

## CCQM-K28: Tributyltin in sediment

Céline S.J. Wolff Briche, Raimund Wahlen and Ralph E. Sturgeon<sup>a</sup>  
LGC, Teddington, Middlesex, UK

<sup>a</sup>Institute for National Measurement Standards, National Research Council of Canada,  
Ottawa, Canada

### Abstract

Key comparison CCQM K-28 was undertaken to assess the measurement capabilities for quantitation of  $(C_4H_9)_3Sn^+$  (TBT) in a prepared marine sediment by National Metrology Institutes (NMIs), which are members of the Comité Consultatif pour la Quantité de Matière (CCQM). It follows a previous pilot study, CCQM-P18. [1, 2]

This exercise was sanctioned by the 8<sup>th</sup> 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.

Eight NMIs initially indicated their interest, with seven ultimately submitting their results. All NMIs relied on isotope dilution mass spectrometry using a species-specific <sup>117</sup>Sn-enriched TBT standard, which was supplied by LGC. No analytical methodology was prescribed for this study. As a result, a variety of extraction approaches was adopted by the participants, including mechanical shaking, sonication, accelerated solvent extraction, microwave assisted extraction and heating in combination with ethylation and direct sampling. Detection techniques included ICP-MS (coupled to GC or HPLC for the separation of Sn species), and GC-MS.

### 1. Introduction

The use of tributyltin (TBT) as an antifouling agent in paints on vessels shorter than 25m has been banned for two decades, in most countries. It can, nevertheless, be found in coastal waters and sediments of most developed countries. TBT in water and in marine sediment samples remain at such levels that the compound continues to pose an ecotoxicological threat in the aquatic environment.

The accurate quantification of organotin species is a challenging task due to their instability leading to possible interconversion reactions between species, low (ng/g) concentration levels and questions concerning extraction efficiency. Different methodologies are available with varying performance [3], but no single methodology can be recommended for consistent use.

This problem was deemed to be of sufficient interest to the analytical and environmental communities that a key comparison, CCQM-K28, of the Comité Consultatif pour la Quantité de Matière (CCQM) was sanctioned at the 8<sup>th</sup> meeting, April, 2002, to task the Inorganic Analysis Working Group to conduct an inter-comparison on the determination of TBT in sediment.

This determination, which follows a successful pilot study (CCQM-P18), broadens the scope and degree of difficulty of measurements heretofore addressed by this Group and is the first key comparison to address the issue of organometallic speciation by the CCQM. 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 content) as well as a test sediment material, and that LGC would make available a species specific calibration standard based on a synthesized  $^{117}\text{Sn}$ -enriched TBT to be used by participants wishing to conduct isotope dilution mass spectrometry (ID-MS). The advantages of such a calibration methodology to the enhancement of data quality have recently been demonstrated by Encinar *et al.* [4], 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-K28**

A call for participation was sent out to all NMIs in October 2002. In December 2002, a 3 mL solution of the  $^{117}\text{Sn}$  enriched TBTCI (with a nominal mass fraction of 110  $\mu\text{g/g}$  in methanol, i.e. 338 nmol/g) was sent to each participant by LGC to be used for ID-MS calibration. In January 2003, all participants were sent one bottle of CRM PACS-2 control sediment (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 two bottles of the sample material (with a nominal range of 100-150 ng/g TBT corresponding to 0.345-0.517 nmol/g) from the NRC. Instructions for handling and storage of all samples and calibration standards were provided to each participant.

Table 1 summarises the NMIs, which initially agreed to participate in this Key Comparison and to which materials were distributed. Results were requested to be submitted to LGC no later than April 30<sup>th</sup>, 2003.

**Table 1. CCQM-K28 participants**

<b>INSTITUTION / ORGANIZATION</b>	<b>COUNTRY</b>	<b>CONTACT</b>
<b>BAM</b> Federal Institute for Materials Research and Testing, Berlin	<b>Germany</b>	T. Win
<b>BNM-LNE</b> Bureau National de Métrologie - Laboratoire National d'Essais	<b>France</b>	B. Lalère
<b>LGC</b> Laboratory of the Government Chemist	<b>United Kingdom</b>	R. Wahlen
<b>NARL</b> National Analytical Reference Laboratory	<b>Australia</b>	L. Mackay
<b>NIST</b> National Institute for Standards and Technology	<b>U.S.A.</b>	M. Schantz
<b>NMIJ</b> National Metrology Institute of Japan	<b>Japan</b>	K. Inagaki
<b>NRC</b> National Research Council of Canada	<b>Canada</b>	R. Sturgeon
<b>SP</b> SP Swedish National Testing and Research Institute	<b>Sweden</b>	B. Magnusson

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-K28 sample was a marine sediment matrix prepared in-house at NRC by gravimetrically blending two NRC marine sediment CRMs: PACS-2 and HISS-1, the latter containing negligible concentrations of TBT and 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 has 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.

The enriched calibration standard was provided by LGC and distributed directly to participants as a 3 mL methanolic solution containing nominally 110 µg/g TBTCl in the form of <sup>117</sup>Sn-enriched material for those laboratories undertaking isotope dilution mass spectrometry. Safety data sheets accompanied the standard, as did instructions for its use and storage. The material was deemed stable for at least 5-6 months at room temperature in their amber vials.

#### **4. Instructions to participants**

Duplicate CCQM-K28 samples were sent in January 2003, with the information documents, to all institutes who had expressed their interest in participating.

The participants were free to choose one or more suitable methods of measurement for 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 sample material;
- instructions for determination of the dry mass correction;
- request for results for a minimum of 6 replicate determinations;
- request for a 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 participants. All seven participants used isotope dilution mass spectrometry, but their extraction and detection methods varied. There are a number of extraction techniques currently in use for determination of TBT, including mechanical shaking, sonication, microwave assisted extraction, heating and accelerated solvent extraction (ASE) used with solvents such as KOH, HCl, acetic acid and methanol. Further, extracts may be either analysed directly by high performance liquid chromatography (HPLC) coupled to ICP-MS or immediately derivatised with alkylating (ethylation) or Grignard reagents (pentylation) prior to separation with gas chromatography (GC) coupled to mass spectrometry (MS) or inductively coupled plasma mass spectrometry (ICP-MS).

**Table 2. Analytical methods and instrumental techniques used by CCQM-K28 participants**

<b>Participant</b>	<b>Method</b>	<b>Instrumentation</b>
BAM	HOAc/MeOH/sonicate/ethylation	GC-MS
LGC	HOAc/MeOH; ASE extraction	HPLC-ICP-MS
BNM-LNE	12 h HOAc/shaking; ethylation	GC-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/ethylation	GC-SF-ICP-MS

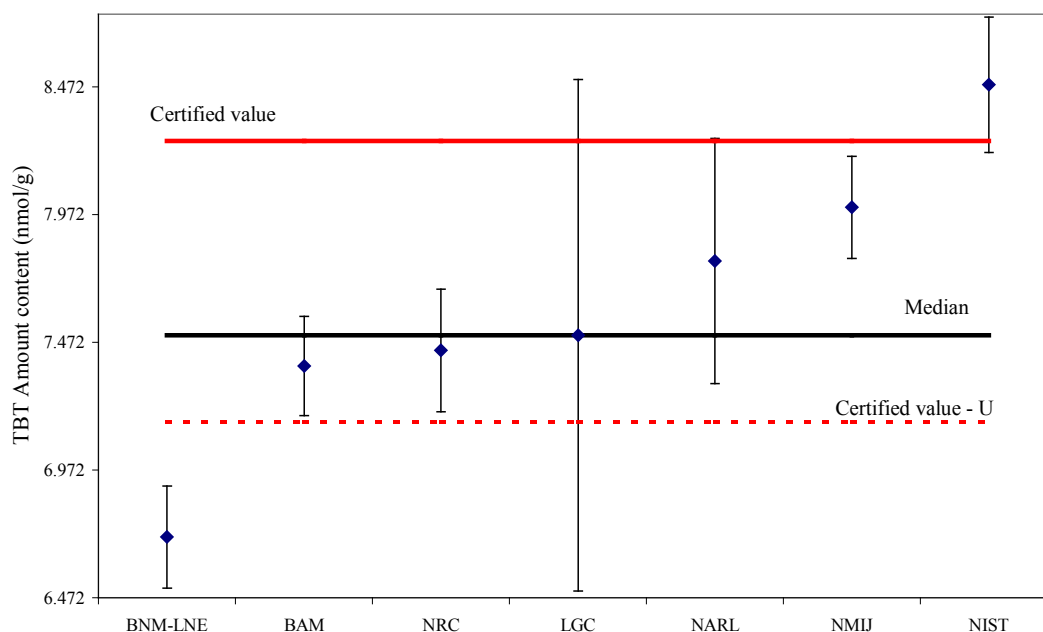
## 6. Results

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, from which recovery data were calculated, with a current certified value of  $0.98 \pm 0.13 \mu\text{g/g}$  (as tin) or  $8.26 \pm 1.10 \text{ nmol/g}$  (as TBT<sup>+</sup>). Results are displayed graphically in Figure 1. The median (all the participants results) is  $7.50 \text{ nmol/g TBT}^+$  ( $890 \text{ ng/g as Sn}$ ). It must be noted that the certified reference material PACS-2 is currently undergoing re-certification for its organotin species, made necessary by corrections for stability over its shelflife.

**Table 3. CCQM-K28 participants' measurement results for PACS-2 material**

<i>participant</i>	<i>reported result nmol·g<sup>-1</sup></i>	<i>expanded uncertainty nmol·g<sup>-1</sup></i>
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	8.00	0.20
NRC	7.44	0.24



**Figure 1: Results of TBT analysis 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 red dotted line represents the lower value of the certified range (expanded uncertainty,  $k=2$ ).

Participant's results for the CCQM-K28 sample are presented in Table 4. Results are displayed graphically in Figure 2. The median is 1.069 nmol/g TBT<sup>+</sup> (126.8 ng/g as Sn) with an associated expanded uncertainty ( $k=2$ ) of 0.041 nmol/g TBT<sup>+</sup> (4.9 ng/g as Sn) after resampling (3.8 %). The sampling distribution for the median is ill-defined in the absence of a known distribution. Resampling ( $n=100000$ ) gave a standard deviation of 0.021 nmol/g TBT<sup>+</sup> (2.5 ng/g as Sn); using the interquartile range estimate of standard deviation and assuming underlying normality gave  $s=0.009$ .

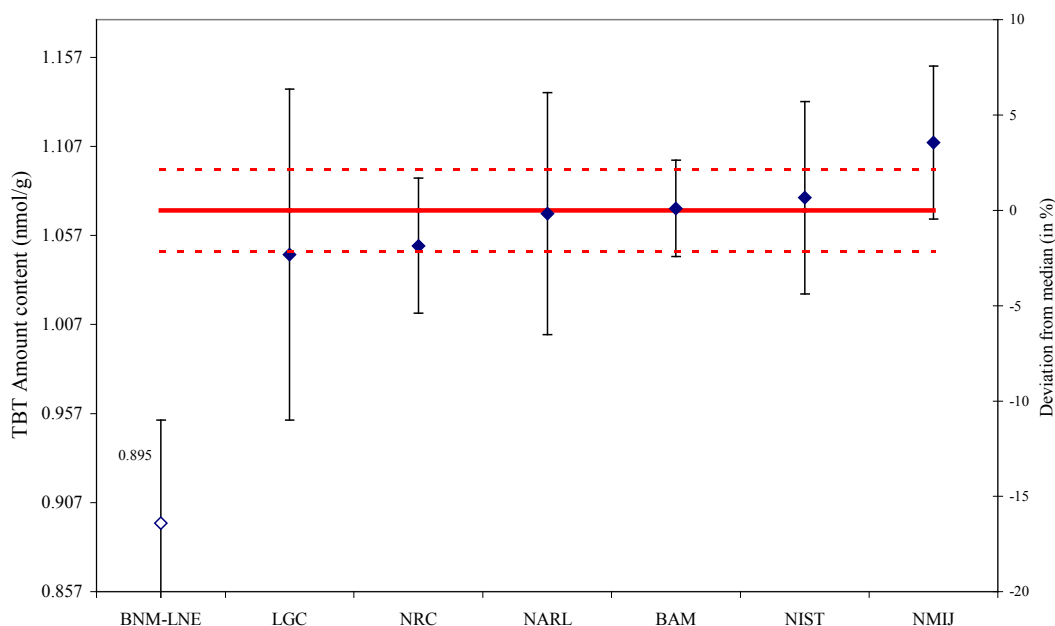
**Table 4. CCQM-K28 participants' measurement results**

<i>participant</i>	<i>reported result nmol·g<sup>-1</sup></i>	<i>expanded uncertainty nmol·g<sup>-1</sup></i>
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

The lowest result (BNM-LNE) is an “outlier” judged by Grubb's test at both the 95% and 99% level of confidence. BNM-LNE was contacted in order to determine if any problems could be identified that would explain the significantly lower value reported compared to the other participants. Some possible GC-MS problems initially suspected were ruled out, but no other explanations were given. After discussion

amongst the participants, it was decided not to include the value submitted by BNM-LNE into the calculation of the key comparison reference value.

The KCRV was thus recalculated as the median of 6 values (excluding BNM-LNE one). The median is 1.071 nmol/g TBT<sup>+</sup> (127.0 ng/g as Sn) with an associated expanded uncertainty (k=2) of 0.023 nmol/g TBT<sup>+</sup> (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<sup>+</sup>). This represents a relative expanded uncertainty of 2.1 %.



**Figure 2: Results of TBT analysis in CCQM-K28 sediment**

The median is represented by the thick line. The dotted lines represent the expanded uncertainty (k=2) associated with the reference value. The dot for BNM-LNE is represented by a white dot as it was not used to calculate the KCRV.

## 7. Conclusion

The reference value for the key comparison CCQM-K28 (KCRV) was calculated using all the participants' results and was chosen to be the median. The CCQM-K28 KCRV is equal to 1.071 nmol/g TBT<sup>+</sup> with an associated expanded uncertainty U = 0.023 nmol/g TBT<sup>+</sup> (2.1 %) using a coverage k = 2. In mass fraction terms, the KCRV corresponds to 127.0 ng/g as Sn with an associated expanded uncertainty U = 2.7 ng/g as Sn.

The IDMS methods available permit accurate fit-for-purpose measurements to be performed for TBT but cannot be extended this to other organotin species such as MBT due to its instability and known extraction problems. The calculated equivalence statements are given in the appendix ( section 9).

## 8. Acknowledgement

The work described here contains the contributions of many scientists:

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## 9. Appendix: equivalence statements

The equivalence statements are calculated according to the BIPM guidelines. The degree of equivalence (and its uncertainty) between an NMI result and the KCRV is calculated according to:

$$D_i = (x_i - x_R) \qquad U_i = 2 \cdot \sqrt{(u_i^2 + u_R^2)}$$

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 combining the standard uncertainty of the NMI results  $u_i$  and the standard uncertainty of the KCRV  $u_R$ . These are given in Table 5. A graphical display is given in Figure 3.

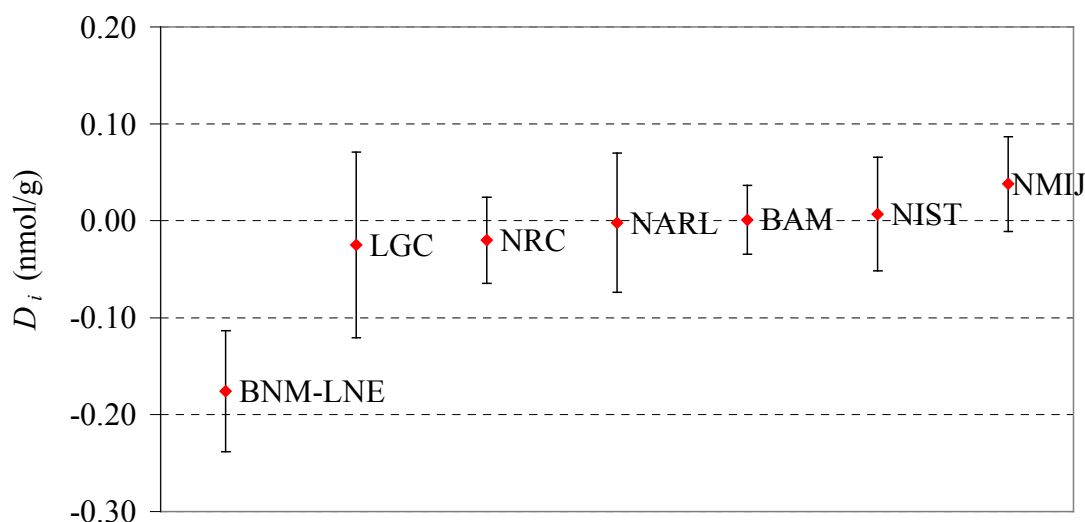
**Table 5: Degree of equivalence between the NMI result and the KCRV**

	$D_I$ (nmol/g)	$U_i$
<b>BNM-LNE</b>	-0.18	0.06
<b>LGC</b>	-0.02	0.10
<b>NRC</b>	-0.02	0.04
<b>NARL</b>	0.00	0.07
<b>BAM</b>	0.00	0.04
<b>NIST</b>	0.01	0.06
<b>NMIJ</b>	0.04	0.05

The degree of equivalence (and its uncertainty) between two NMI results can be calculated according to the following equations:

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

where  $D_{ij}$  is the degree of equivalence between the NMI result  $x_i$  and  $x_j$  and  $U_{ij}$  is the expanded uncertainty ( $k=2$ ) of  $D_{ij}$ , calculated by combining the standard uncertainty of the NMI results  $u_i$  and  $u_j$ .



**Figure 3: Graphical display of the degrees of equivalence for CCQM-K28**

## 10. References

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