Certified Reference Material

National Research Council Canada | Conseil national de recherches Canada

HIPA-1, SOPH-1 and PACS-2

Sediment Certified Reference Materials for the Determination of Tributyltin and Dibutyltin

This suite of certified reference materials are intended for the calibration of instruments and evaluation of methods for the determination of $(C_4H_9)_3Sn^+$ (tributyltin, TBT) and $(C_4H_9)_2Sn^{2+}$ (dibutyltin, DBT) in sediments or materials of a similar matrix.

Certified Value for Butyltins, ng/g (as Sn)

	HIPA-1	SOPH-1	PACS-2
TBT	78 ± 9	125 ± 7	890 ± 105
DBT		174 ± 9	1047 ± 64

Due to a lack of independent methods only an information value of 6 x10^2 ng/g for MBT in PACS-2 is provided. Care should be taken not to attribute more reliability to this number than is warranted.

The certified values are based on the unweighted mean of results from data submitted by laboratories participating in several recent Comité Consultatif pour la Quantité de Matière (CCQM) comparisons. The expanded uncertainty (U_{CRM}) in the certified value is equal to $U = ku_c$ where u_c is the combined standard uncertainty calculated according to the ISO Guide [1] and k is the coverage factor. The value of u_c is determined from the combined uncertainties associated with the various methods (u_{char}) as well as uncertainties associated with homogeneity (u_{hom}) and stability (u_{stab}).

It is intended that U_{CRM} encompasses every aspect that reasonably contributes to the uncertainty of the measurand [2,3]. A coverage factor (k) of 2 was applied.

Background

CCQM-P18, CCQM-P43 and CCQM-K28 were undertaken in 2002 and 2003 to assess the current capabilities of interested National Metrology Institutes (those which are members of the Consultative Committee for Amount of Substance) and selected outside 'expert' laboratories to quantitate tributyltin and dibutyltin in a prepared marine sediment.

These exercises were sanctioned by the CCQM as an activity of the Inorganic Analysis Working Group, and were jointly piloted by the Institute for National Measurement Standards of the National Research Council Canada (NRC) and LGC Ltd (UK).

A detailed report addressing CCQM-P18 is published in Metrologia [4].

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Preparation of material

HIPA-1 and SOPH-1 were prepared in-house at NRC following 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.

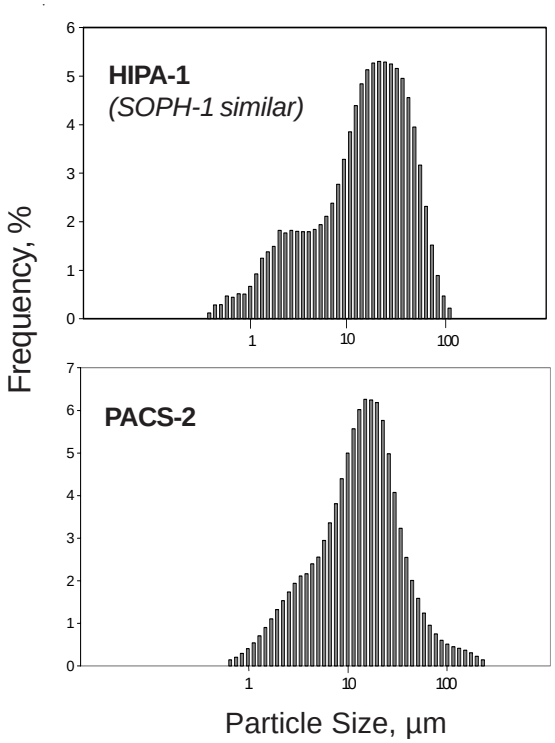
HISS-1 was collected from the Hibernia Shelf, off the coast of Newfoundland. PACS-2 was collected in the harbour of Esquimalt, B.C. Both sediments were freeze dried and screened to pass a No. 120 (125 µm) screen and blended by Institute staff using the facilities of CANMET, Mining and Mineral Sciences Laboratories, a division of Natural Resources Canada, in Ottawa.

Table 1.
Particle Size, µm

	HIPA-1	SOPH-1	PACS-2
Median	14.5	12.0	12.9
Mean	18.1	13.8	19.2
Mode	19.6	18.6	14.2

The particle size distribution was characterized at NRC using a Horiba LA 920 Laser Scattering Distribution Analyser.

Figure 1.
Particle Distributions



Storage and Sampling

To ensure the stability of the organotin species it is necessary to store these materials at a temperature of -20°C. Prior to use, the bottle should be well mixed by rotation, shaken and tightly closed immediately thereafter.

Characterisation

Mean values submitted by selected laboratories participating in CCQM P-18, CCQM P-43 and CCQM K-28 were used to calculate the certified value and the uncertainty of characterization (u_{char})[5].

Homogeneity

These materials were tested for homogeneity at NRC. Also, randomly bottles were selected for the analysis by the participating laboratories. Results from different bottles, as determined by ID-GC-ICP-MS, resulted in an uncertainty as reported in Table 2.

The homogeneity is warranted for samples of 500 mg and above.

Stability

Based on a 5 year study of the stability of tributyltin in PACS-2, an uncertainty component was assigned [6]. Similar behaviour from HIPA-1 and SOPH-1 is expected.

An uncertainty component associated with the short term stability (transport) was evaluated but considered insignificant. Measurements were conducted on samples stored for one month at -20°C, +4°C and 22°C.

Table 2.
Uncertainty Components for HIPA-1, SOPH-1 and PACS-2

Source	uncertainty components, ng/g				
	TBT			DBT	
	HIPA-1	SOPH-1	PACS-2	SOPH-1	PACS-2
u_{char}	2.4	1.4	15	2.6	22
u_{hom}	3.5	2.2	47	3.0	19
u_{stab}	1.6	2.5	19	2.3	14
u_c	4.5	3.6	53	4.6	32
U_{CRM}	**9.0**	**7.2**	**105**	**9.2**	**64**

Table 2. Analytical Methods and Instrumental Techniques used in the Certification of HIPA-1.

Calibration	Extraction Method	Instrumentation
ID-MS	(a)HOAc/MeOH/sonicate/ethylation (b)HOAc/MeOH/microwave/ethylation	GC-MS GC-AED
SA-IS	KOH/MeOH/heat/ethylation	GC-FPD
ID-MS	HCl/tropolone/hexane; ASE extraction; Grignard pentylation	GC-MS
ID-MS	HOAc/MeOH ; ASE extraction	HPLC-ICP-MS
ID-MS	12 h HOAc/shaking; ethylation	GC-MS
ID-MS	(a)HOAc/microwave (b)HOAc/microwave/ethylation	HPLC-ICP-MS GC-MS
ID-MS	HOAc/MeOH/tropolone; microwave; ethylation	GC-ICP-MS
ID-MS	HOAc/microwave	HPLC-ICP-MS
^{117}Sn ^{119}Sn	HOAc/MeOH/sonicate/ethylation	GC-ICP-MS
ID-MS SA-IS	HOAc/microwave/ethylation	GC-ICP-MS
ID-MS	HOAc/microwave/ ethylation	GC-MS
ID-MS	Ultrasonication (HBr), shaking (tropolone in DCM)	GC-ICP-MS
ID-MS	MAE (MeOH, HoAc, tropolone)	LC-ICP-MS

Methods

Table 2 summarizes the calibration procedure, extraction method and detection technique used by individual laboratories participating in the P-18 and K-28 exercises. A species specific calibration standard based on synthesized ^{117}Sn- enriched TBT was supplied by LGC Ltd. to those participants using isotope dilution mass spectrometry (ID-MS). Several laboratories used the method of standard additions (SA) for quantitation.

Detection was 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.

Expiration of Certification

The certified values stated for HIPA-1, SOPH-1 and PACS-2 are valid until September 2007 within the measurement uncertainty specified, provided the CRM is handled and stored in accordance with instructions herein. The stability of these CRMs will continue to be monitored. Our web site at http://inms-ienm.nrc-cnrc.gc.ca/calserv/chemical_metrology_ e.html#certified should be consulted for any new information.

Instructions for Drying

A separate aliquot of the sediment should be used to obtain a dry weight correction factor. Drying for two hours at 105°C has proved to be a relatively simple method to achieve a dry weight.

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The results listed in this certificate are traceable to the SI through gravimetrically prepared standards of established purity and international measurement intercomparisons. As such, they serve as suitable reference materials for laboratory quality assurance programs, as outlined in ISO/IEC 17025. PACS-2 is registered at the Bureau International des Poids et Mesures (BIPM) in Appendix C of the Comité International des Poids et Mesures database listing Calibration and Measurement Capabilities accepted by signatories to the Mutual Recognition Arrangement of the Metre Convention.

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