BAM and the University of Oviedo indicated that their method of choice was (1) and that their method (2) should be used as supportive information only.

Due to the late arrival of the reference material in their laboratory, the usual procedure adopted by PUC to eliminate sulphur interferences using dimethyldioxirane could not be used. The reagent is unstable and must be freshly prepared through a time consuming procedure not matching the deadline for the results' delivery.

Shortly after the measurements were finished, the University of Pau noticed that their microwave system was inoperative so there are some doubts about their extraction efficiency and reproducibility.

6. CCQM-P43 Participants' results for the analysis of DBT

In only a few cases was the functional relationship for ID-MS (i.e., equation or other approach) and a list of quantities defined along with associated quantified uncertainty components made available by the participants in their submitted reports. As a consequence, there are cases where it was not possible for the co-ordinating laboratories to re-evaluate the results based on the information provided.

Participants' results for the control CRM marine sediment reference material PACS-2 are presented in Table 3, with a current certified value of $1.09 \pm 0.15 \mu\text{g/g}$ (as Sn) or $9.18 \pm 1.26 \text{ nmol/g}$ (as DBT^+). Results are displayed graphically in Figure 1. The median, calculated from these data (without BAM-2 and Oviedo-2, as noted above), is $9.02 \text{ nmol/g DBT}^+$, corresponding to an average recovery of the target analyte of 99.0 %.

Table 3: CCQM-P43 participants' measurement results for DBT in PACS-2

<i>participant</i>	<i>reported result nmol·g⁻¹</i>	<i>expanded uncertainty nmol·g⁻¹</i>
BAM-1	8.213	0.557
BAM-2	7.787	0.245
BNM-LNE	8.090	0.440
KRISS	8.712	0.220
LGC	9.480	1.300
NARL	8.960	0.830
NIST	9.019	0.647
NMIJ	9.13	0.129
NRC	9.500	0.290
Univ. Oviedo-1	9.095	0.194
Univ. Oviedo-2	9.653	0.670
PUC	11.787	0.540
Univ. Pau	8.0230	0.14682

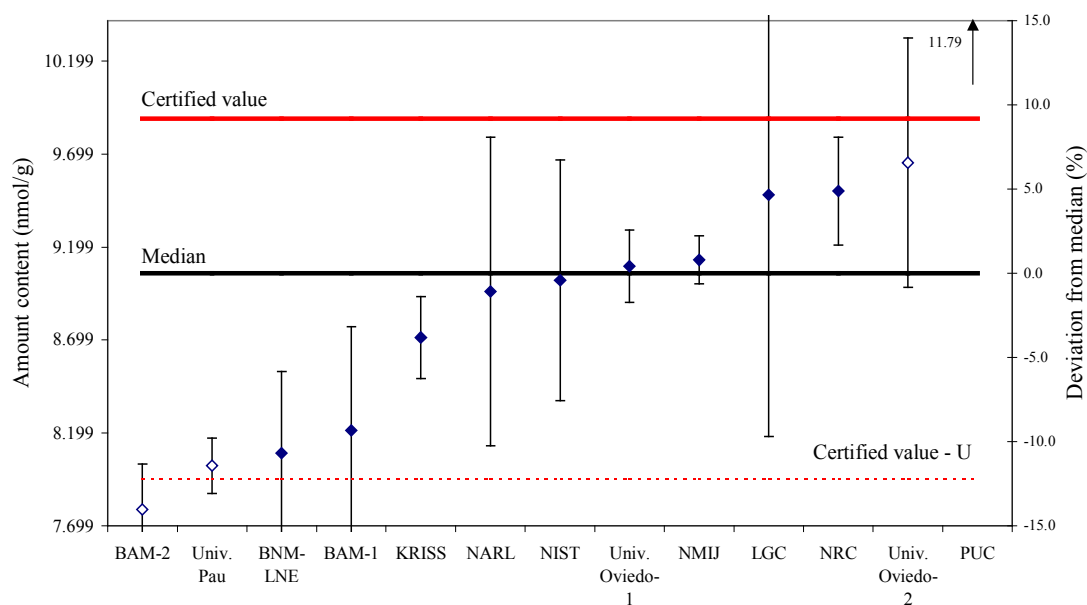


Figure 1: Results for DBT determination in PACS-2 material

The median is represented by the thick black line. The dotted line represents the lower value of the certified range. The certified value is represented by the thick red line. BAM-2, Oviedo-2, Univ. Pau and PUC results were not included in the calculation of the median. The white filled dots represents values that were not used in the calculation of the median.

Participants' results for the marine sediment CCQM-P43 sample are presented in Table 4. Results are displayed graphically in Figure 2. The median, calculated from

these data (without BAM-2, Oviedo-2 as noted above), is 1.482nmol/g DBT⁺ (176 ng/g as Sn). The sampling distribution for the median is ill-defined in the absence of a known distribution. Resampling (n=100000) gave a standard deviation of 0.054nmol/g DBT⁺ (3.6%), using the interquartile range estimate of standard deviation and assuming underlying normality gave s=0.047

Table 4: CCQM-P43 participants' measurement results for DBT

<i>participant</i>	<i>reported result nmol·g⁻¹</i>	<i>Expanded uncertainty nmol·g⁻¹</i>
BAM-1	1.280	0.038
BAM-2	1.504	0.125
BNM-LNE	1.205	0.080
KRISS	1.466	0.071
LGC	1.500	0.150
NARL	1.550	0.140
NIST	1.371	0.078
NMIJ	1.482	0.041
NRC	1.530	0.054
Univ. Oviedo-1	1.542	0.047
Univ. Oviedo-2	1.522	0.110
PUC	1.570	0.150
Univ. Pau	1.371	0.082

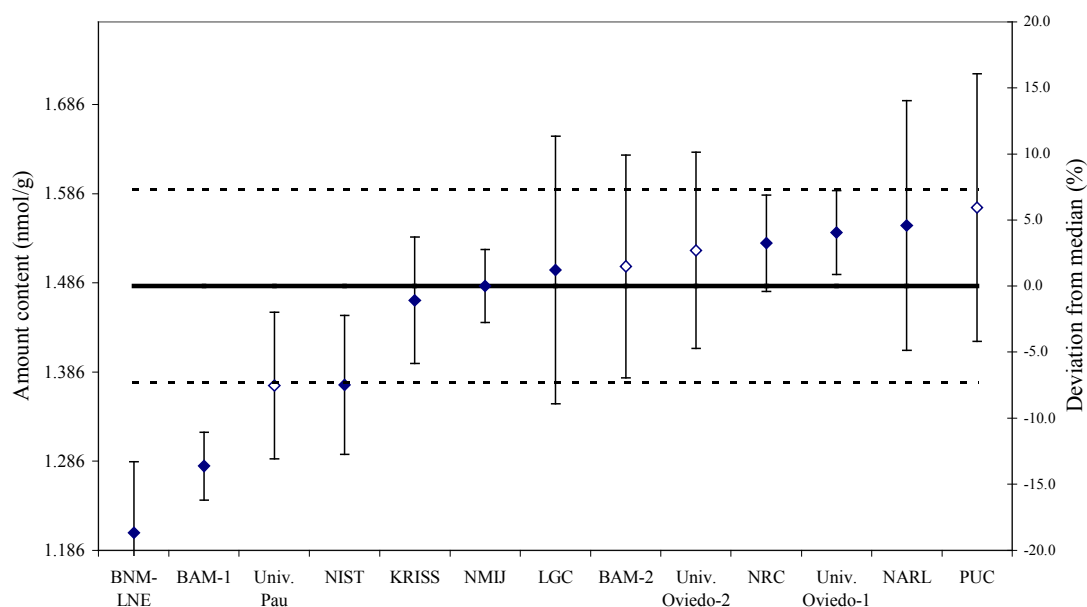


Figure 2: Results for DBT determination in CCQM-P43 material

The median is represented by thick line and the expanded uncertainty range is represented by the dotted lines. BAM-2 and Oviedo-2 were not included in the calculation of the mean and median. As two other participants mentioned problems

(the University of Pau and PUC), their results were also not included in the calculation of the reference value. The white filled dots represents values that were not used in the calculation of the reference value (median).

The reference value for the pilot study CCQM-P43 regarding the amount of DBT in a sediment was calculated using participants' results and was chosen to be the median. The CCQM-P43 reference value is equal to 1.48 mol/g DBT⁺ (176 ng/g as Sn) with an associated expanded uncertainty $U = 0.11 \text{ mol/g DBT}^+$ (corresponding to 13 ng/g as Sn, i.e. 7.3 %).

7. CCQM-P43 and CCQM-K28 Participants' results for the analysis of TBT

As the material was used for a key comparison in parallel with the pilot study, a brief summary of the results is given here.

Table 5: CCQM-K28 and CCQM-P43 participants' measurement results for TBT in PACS-2

<i>participant</i>	<i>reported result nmol·g⁻¹</i>	<i>expanded uncertainty nmol·g⁻¹</i>
National Metrology Institutes (NMI), participating in CCQM-K28 for TBT		
BAM	7.38	0.194
BNM-LNE	6.71	0.2
LGC	7.5	1.0
NARL	7.79	0.48
NIST	8.480	0.265
NMIJ	8.03	0.2
NRC	7.44	0.24
"Expert" non NMI laboratories, participating in CCQM-P43 for TBT		
Oviedo-1	7.527	0.231
Oviedo-2	7.925	0.362
PUC	12.32	0.45
Umeå	7.56	0.44

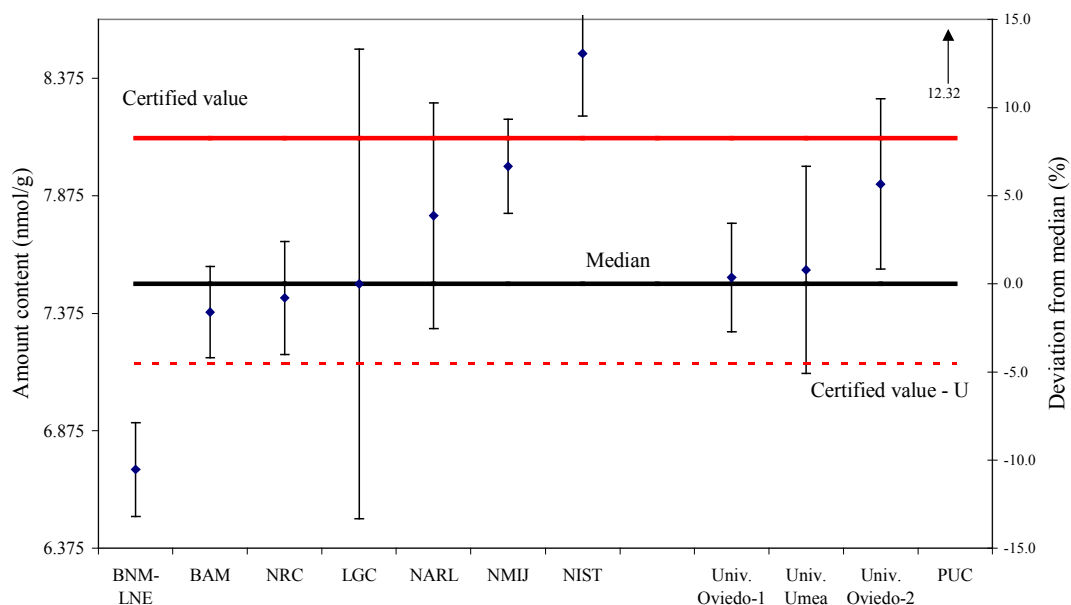


Figure 3: Results for determination of TBT in PACS-2 material

The median is represented by the thick black line. The certified value is represented by a thick red line, and the dotted red line represents the lower value of the certified range.

Table 6: CCQM-K28 and CCQM-P43 participants' measurement results for TBT

<i>participant</i>	<i>reported result nmol·g⁻¹</i>	<i>expanded uncertainty nmol·g⁻¹</i>
National Metrology Institutes (NMI), participating in CCQM-K28 for TBT		
BAM	1.072	0.027
BNM-LNE	0.895	0.058
LGC	1.046	0.093
NARL	1.069	0.068
NIST	1.078	0.054
NMIJ	1.109	0.043
NRC	1.051	0.038
"Expert" laboratories but non NMI, participating in CCQM-P43 for TBT		
Oviedo-1	1.085	0.036
Oviedo-2	1.100	0.045
PUC	1.310	0.09
Umeå	1.15	0.10

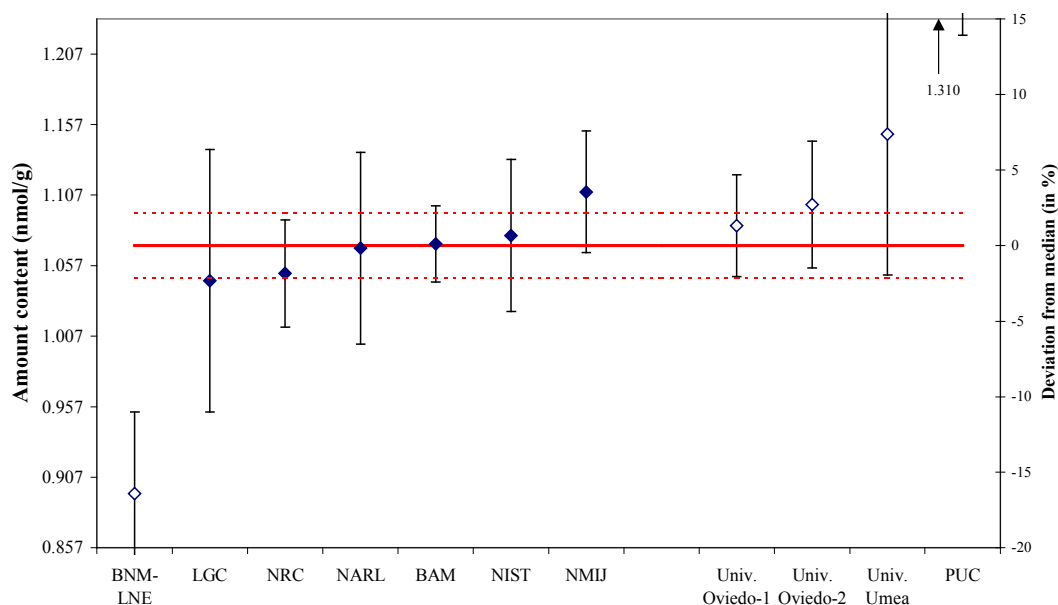


Figure 4: Results for determination of TBT in CCQM-K28 and CCQM-P43 sediment

The median is represented the thick line. The dotted lines represent the expanded uncertainty associated with the reference value. The white filled dots represents values that were not used in the calculation of the reference value.

The reference value for the key comparison CCQM-K28 (KCRV) was calculated using only 6 participating NMIs' results (excluding BNM-LNE one) and was chosen to be the median. The median is 1.071 nmol/g TBT⁺ (127.0 ng/g as Sn) with an associated expanded uncertainty (k=2) of 0.023 nmol/g TBT⁺ (2.7 ng/g as Sn). The expanded uncertainty is calculated from the maximum of the theoretical sampling distribution for the median based on standard deviation of the mean (0.011 nmol/g TBT⁺). This represents a relative expanded uncertainty of 2.1 %. Details are given in the CCQM-K28 report.[4]

8. Acknowledgement

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9. References

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