

CCQM - P-18 Pilot Study:

Tributyltin in Sediment

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Abstract

CCQM P-18 was undertaken to assess the current capabilities of interested National Metrology Institutes (those which are members of the CCQM) and selected outside 'expert' laboratories to quantitate $(C_4H_9)_3Sn^+$ (TBT) in a prepared marine sediment. This exercise was sanctioned by the 7th CCQM meeting, April 4-6, 2001, as an activity of the Inorganic Working Group and was jointly piloted by the Institute for National Measurement Standards of the National Research Council of Canada and the Laboratory of the Government Chemist, Teddington, UK. A total of 14 laboratories initially indicated interest (10 NMIs, and 4 external labs), from which results were submitted by 7 NMIs and 4 external participants. Two external laboratories utilized a standard calibration approach based on a natural abundance TBT standard, whereas all NMIs relied upon isotope dilution mass spectrometry for quantitation. For this purpose, a species specific ^{117}Sn -enriched TBT standard was supplied by the LGC. No sample preparation methodology was prescribed by the piloting laboratories and, by 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 (with GC and HPLC sample introduction), GC-MS, GC-AED and GC-FPD. Recovery of TBT from a control standard (NRCC CRM PACS-2 marine sediment) averaged $93.5 \pm 2.4 \%$ ($n = 14$). Results for the pilot material averaged 0.680 ± 0.015 nmol/g ($n = 14$) with a median value of 0.676 nmol/g. Overall, performance was comparable to state-of-the-art expectations and the satisfactory agreement amongst participants allows for consideration of a follow-up Key comparison.

Introduction

Organotin compounds are ubiquitous contaminants in the environment, several of which exhibit deleterious effects in aquatic ecosystems. In particular, the use of tributyltin as a marine antifouling agent has led to its near global dispersal and it is now prominent in the coastal waters of all developed nations [1]. Tributyltin (TBT) persists in sediments, despite international efforts to curtail its usage in TBT-based paints since 1982 in France and subsequently in other countries. TBT levels in water and in marine sediment samples remain relatively high and 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. Pellegrino *et al.* [2] and Quevauviller *et al.* [3] recently summarized methodologies and performance characteristics for numerous current approaches, only to conclude that no single methodology can be recommended for consistent use.

This problem was deemed to be of sufficient interest to the analytical and ecotoxicological communities that pilot study P-18 of the Comité Consultatif pour la Quantité de Matière (CCQM) was sanctioned at the 7th meeting, April, 2000, to task the Inorganic Working Group to conduct an inter-comparison on the determination of TBT in sediment. This determination broadens the scope and degree of difficulty of measurements heretofore addressed by this Group and is the first to address the issue of organometallic speciation by the CCQM. The exercise was jointly piloted by the Institute for National Measurement Standards of the National Research Council of Canada (NRC), Ottawa, and the Laboratory of the Government Chemist (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 the LGC would make available a species specific calibration standard based on a synthesized ¹¹⁷Sn-enriched TBT to be used by participants wishing to conduct isotope dilution mass spectrometry (ID-MS). The advantages of application of such 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 enriched isotopic species.

Participation in CCQM P-18

A call for participation was sent out to all NMIs in October, 2000, at which time several external laboratories identified as expert in the technique were also individually invited to contribute to the effort. By the end of April, 2001, all respondents were sent one bottle of CRM PACS-2 control sediment and two bottles of the pilot material from the NRC along with calibration standards from the LGC comprising either a 100 : 1 aliquot of >99 % purity TBTCI standard and/or a vial containing a nominal 90.5 : g/g methanolic solution of the ¹¹⁷Sn enriched TBTCI to be used for ID-MS calibration. Instructions for handling and storage of all samples and calibration standards were provided to each participant.

Table 1 summarizes the NMIs and invited external laboratories which initially agreed to participate in this pilot study and to which materials were distributed. Results were requested to be submitted to NRC no later than October 1, 2001. CENAM and KRISS subsequently announced their

withdrawal from the study on November 15 and 23, respectively. NIST had neither withdrawn nor submitted data by the deadline, and was provided with an extension to January 30, 2002 as they expressed continued interest in being able to participate. NIST subsequently withdrew on February 14, 2002, citing instrumentation problems. Several laboratories submitted more than one independent result, based on an alternative detection methodology, calibration strategy or extraction procedure. In such case, the resultant mean was treated as an independent value and is delineated as the appropriate laboratory acronym accompanied by a numerical suffix (e.g., NARL-1).

Table 1. CCQM P-18 initial study participants

INSTITUTION / ORGANIZATION	COUNTRY	CONTACT
BAM Federal Institute for Materials Research and Testing, Berlin	Germany	T. Win
CENAM Centro Nacional de Metrologia	Mexico	E. Castro
Crompton Crompton GmbH Research Analytic	Germany	P. Schultze
IRMM Institute for Reference Materials and Measurements	European Union	H. Schimmel
KRISS Korean Research Institute of Standards and Science	Korea	D. Kim
LGC Laboratory of the Government Chemist	United Kingdom	R. Wahlen
LNE Laboratoire National d'Essais	France	B. Lalere
Limnol. Limnologisches Institut Dr. Nowak	Germany	T. Brandsch
NARL National Analytical Reference Laboratory	Australia	L. Mackay
NMIJ National Metrology Institute of Japan	Japan	K. Inagaki
NIST National Institute for Standards and Technology	U.S.A.	M. Schantz
NRCC National Research Council of Canada	Canada	R. Sturgeon
Oviedo University of Oviedo, Dept. of Chemistry	Spain	J.I. Garcia Alonso
Pau Université de Pau et des Pays de l'Adour, Lab. de Chimie	France	O. Donard

Samples and Calibration Standards

The P-18 pilot sample sediment was prepared in-house at NRC following careful 9:1 (*m/m*) gravimetric blending of two NRC CRM marine sediments, PACS-2 and HISS-1, the latter containing negligible concentrations of TBT and thus serving as a solid, inert diluent. The mixture was tumbled for 12 days at room temperature in a large glass container and sample homogeneity ascertained through measurement of several certified minor elements. ICP-AES was used for this purpose following a complete decomposition of sub-samples using pressurized microwave digestion with a mixed acid. Samples were withdrawn over a period of several days in an effort to track the progress of the blending process. Final variability within the blend was < 3% RSD and < 1% from target values of TBT based on the dilution factor. The sample was then partitioned into 336 pre-cleaned glass bottles, each containing nominal 25 g amounts of sample. All bottles were gamma-irradiated (minimum 2.5 Mrad) to ensure long-term stability and then labelled and packaged in trilaminate foil pouches. Analysis of randomly selected bottles of P-18 samples before and after gamma-irradiation revealed that this process altered the TBT content, as expected [5]. The concentration of TBT in irradiated samples was determined (in-house) to be 13 % lower than in non-irradiated samples. A homogeneous distribution of TBT between bottles was also verified. No significant difference was noted for the within bottle (8 determinations) *versus* between bottle homogeneity, as initially assessed by the precision of the NRC in-house SPME-GC-MS results [12.4 % RSD, (1s, n = 14) for 7 bottles]. The decision to proceed with sample distribution was based on an examination of available literature relating to TBT determinations in sediment, and the state-of-the-art characterizing CRMs certified for TBT, suggesting that this level of homogeneity would be fit for purpose (it was typical of that characterizing available water, sediment and tissue CRMs [6,7]). Subsequent, more detailed studies, using a more precise species specific isotope dilution MS technique, have shown that the distributed pilot sediment was quite homogeneous with respect to TBT, having less than 5 % variation between bottles (1s, n = 12), based on 1 g test samples.

Calibration standards were provided by LGC and were distributed direct to participants as requested, i.e., either a >99 % purity natural abundance TBTCI standard (100 : 1 in a sealed vial) or both this standard as well as a 4 ml methanolic solution containing nominally 90.5 : g/g TBTCI in the form of ¹¹⁷Sn-enriched material for those laboratories undertaking isotope dilution mass spectrometry. Safety data sheets accompanied the standards, 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.

Instructions to the Participants

The information packages distributed to the participants from both the NRCC and the 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, itemized 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.

A subsequent communiqué from the NRCC clarified that all participants were to report results as nmol/g of *total* TBT cation (inclusive of all isomers), based on a dry mass basis.

Methods and Instrumentation Used

As noted earlier, the choice of protocol presented in the instructions document was left to the discretion of the participant. Apart from a decision to employ ID-MS or calibration with a natural abundance standard in combination with selected internal organotin standards [standard additions calibration with an accompanying internal standard (SA-IS) and external calibration (EC) with and without the internal standard] there are a number of extraction techniques currently in use for determination of TBT [2], 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) in tandem with mass spectrometry (MS), flame photometry (FPD), atomic emission (microwave induced plasma) and inductively coupled plasma mass spectrometry (ICP-MS) or by high performance liquid chromatography (HPLC) coupled to ICP-MS. Table 2 summarizes the methods used by the individual participants. The Department of Physical and Analytical Chemistry of the University of Oviedo, Oviedo, Spain utilized ID-MS based on the LGC supplied ^{117}Sn enriched calibration material and also based on an in-house synthesized ^{119}Sn enriched TBTCI spike. For analysis of the P-18 material, the majority of participants selected 0.5 - 1 g sub-samples for work-up, the exceptions were 0.25-0.35 g (LGC, Univ. of Pau, Univ. of Oviedo), and 2.0 g (NRC). No target value for uncertainty was specified at the commencement of this study.

The majority of the participants applied ID-MS, except for Crompton GmbH Research Analytic and Limnologisches Institut Dr. Nowak. A standard additions (SA) approach was taken by Crompton GmbH Research Analytic wherein a natural abundance TBTCI and several organotin reference standards, i.e., tetrapropyltin, tripropyltin, diheptyltin and monoheptyltin chlorides, were used to normalize for response. The Limnologisches Institut relied on an external calibration (EC) but also incorporated tripropyltin chloride as the internal standard during the derivatization step.

Table 2. Analytical methods and instrumental techniques used by CCQM P-18 participants.

Participant	Calibration	Method	Instrumentation
BAM	ID-MS	(a)HOAc/MeOH/sonicate/ethylation (b) HOAc/MeOH/microwave/ethylation	(1) GC-MS (2) GC-AED
Crompton	SA-IS	KOH/MeOH/heat/ethylation	GC-FPD
IRMM	ID-MS	HCl/tropolone/hexane; ASE extraction; Grignard pentylation	GC-MS
LGC	ID-MS	HOAc/MeOH; ASE extraction	HPLC-ICP-MS
LNE	ID-MS	12 h HOAc/shaking; ethylation	GC-MS
Limnol.	EC-IS	KOH/MeOH/heat/ethylation	GC-FPD
NARL	ID-MS	(a) HOAc/microwave (b) HOAc/microwave/ethylation	(1)HPLC-ICP-MS (2)GC-MS
NMIJ	ID-MS	HOAc/MeOH/tropolone; microwave; ethylation	GC-ICP-MS
NRCC	ID-MS	HOAc/microwave	HPLC-ICP-MS
Oviedo	ID-MS:(1) ¹¹⁷ Sn and (2) ¹¹⁹ Sn	HOAc/MeOH/sonicate/ethylation	GC-ICP-MS
Pau	(1) ID-MS (2) SA-IS (3) EC	HOAc/microwave/ethylation	GC-ICP-MS

Results

In only 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 piloting laboratories to re-evaluate the results based on the information provided.

Participant's results for the control CRM marine sediment reference material PACS-2 are presented in Table 3, from which recovery data were calculated, based on the certified value of 0.98 ± 0.13 : g/g (as tin) or 8.26 ± 1.10 nmol/g (as TBT cation). Results are displayed graphically in Figure 1. The mean result, calculated from these data, is 7.72 ± 0.18 (n = 14) nmol/g TBT cation with a

median of 7.71, corresponding to an average recovery of the target analyte of $93.5 \pm 8.2 \%$ (1s). With the exceptions of Univ. of Pau and NMIJ, no uncertainty budgets were developed for the determination of TBT in PACS-2, hence only data for the sample standard deviation (1s) reported by each participant is presented in Table 3 and illustrated in Figure 1.

Table 3. Results for determination of TBT in PACS-2* CRM

Participant	Total TBT cation, nmol/g (mean \pm 1s, [n])	% Recovery of Certified Value	Report Date
BAM	(2) 7.72 ± 0.21 [4]	93.5 ± 2.5	October 1, 2001
Crompton	7.56 ± 0.33 [4] (SA) ^a	91.5 ± 4.4	November 18, 2001
IRMM	8.55 ± 0.26 [4]	103.5 ± 3.1	September 27, 2001
LGC	6.93 ± 0.26 [3]	83.9 ± 3.8	October 1, 2001
LNE	7.21 ± 0.47 [3]	87.3 ± 6.5	October 10, 2001
Limnol.	6.42 ± 0.17 [3] (EC) ^b	77.7 ± 2.6	September 27, 2001
NARL	(1) 7.85 ± 0.24 [3] (2) 7.69 ± 0.14 [3]	(1) 95.0 ± 2.9 (2) 93.1 ± 1.7	September 29, 2001
NMIJ	8.16 ± 0.12 [3]	98.5 ± 1.4	October 9, 2001
NRCC	8.57 ± 0.05 [3]	103.8 ± 0.6	September 14, 2001
Oviedo	7.22 ± 0.46 [3] (¹¹⁹ Sn)	87.8 ± 5.6	September 18, 2001
Pau	(1) 8.15 ± 0.18 [6] (2) 8.83 ± 0.73 [3] (SA) ^a (3) 7.26 ± 0.22 [3] (EC) ^b	98.7 ± 1.7 106.9 ± 8.8 87.9 ± 2.7	September 21, 2001

*reference value: 8.26 ± 1.10 nmol/g (95% CI).

^astandard additions (with tripropyltin and other organotin species serving as internal standards).

^bexternal calibration (with tripropyltin chloride serving as internal standard)

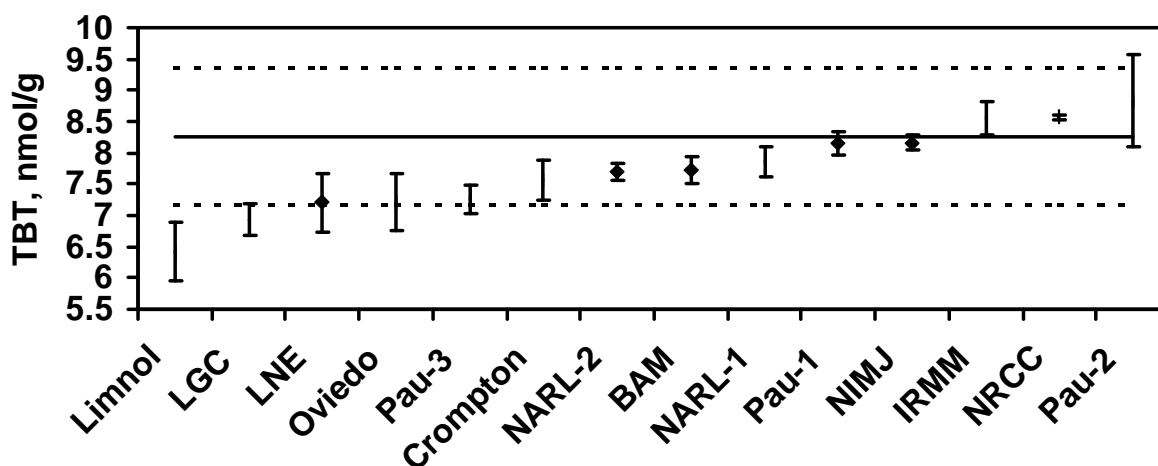


Figure 1: Results for TBT in PACS-2 CRM sediment. Error bars represent $\pm 1s$. Horizontal lines represent CRM PACS-2 certified value and associated 95 % confidence interval.

Explicit experiments aimed at elucidating recovery of TBT were not *reported* by any participant; values summarized in Table 3 were thus calculated from the ratio of determined TBT : certified value in PACS-2. For the purposes of this calculation, it was assumed that the *efficiency* of extraction of the endogenous TBT from the sediment was identical to that of the added spike. As application of ID-MS (or analyte standard addition) is based on the premise that complete equilibration of the added spike occurs in both the chemical and physical domains, if the resulting data are to be accepted, then it must also be accepted that the recovery data are also accurate. A standard additions approach was used by both Univ. Pau (Pau-2) and Crompton GmbH Research Analytic; it was assumed, as in the case of ID-MS, that these added spikes were fully equilibrated with the sample prior to extraction. The Limnologisches Institut Dr. Nowak utilized an external calibration approach, as did Univ. of Pau (Pau-3). It is not possible to draw any firm conclusions from these data regarding an optimum methodology for the extraction of TBT from the PACS-2 sediment; a variety of approaches (Table 2) appear appropriate, encompassing several solvent mixtures (HOAc, HCl, MeOH, KOH, tropolone, hexane) but highest recoveries are generally associated with microwave and accelerated solvent extraction assisted procedures. Further, there is no relationship between sub-sample size and final results. It is noteworthy that a simple standard additions approach (Pau-2 and Crompton GmbH, Research Analytic) also yields acceptable data within the uncertainty of the certified value when either microwave assisted extraction or simple methanolic KOH with heating is applied, indicating that spike equilibration is readily achieved with this matrix and discordant results generated using ID-MS are likely not attributable to this factor.

Results for the determination of total TBT cation (all isomers, dry weight basis) in the pilot sediment are summarized in Table 4 and graphically presented in Figure 2. A recovery factor, based on the analysis of PACS-2 (Table 3) was used to correct data submitted for the pilot sediment from the Limnologisches Institut; no other participant's data were similarly treated (it was assumed that the two matrices behaved identically with respect to extraction efficiency). Data provided by BAM were pooled results obtained from using both ID GC-MS and GC-AED detection. The uncertainties associated with all data are, unless noted otherwise, expanded uncertainties, having a nominal coverage factor of $k = 2$. As there was no consistent treatment of uncertainties presented by the participants, particularly from the 4 external laboratories, a simple mean and associated standard deviation of the mean of all results along with the median value for the TBT concentration have been calculated [8], i.e., mean = 0.680 ± 0.015 ($n = 14$); median = 0.676 nmol/g TBT.

Table 4. Results for the determination of TBT in P-18 pilot sediment

Participant	nmol/g (total TBT cation), mean \pm 1s [n]	nmol/g (total TBT cation), mean \pm U_c	k
BAM	(1 & 2) 0.669 ± 0.033 [7]	0.669 ± 0.030	2.2
Crompton	0.623 ± 0.032 [4]	0.623 ± 0.101^a	CI
IRMM	0.800 ± 0.051 [12]	0.800 ± 0.054	2
LGC	0.657 ± 0.033 [11]	0.657 ± 0.082	2
LNE	0.586 ± 0.008 [6]	0.586 ± 0.031	2
Limnol.	0.551 ± 0.036 [6]	0.551 ± 0.029 (0.709 ± 0.037) ^b	
NARL	(1) 0.686 ± 0.015 [6] (2) 0.678 ± 0.016 [6]	(1) 0.686 ± 0.044 (2) 0.678 ± 0.034	2.0
NMIJ	0.674 ± 0.015 [6]	0.674 ± 0.025	2
NRCC	0.748 ± 0.015 [6]	0.748 ± 0.052	2
Oviedo	(1) 0.637 ± 0.035 [10, (¹¹⁹ Sn)] (2) 0.611 ± 0.044 [11, (¹¹⁷ Sn)]	(1) 0.637 ± 0.056 (¹¹⁹ Sn) (2) 0.611 ± 0.044^c (¹¹⁷ Sn)	?
Pau	(1) 0.722 ± 0.022 [6] (2) 0.722 ± 0.017 [3]	(1) 0.722 ± 0.043 (ID) (2) 0.722 ± 0.020 (SA)	2

^a SA-IS results, uncertainty is a 95 % CI ($n=3$)

^b EC-IS results, value corrected for recovery (Table 3) given in parentheses.

^cuncertainty reported as standard deviation of mean ($n = 11$).

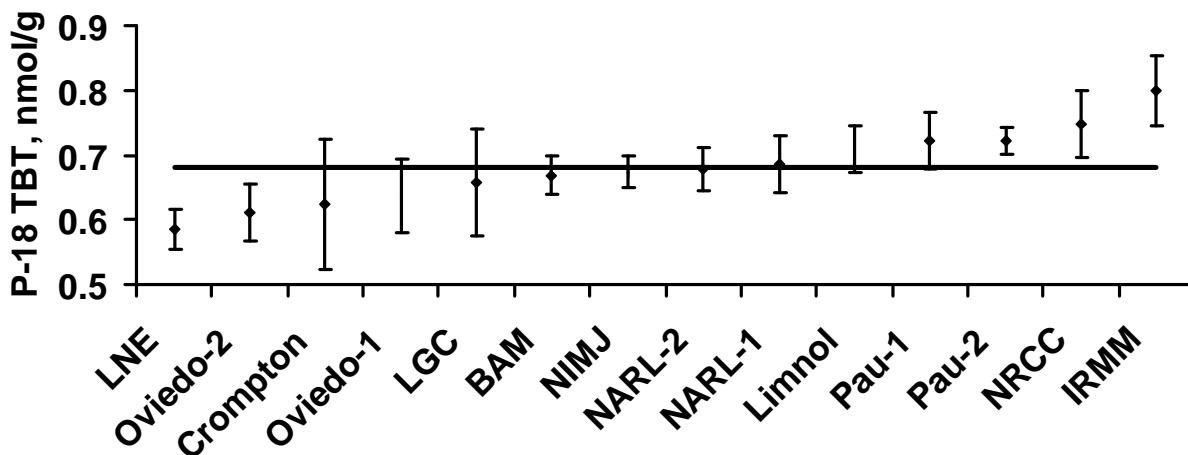


Figure 2. Results for TBT in P-18 pilot sediment. Error bars depict combined expanded uncertainties. Horizontal line represents simple mean of all data. Note: error bars for Oviedo-2 represent sample standard deviation ($\pm 1s$, $n = 11$), those for Crompton GmbH Research Analytic are their 95 % *CI*.

Detection limits, estimated by all participants, are summarized in Table 5. There was no common method used to estimate this figure of merit, some participants choosing to define the LOD as the concentration giving a response equivalent to three times the standard deviation of the blank, others deriving this figure of merit from a regression analysis of their calibration curve, noting that the value will change depending on the concentration range (and hence sample mass processed) in question.

Table 5. Estimated detection limits for TBT in sediment

Participant	Estimated Detection limit, pmol/g TBT cation	Detection technique
BAM	6.3	GC-AED
Crompton	170	GC-FPD
IRMM	13	GC-MS
LGC	70	HPLC-ICP-MS
LNE	60	GC-MS
Limnol.	72	GC-FPD
NARL	20	HPLC-ICP-MS
NMIJ	9.3	GC-ICP-MS
NRCC	49	HPLC-ICP-MS
Oviedo	14	GC-ICP-MS
Pau	0.13 (¹¹⁷ Sn); 0.25 (¹²⁰ Sn)	GC-ICP-MS

Discussion

Results for determination of TBT in the PACS-2 control sample were acceptable for the majority of the participants. This is illustrated by the data in Table 3 and Figure 1. Results submitted by LGC and the Limnologisches Institut were biased low with respect to the accepted measurement window defined by the certified value and associated 95 % *CI*, and data for LNE and the Univ. of Oviedo are just inside this “window”. This is also reflected in the recovery data, summarized in Table 1, wherein these laboratories attained TBT recoveries of less than 88 %.

The majority of laboratories subjected the sediments to a vigorous and efficient extraction procedure relying on microwave assisted or accelerated solvent extraction techniques. Although the data base is small in this study, it is suggestive that low recoveries of TBT from PACS-2 are systematically obtained by those laboratories utilizing the potentially less efficient extraction techniques, such as sonication (Oviedo), mechanical shaking (LNE) or heat (Crompton GmbH Research Analytic and Limnologisches Institut Dr. Nowak). Nevertheless, results from LGC are inconsistent with this general conclusion, as an accelerated solvent extraction approach was used for sample extraction in

this laboratory. Further, despite use of only heat, Crompton GmbH Research Analytic achieved acceptable results, and data obtained by NARL (not presented in the Tables) following application of a sonication extraction process were in good agreement with their microwave assisted extraction results (i.e., <0.7 % divergent), suggesting that the source of the problem with the Limnologisches Institut Dr. Nowak was simply the use of an EC protocol (also evident in Pau-3 data).

The TBT target value for the P-18 sediment (based on a 10-fold gravimetric dilution of PACS-2) was 0.83 nmol/g TBT cation. The resultant calculated mean of 0.680 ± 0.015 ($n = 14$) obtained in this study reveals a significant disparity between the target and obtained TBT concentration. This appears to be a consequence of the gamma-irradiation sterilization process, which is known to degrade TBT (amongst other species) [5]. As a consequence, the approximate target value of 100 - 150 ng/g (as Sn) originally suggested in the covering letter to participants was considerably lower than anticipated and resulted in a rewarding scrutiny of data by all participants. As noted earlier, in-house measurements indicated that the irradiated samples were 13 % lower in TBT content than non-irradiated samples. An examination of the participants data confirmed this; the ratio of reported TBT in the PACS-2 compared to the P-18 material should be 10.0 (based on the gravimetric dilution factor) whereas an average of 8.61 was achieved with a range of values from 8.13 to 9.48 (based on uncorrected data for Limnologisches Institut Dr. Nowak).

For the Limnologisches Institut laboratory, for which an external calibration approach was used, a correction factor for TBT recovery, based on their reported PACS-2 data, was subsequently applied to their P-18 data. This was based on the assumption that a matrix effect occurred and that the added internal standard (i.e., tripropyltin) served to only correct/compensate for volumetric factors. No other participant's P-18 sample data were likewise corrected. It is acknowledged that this is not a completely suitable approach as the uncertainty in the correction factor (assumed to be zero) will, in fact, be large because of the uncertainty in the certification range for the PACS-2. It may thus be prudent to exclude data for the pilot material from all laboratories submitting results for PACS-2 which were outside the reference range (i.e., the Limnologisches Institut and LGC).

The mean for Oviedo-2 appears biased low and it is to be noted that the measure of uncertainty used in this figure for this laboratory is a sample standard deviation ($n=11$). These results were obtained on samples subjected to ultrasonic extraction in vessels that were later deemed (by the participant) to be of inappropriate geometry and hence the extraction efficiency was questionable.

Dry mass correction for sample humidity is relatively insignificant when compared to other variables likely responsible for the spread in the reported values. Moisture correction in the P-18 material ranged from a high of 0.98 % (Pau) to a low of 0.14 % (LNE) with a mean of 0.64 ± 0.24 % ($1s$).

Major sources contributing to overall uncertainty identified by the participants are summarized in Table 6 and were frequently related to the measurement of the reference-to-spike ratio in the blends. Only NARL noted the need to consider a correction factor (1.000) associated with possible degradation of the TBT to DBT during the extraction procedure and included a relative uncertainty component (0.97%) associated with this term. The LGC, IRMM, NARL and NMII provided explicit estimates of the contribution to overall uncertainty arising from the extraction efficiency. NMII

equated it to the relative standard error of the mean of independent sample measurements (0.0092) and included this factor (E = 1.000) in their equation for the ID-MS expression for the result. NARL did likewise, assessing the extraction uncertainty (0.0017) from measurement of successive extractions of the P-18 material. IRMM equated the uncertainty of the extraction process with the relative uncertainty of the limit of detection and propagated this component into their overall expression for expanded uncertainty. LGC equated the uncertainty associated with the extraction process to the blend-to-blend variation of the results over 11 determinations. The question of extraction efficiency is one that needs to be resolved; it impacts on results of speciation measurements substantially more than on previous inter-comparisons of total metal recoveries from various matrices [9,10].

Table 6. Major sources of uncertainty

Participant	Dominant Source
BAM	method precision int. standard/analyte ratio
Crompton	calibration function
IRMM	LOD (extraction efficiency)
LGC	ref/spike ratio measurement (extraction component, 65%)
LNE	ref/spike ratio measurement
Limnol.	sample workup
NARL	(1) blank and degradation of TBT to DBT (2) method precision and blank
NMIJ	primary Std extraction efficiency
NRCC	ref/spike ratio measurement
Oviedo	primary Std assay ratio measurement
Pau	unclear

Several participants provided information arising from the reverse spike ID-MS determination of the concentration of TBT in the LGC isotopically enriched calibration standard. As supplied, this

standard was stated to contain 90.5 : g/g TBTCI (as Sn). Pau reported this standard to be 98.1 ± 1.1 : g/g; Oviedo, 100.1; NRC, 105.5 ± 1.4 and NMIJ, 101.5. Clearly, there may have been a need to precede this Pilot exercise with a determination of TBT in a simple calibration solution, as practised in some of the earlier CCQM inter-comparisons and it would have been useful to ask those participants using ID-MS to provide an independent measure of the concentration of the calibration standard by reverse spike techniques. Perhaps in this manner some trend in the data may arise which will relate scatter to calibration and not extraction efficiency.

Despite a 10-fold decrease in the concentration of TBT in the P-18 test sediment compared to the PACS-2 control, the precision of determination was not degraded for this material (8.4 % RSD vs 8.2 % for PACS-2, 1s data). It is likely that this arises because there is no detectable blank reported by most participants and the concentration of TBT in the sample was typically 20-100-fold above reported detection limits (cf. Table 5). In this connection, no single detection system can be recommended for application at this concentration and it is likely that the skill and experience of the operator is more important than the hardware available. It is also significant that the performance of the external laboratories is not at all inferior to that of the NMI participants as, in many cases, they have historically had more experience with the determination of this analyte than most NMI laboratories.

Only one of the participants (NARL) discussed the issue of isomer resolution when using GC techniques. This issue was originally raised by NARL, which prompted issue of a statement by the pilot laboratories that if isomer resolution was achieved, the integrated response from all was to be taken as a measure of quantitation. Additionally, as noted earlier, none of the participants raised concerns over potential degradation of TBT to DBT during sample work-up, although this issue could have been easily addressed by those using ID-MS techniques [4].

Summary statistics for this study are given in Table 7. In view of the disparate treatments used to arrive at the associated expanded measurement uncertainties, a median is the preferred statistic [8] characterizing these data.

Challenges in CCQM P-18

This the first time the CCQM has challenged participants with the quantitation of an organometallic analyte. Determination of tributyltin chloride requires significant sample preparation to ensure reproducible extraction of the TBT without decomposition, as well as derivatization of the analyte prior to detection (in most cases). Estimated limits of detection suggest that the determination is being attempted by some participants at a level only 4-fold above their LOD. Precision and accuracy can be enhanced through application of ID-MS techniques but equilibration must be assured if results are to be acceptable. More attention should be given to the impact of extraction efficiency on the overall results and associated uncertainty.

With respect to the question, “how far does the light shine”, it should be emphasized that the extremely good results obtained in this Pilot study are probably limited entirely to the determination

of TBT, and likely DBT, in a sediment matrix. Application to tissue matrices or MBT or, indeed, to any other organometallic species, cannot be confidently extrapolated.

Table 7. Summary Statistics Amongst Participants for P-18 sample

TBT	All Participants
(in nmol/g)	
Mean	0.680
Median	0.676
Sample standard deviation, 1s	0.057
Standard deviation of mean	0.015
ts / %n (95 % confidence)	0.033 (n = 14)
(in percent)	
1s	8.4
RSD of mean	2.3
ts / %n (95 % confidence)	4.9
Range ^a	31

^a(highest value-lowest value)/mean

Conclusion

The Inorganic Working Group is in a position to recommend the organization of a Key Comparison, if the CCQM so desires, with objectives similar to those of P-18. An expanded uncertainty of < 5 % can be realistically targeted. Additionally, a microwave assisted or accelerated solvent extraction technique can be recommended for sample treatment with species specific isotope dilution mass spectrometry for quantitation. It may be of interest to acquire information values and their associated statistics for MBT and DBT using the same methodologies.

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References

1. S. Tanabe, *Marine Pollution Bulletin*, **39**, 62 (1999).
2. C. Pellagrino, P. Massanisso and R. Morabito, *Trends Anal. Chem.* **19(2)**, 97 (2000).
3. P. Quevauviller, M. Astruc, R. Morabito, F. Ariese and L. Ebdon, *Trends Anal. Chem.*, 19(2), 180 (2000).
4. J.R. Encinar, P.R. Gonzalez, J.I. Garcia Alonso and A. Sanz-Medel, *Anal. Chem.*, **74**, 270 (2002).
5. D.W. Allen, J.S. Brooks, J. Unwin and D. McGuinness, *Appl. Organometal. Chem.*, **1**, 311 (1987).
6. R. Morabito, H. Muntau, W. Cofino and Ph. Quevauviller, *J. Environ. Monitor.* **1**, 75 (1999).
7. IAEA database for CRMs www.iaea.org/programmes/nahunet/e4/nmrm/index.htm
8. M. Cox in "Advanced Mathematical and Computational Tools in Metrology IV", P. Ciarlini, A.B. Forbes, F. Pavese and D. Richter (Eds.), World Scientific Publishing Co., 2000, pp. 45-65.
9. V.J. Barwick and S.L.R. Ellison, *Analyst*, 124, 981 (1999).
10. P. Quevauviller and R. Morabito, *Trends Anal. Chem.*, 19, 86 (2000).