APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 8, 629–637 (1994)

Certified Reference Material (CRM 462) for the Quality Control of Dibutyl- and Tributyl-tin Determinations in Coastal Sediment

Ph. Quevauviller,* M. Astruc,† L. Ebdon,‡ V. Desauziers,†§ P. M. Sarradin,† A. Astruc,† G. N. Kramer¶ and B. Griepink||

*European Commission, Measurements and Testing Programme (BCR), rue de la Loi 200, B-1049 Brussels, Belgium, †Université de Pau et des Pays de l'Adour, Laboratoire de Chimie Analytique, Avenue de l'Université, F-64000 Pau, France, ‡University of Plymouth, Department of Environmental Sciences, Drake Circus, Plymouth PL4 8AA, UK, and ¶European Commission Institute for Reference Materials and Measurements, Steenweg op Retie, B-2440 Geel, Belgium

Determinations of tributyltin (TBT) species, along with the degradation products mono- and dibutyltin (MBT and DBT), are routinely carried out by a number of laboratories to ascertain the level of organotin contamination of the marine environment, particularly in water, sediment and biota. In order to improve and control the quality of such analyses the EC Community Bureau of Reference, BCR (Measurements and Testing Programme), has organized two interlaboratory studies on TBT in water and TBT in a spiked sediment which were followed by a certification campaign for butyltins in a coastal sediment (CRM 462). This material was collected in the Arcachon Bay (France), then carefully prepared (controlled oven drying) and its homogeneity and long-term stability were verified. This paper presents the certification work performed. The certified values for TBT and DBT are 70 ± 14 ng g^{-1} (as TBT cation) and 128 ± 16 ng g^{-1} (as DBT cation), respectively.

Keywords: Certified Reference Material, coastal sediment, analytical quality control, tributyltin, dibutyltin

INTRODUCTION

Tributyltin (TBT) is released in the marine environment from the leaching of TBT-based antifouling paints used on boats and ships. This compound is known to be highly toxic to marine organisms even at very low concentrations and is a potential source of major mortality of the shellfish population.[1–3] Several EC laboratories monitor the TBT levels in water, sediment and biota to verify that the legislation on the use of TBT-based antifouling paints is respected, or effective (e.g. national regulations in France, Great Britain and The Netherlands, and EC directives on the protection of the marine environment). In addition to TBT, its degradation products mono- and di-butyltin (MBT and DBT) are often determined. A wide variety of analytical techniques have been developed within the last decade for the determination of butyltins and the number of determinations carried out in quality-control and research laboratories has increased considerably in the last few years. The methods currently used involve various analytical steps such as extraction, derivatization, separation and final detection, which multiply the risks of analytical errors.[4] Some of these techniques are far from being validated. A programme for evaluating the performance of these methods has been organized by the Community Bureau of Reference (BCR—now Measurements and Testing Programme) of the European Commission.[5] It was recognized that there was a stong need to control the quality of TBT determinations in sediment by using a Certified Reference Material (CRM) with composition close to representative moderately contaminated samples. The existing sediment CRM produced by the National Research Council of Canada (PACS-1) was considered to be suitable for controlling the quality of analysis of highly polluted sediments owing to its

---

§ Present address: Ecole des Mines d'Alès, 6 avenue de Clavières, F-30319 Alès Cédex, France.

|| Present address: European Commission, PHARE Programme, Rue de la Loi 200, B-1049 Brussels, Belgium.

CCC 0268–2605/94/070629–09

Received 22 February 1994
Accepted 8 August 1994

high TBT mass fraction (1.27 ± 0.22 $\mu g\ g^{-1}$) but it could not be used for the quality control of analysis of coastal sediment with lower TBT contents (typical TBT levels in coastal sediments range from 50 to 200 $ng\ g^{-1}$ of TBT).[6,7] Consequently, the BCR was invited to produce a sediment with TBT levels representative of moderate coastal contamination. This material (CRM 462) was prepared in 1989 and has been certified for its content of TBT and DBT. This paper presents the certification work performed.

BACKGROUND OF THE PROJECT

Intercomparisons were organized within the BCR programme for improving the quality of tin speciation analyses.[4] This programme involved 15 laboratories from seven European countries (see Acknowledgements). The first 'round-robin' dealt with the analysis of solutions containing pure analytes (TBT and mixtures of MBT, DBT and triphenyltin). No systematic errors could be detected in the final determination techniques tested at this stage. A second exercise was undertaken in 1989 on the determination of TBT in a spiked sediment (collected from Laggo Magiore, Italy, and prepared at the EC Joint Research Centre of Ispra[5]). The results of this interlaboratory trial did not reveal any systematic errors in the different analytical methods compared. Figure 1 shows the results obtained in this second intercomparison. The coefficient of variation (CV) obtained between laboratories (25%) was considered to reflect the state-of-the-art at that time and the group of analysts recommended proceeding with the organization of a certification campaign. The participants recognized, however, that better agreement should be achieved for certification. No particular source of error due to a method could be detected and the analytical techniques used in this intercomparison were therefore found suitable for certification. Another interlaboratory exercise was therefore organized to attempt the certification of TBT in a harbour sediment (RM 424). This work is described in detail in this issue;[8] as discussed, the results at that stage could not allow the certification of this material. Consequently, the BCR decided to organize a second certification campaign on TBT in a sediment (CRM 462) containing a higher level of TBT (i.e. around 100 $ng\ g^{-1}$ of TBT) and being representative of coastal environments.

PARTICIPATING LABORATORIES

The candidate reference material of sediment was collected by the University of Pau (France) and prepared at the Institute for Reference Materials and Measurements (IRMM, Geel, Belgium). The verification of the homogeneity and stability was carried out by the University of Pau as described below.

The following laboratories participated in the Certification campaign:

CIBA–Geigy, Bensheim, Germany;
CID–CSIC, Department of Environmental Chemistry, Barcelona, Spain;
ENEA, Casaccia Research Centre, Rome, Italy;
Ministry for Agriculture Fisheries and Food, Burnham-on-Crouch, UK;
University of Antwerp, Department of Chemistry, Antwerp, Belgium;

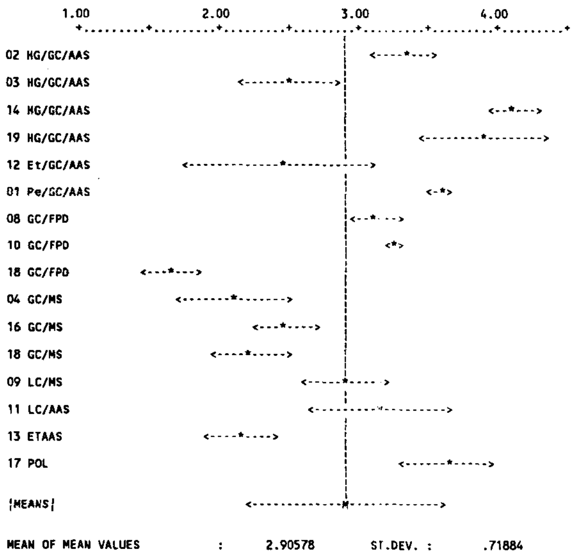

Figure 1 Second intercomparison on TBT in a spiked sediment (content as TBTAc mass fraction in $\mu g\ g^{-1}$). The laboratory codes are indicated along with the methods used (abbreviations are as defined in Table 3). The results plotted correspond to five replicate determinations. 'MEANS' is the mean of laboratory means with its standard deviation.

University of Bordeaux I, Laboratory of Molecular Photophysics and Photochemistry, Talence, France;
University of Pau, Laboratory of Analytical Chemistry, Pau, France;
University of Plymouth, Department of Environmental Sciences, Plymouth, UK;
University of Seville, Department of Chemistry, Seville, Spain.

CERTIFICATION PROCEDURE

The accuracy of measurements is one of the strongest requirements to ensure the worldwide comparability of data. One of the best methods for any laboratory to verify that good accuracy has been achieved is to monitor the analytical procedure by means of a so-called matrix reference material certified in a reliable manner.[9, 10] The use of Certified Reference Materials (CRMs) is a good means of linking the user's results to the basic material and, therefore, to the results of the international community. A laboratory which measures a CRM by its own procedure and finds a value in disagreement with the certified value is thus warned that its measurement includes an error, the source of which must be identified.[11]

Each laboratory that took part in the certification exercise was requested to make a minimum of five independent replicate determinations on at least two different bottles of the CRM on different days.

The requirements listed below were followed by the certifying laboratories to achieve accuracy.

(1) In the meeting of the analysts participating in the certification, the sources of error and the measures taken to eliminate them were discussed. Errors related to a particular technique or analytical step could not be detected.
(2) The laboratories participating in the certification exercise applied their methods correctly. They used at least the following quality-control steps:
    (a) determinations were performed only when the method was under statistical control;
    (b) wherever possible, the performance of the method was verified by analysing available Certified Reference Materials or other well-characterized materials of similar matrix and trace-element composition.

FEASIBILITY STUDY ON MATERIAL STABILIZATION

One of the major requirements for the preparation of a CRM is its stabilization. This should be achieved in such a way that the pattern of compounds is not changed (i.e. no degradation) and the long-term stability of the material is achieved. Gamma-irradiation is a procedure which has been used for this purpose; however, it has been mainly carried out to stabilize materials to be certified for their total element content. In the case of organotin compounds, it was suspected that gamma-irradiation would lead to a degradation of TBT, which was confirmed by a literature search performed within the BCR.[12] Consequently, heating procedures were tested on a test sediment portion to investigate the feasibility of stabilizing the material and the possible effects on the stability of butyltin compounds. The aim of this study was to stop possible microbial activities (risk of microbial degradation of TBT) by a heating procedure which would preserve the organotin content of the sediment. A small amount of sediment sample was collected in the Arcachon Bay, France, and air-dried at ambient temperature (*ca* 20 °C) on a polythene film in a clean room for seven days. The material was ground in a porcelain crucible and sieved at 80 μm mesh. The powder obtained was homogenized manually and bottled in 20 glass bottles, each containing *ca* 50 g of sediment. After bottling, five flasks were wrapped in aluminium film (to protect against light) and were placed in a cupboard at ambient temperature and kept as test samples. The other bottles were treated as follows:

(1) five bottles were heated at 80 °C for 6 h;
(2) five bottles were heated at 120 °C for 2 h;
(3) five bottles were heated at 120 °C for 6 h.

The effect of heat on butyltin stability was assessed by determining TBT in duplicate in each bottle. The determination was carried out by acetic acid (HAc) extraction, hydride generation (using $NaBH_4$), cryogenic condensation in a U-tube filled with chromatographic material (Chromosorb GAWHP, 80–100 mesh) followed

Table 1 Effects of heat on tributyltin stability

Conditions	+20 °C	6 h at 80 °C	2 h at 120 °C	6 h at 120 °C
TBT content[a]	102 ± 16	102 ± 17	105 ± 24	85 ± 17

[a] The TBT contents are given as mass fractions (ng g^{-1}) of Sn.

by thermal separation (based on the different organotin hydride sublimation points) and AAS detection in a quartz furnace electrically heated to 950 °C (University of Pau).

The results obtained are presented in Table 1 as mass fractions of Sn).

A statistical treatment (*F*-test) did not reveal any significant difference between the sets of results. It was therefore concluded that the heating procedures applied did not entail significant losses of TBT by degradation. Previous results obtained at the University of Pau had, however, shown that drying at 80 °C for a longer period (e.g. overnight) could induce degradation of TBT. Hence, the procedure recommended for the preparation of the candidate CRM was drying at 60 °C for for 48 h, grinding and sieving, followed by heat sterilization at 120 °C for 2 h.

Preliminary experiments were also performed in order to evaluate the stability of butyltins in the test material over a three-month period in the dark. The test material was stored at −20 °C, +20 °C and +40 °C and MBT, DBT and TBT were determined in six replicates at each temperature after one, two and three months. A statistical treatment of the results (*T*-test) did not reveal any significant changes in the butyltin contents with respect to the storage conditions tested. It was therefore concluded that the preparation of a coastal sediment for the certification of butyltin compounds could be undertaken safely.

PREPARATION OF THE CANDIDATE CRM

Collection

The coastal sediment to be used as a candidate Certified Reference Mateial (CRM 462) was collected in the southern part of the Arcachon Bay (France) in a small harbour (Larros). The first 10-cm layer was collected with a shovel and stored in plastic containers. After decantation, the sediment sample was air-dried for seven days at ambient temperature on a cotton sheet in a well-ventilated room, and stored at −20 °C in polythene bags. The material (about 180 kg dry mass) was then stored in ice boxes for transportation to IRMM.

Homogenization and bottling

The material was dried at 55 °C in air for 100 h. The moisture content determined at this stage was less than 3%. The material was then sieved through a sieve of 1 mm mesh size and finely ground using a jet mill grinding device with a classifier. This procedure allowed a powder with a closely defined particle size distribution (less than 75 µm) and a sharp maximum size limitation (no oversized particles) to be obtained. The material was then sterilized by heating at 120 °C for 2 h, homogenized in a mixer for 2 h and finally stored in 60-ml well-cleaned brown glass bottles with polyethylene inserts and plastic screw caps, each containing *ca* 25 g of powder.

The moisture content of the material was determined by Karl Fischer titration on ten samples selected during the bottling procedure. The mean moisture mass fraction measured was 2.70 ± 0.40%.

HOMOGENEITY

Between-bottle homogeneity was verified by the determination of DBT and TBT on intakes of 1 g taken from 20 bottles which were set aside at regular intervals during the whole period of bottling. Within-bottle homogeneity was assessed by ten replicate determinations on the well-mixed contents of one bottle. Each bottle was shaken manually for 5 min to eliminate segregation which might have occurred during transport and storage.

The determinations of DBT and TBT were carried out using the method previously described in the feasibility study (see above). Calibrations were performed by standard additions. The uncertainty of the method of separation and final determination was assessed by fine replicate determinations of each butyltin compound on one extract solution; the CV of the method does, therefore, not comprise the CV introduced by the extraction procedure. The CVs for DBT and TBT

Table 2 Within- and between-bottle homogeneity, CV ± U_{CV} (%)

Compound	Between-bottle[a]	Within-bottle[b]	Method of final determination[c]
DBT	9.6 ± 1.5	5.6 ± 1.2	6.0 ± 1.3
TBT	15.8 ± 2.5	10.0 ± 2.2	9.0 ± 2.0

[a] Single determination on the content of each of 20 bottles.
[b] 10 replicate determinations on the content of one bottle.
[c] 10 replicate determinations of an extract solution.
Uncertainty on the CVs: $U_{CV} \approx CV/\sqrt{2n}$.

are presented in Table 2. An *F*-test at a significance level of 0.05 did not reveal significant differences between the within- and between-bottle variances. The within-bottle CV is very close to the CV of the method and, therefore, no inhomogeneity of the material was suspected. It was hence concluded that the material is suitable for use as a CRM and is homogeneous at least at an analytical portion of 1 g and above for DBT and TBT.

STABILITY

The stability of the butyltin content was tested to determine the suitability of this material as a reference material. Bottles were kept at respectively −20 °C, +20 °C and +40 °C over a period of 12 months and DBT and TBT were determined at regular intervals during the storage period Tests were made at the beginning of the storage period and after one, three, six and 12 months. Samples were analysed using the procedures detailed above for the feasibility study. DBT and TBT were each determined ten times on each occasion of analysis.

The samples stored at −20 °C were used as references for the samples stored at +40 °C and at +20 °C. The ratios (R_T) of the mean values ($\bar{X}_T$) of five measurements made at +20 °C and +40 °C, respectively, and the mean value ($\bar{X}_{-20\,°C}$), from five determinations made on the same occasion of analysis on samples stored at a temperature of −20 °C, were calculated. The uncertainty U_T was obtained from the coefficient of variation (CV) of five measurements obtained at each temperature:

$$U_T = (CV_T^2 + CV_{-20\,°C}^2)^{1/2} . R_T$$

In the case of ideal stability, the ratio R_T should be 1. In practice, however, there are some random variations due to the error on the measurement. As shown in Fig. 2(a) for DBT at +20 °C, the value 1 exists in almost all cases between $R_T - U_T$ and $R_T + U_T$. The uncertainty on the CV can account for the deviations observed. For TBT at +20 °C (Fig. 2b), the content decreased after three months of storage and stabilized afterwards. This decrease was assessed to be due to a degradation of TBT directly to MBT as previously observed,[13] because of a corresponding increase of MBT content after three months (from 66 to 93 ng g^{-1} as Sn). In the case of storage at +40 °C, both DBT and TBT displayed strong losses after three months which were likely to be due to a degradation of these compounds to MBT and inorganic tin (Figs 2a and 2b).

On the basis of the results, the following conclusions were drawn.

(1) DBT is stable at +20 °C in the dark.
(2) TBT displayed losses at the start of the storage period but the content stabilized after three months. It is hence concluded that TBT remained stable at +20 °C in the CRM in the dark; however, in order to avoid any risk of organotin degradation during long-term storage, it was decided to store the material at +4 °C in the dark.
(3) Both DBT and TBT are unstable at +40 °C. However, the two compounds are stable at this temperature for at least one month (Figs 2a and 2b), which indicates that the material could be transported safely under more extreme conditions.

TECHNIQUES USED FOR CERTIFICATION

The techniques used in the certification involved solvent of acid extraction, derivatization (e.g. Grignard reaction or hydride generation), separation by gas chromatography (GC) or high-performance liquid chromatography (HPLC), and various methods of final detection (e.g. quartz furnace atomic absorption spectrometry, flame photometric detection etc.). Table 3 gives an account of the techniques used by each laboratory in the certification; more detailed descriptions can be found in the certification report.[14]

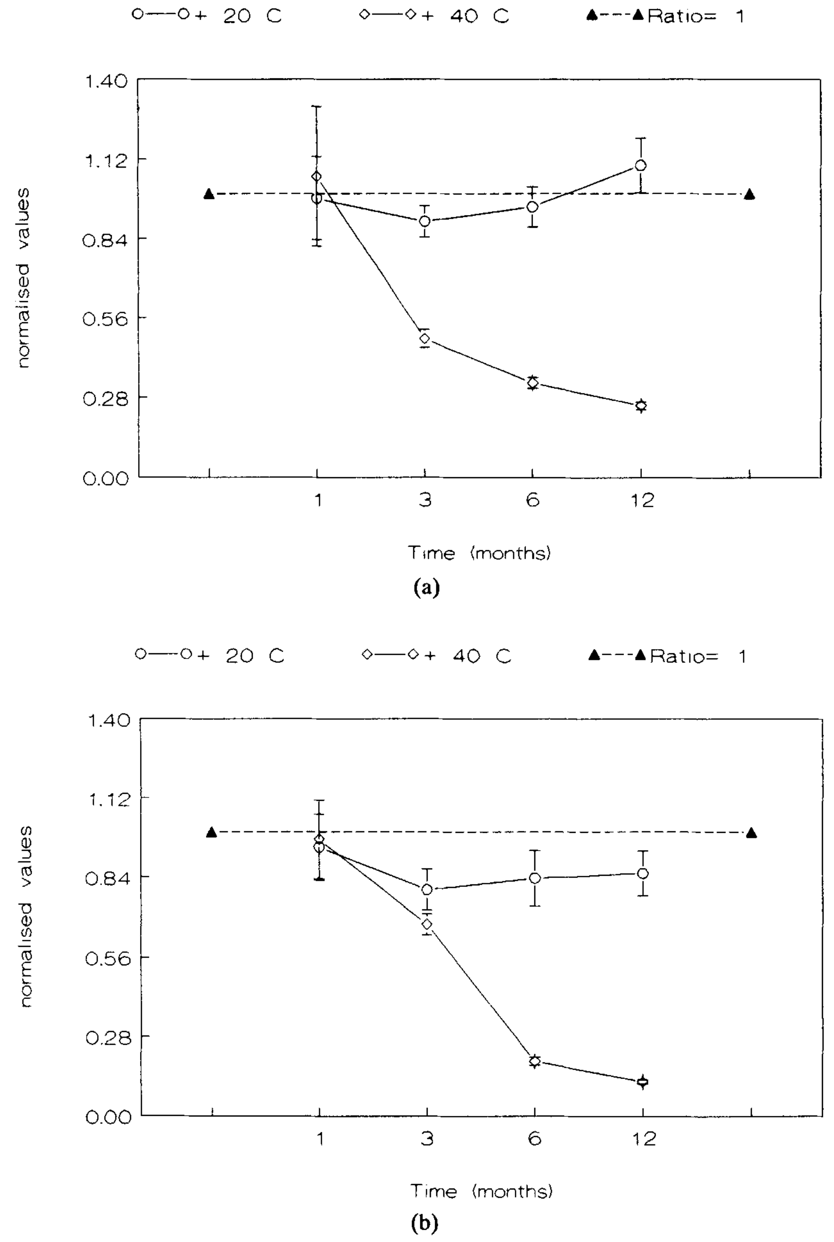

Figure 2 Stability tests of coastal sediment CRM 462: $R_T = \bar{X}_T/\bar{X}_{-20\,^\circ C}$, where $\bar{X}_T$ = mean of 10 replicates at temperature T ($+20\,^\circ$C or $+40\,^\circ$C), and $U_T = (CV_T^2 + CV_{-20\,^\circ C}^2)^{1/2} . R_T$, where CV_T = coefficient of variation of 10 replicates at temperature T. (a) Stability tests of DBT at +20 and +40 °C; (b) stability tests of TBT at +20 and +40 °C.

TECHNICAL DISCUSSION

The results submitted in the certification were discussed amongst all participants in a technical meeting; they were presented in the form of bar-graphs showing the laboratory codes and the methods used, the indiviudal means and standard deviations and the mean of laboratory means with its standard deviation. Figures 3(a) and 3(b) show the sets of results for TBT and DBT after technical scrutiny.

Table 3 Summary of the analytical methods used in the Certification

Laboratory code	Sample pre-treatment, derivatization separation and calibration[a, b]	Final determination[a]
01	Extraction with acetic acid/hexane/DDTC in pentane. Pentylation with Grignard reagent. Capillary GC separation. TBTOAc and $\mathrm{DBTCl_2}$ as calibrants. TPrT as internal standard. Calibration graph.	QFAAS (wavelength 286.4 nm). Addition of air/$\mathrm{H_2}$.
02	Acetic acid extraction. Hydride generation with $\mathrm{NaBH_4}$. Cryogenic trapping (U-tube) and GC separation (packed column). TBTCl and $\mathrm{DBTCl_2}$ as calibrants. Standard additions.	QFAAS (wavelength 286.4 nm). Addition of $\mathrm{H_2/O_2}$.
03	Acetic acid extraction. Hydride generation with $\mathrm{NaBH_4}$. Cryogenic trapping (U-tube) and GC separation (packed column). TBTCl and $\mathrm{DBTCl_2}$ as calibrants. Calibration graph. TET as internal standard.	QFAAS (wavelength 224.6 nm). Addition of $\mathrm{H_2/O_2}$.
04	Diethyl ether/HCl/tropolone extraction. Pentylation with Grignard reagent. Capillary GC separation. TBTO and $\mathrm{DBTCl_2}$ as calibrants. DHTC as internal standard. Calibration graph.	Mass spectrometry of masses 247, 249, 303 and 305 for TBT, and masses 307 and 319 for DBT.
05	HCl/methanol/tropolone extraction. Pentylation with Grignard reagent. Capillary GC separation. TBTCl and $\mathrm{DBTCl_2}$ as calibrants. TPrT as internal standard. Calibration graph.	Mass spectrometry of masses 301, 303 and 305 for TBT, and masses 305, 317 and 319 for DBT.
06	For TBT, supercritical fluid extraction ($\mathrm{CO_2}$/HCl/MeOH); for DBT, MeOH/HCl extraction. Ethylation with Grignard reagent. Capillary GC separation. TBTCl and $\mathrm{DBTCL_2}$ as calibrants. TPrT as internal standard. Calibration graph.	FPD (wavelength 610 nm). Addition of $\mathrm{N_2}$.
07	HBr/tropolone extraction. Pentylation with Grignard reagent. Capillary GC separation. TBTCl and $\mathrm{DBTCl_2}$ as calibrants. $\mathrm{DMTPe_2}$ as internal standard. Calibration graph.	FPD (wavelength 610 nm). Addition of $\mathrm{H_2}$/air.
08	NaOH/hexane extraction. Hydride generation with $\mathrm{NaBH_4}$. Capillary GC separation. TBTO and $\mathrm{DBTO_2}$ as calibrants. TPrT as internal standard. Calibration graph.	FPD (wavelength 610 nm). Addition of $\mathrm{N_2}$
09	Acetic acid extraction. Back-extraction with toluene. HPLC separation. TBTOAc and $\mathrm{DBTAc_2}$ as calibrants. Standard additions.	ICP–MS of mass 120.

[a] Abbreviations (techniques): ETAAS, electrothermal atomic absorption spectrometry; FPD, flame photometric detection; GC, gas chromatography; HG, hydride generation; HPLC, high-performance liquid chromatography; ICPMS, inductively coupled plasma mass spectrometry; MS, mass spectrometry; Pe, pentylation; QFAAS, quartz furnace atomic absorption spectrometry. Abbreviations (chemical groups, compounds): E, ethyl; Pr, propyl; Pe, pertyl.

Tributyltin

Poorer extraction recoveries for TBT in CRM 462 were often observed in comparison with recoveries obtained from other sediment materials. Some laboratories found lower recoveries if the spike was allowed to equilibrate longer. The previous interlaboratory excercise on TBT-spiked sediment had identified the need to allow spikes to equilibrate at least overnight to obtain a realistic assessment of extraction recoveries.

The evaluation of polarographic methods showed that there were major problems with this sample. The surfactants present made it difficult to detect TBT and polarography was, therefore, a method not recommended for this certification.

In some cases (e.g. Laboratories 04, 07 and 08), the uncertainty over extraction recoveries was not taken into account in the overall uncertainty of the laboratory means, which explains the poor standard deviations observed.

It was agreed to certify the TBT content.

Dibutyltin

As shown in Fig. 3(b), the overlap obtained between the different sets of results and the range of techniques used was found satisfactory and, as no doubts were thrown on the results presented, it was agreed to certify the DBT content.

Monobutyltin

A high scatter of results was observed for MBT which prevented certification. Many laboratories reported problems in the extraction step. The addition of complexing agents such as diethyldith-

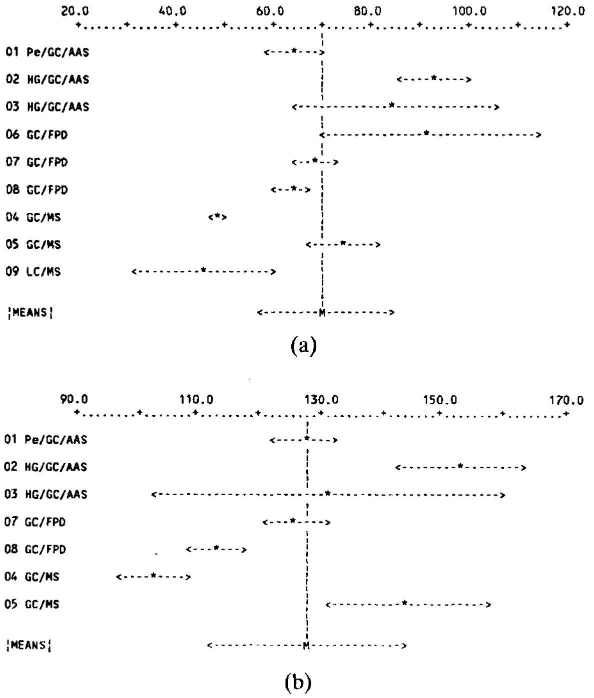

Figure 3 Bar-graphs of TBT and DBT (certified values in CRM 462). The results correspond to five replicate determinations. 'MEANS' is the mean of laboratory means with 95% confidence interval. (a) Tributyltin in ng g^{-1} (as TBT); (b) dibutyltin in ng g^{-1} (as DBT).

iocarbamate or sodium dithiocarbamate may enhance the extraction recovery. However, the addition of complexing agents was found to hinder the hydride generation of a volatile species for MBT. Considering the high spread of results (ranging from 13 to 244 ng g^{-1} as MBT) and the doubts still remaining on the different techniques used, it was decided not to give any indicative values for MBT which could be misused by laboratories. Further efforts should be made to improve the state-of-the-art of MBT determination before contemplating certification of this compound at the ng g^{-1} level. A similar lack of agreement on MBT results has already been shown in a recent comparison of analytical techniques;[15] this study confirmed, however, that the techniques used for DBT and TBT determinations were satisfactory.

CERTIFIED VALUES

Following the technical evaluation, the sets of accepted results were submitted to statistical tests (Kolmogorov–Smirnov–Lilliefors, Nalimov, Bartlett and Cochran tests, and one-way analysis of variance) which are described in detail in the certification report.[13] The certified values (unweighted mean of *p* accepted sets of results) and their uncertainties (half-width of the 95% confidence intervals) are given in Table 4 as mass fractions (based on dry mass). The two compounds are certified as mass fractions (ng g^{-1}) of, respectively, $Sn(C_4H_9)_3^+$ (TBT) and $Sn(C_4H_9)_2^{2+}$ (DBT).

Table 4 Certified mass fractions of TBT and DBT in CRM 462

Compound	Certified value[a] (ng g^{-1})	Uncertainty (ng g^{-1})	*p*
TBT	70	14	9
DBT	128	16	7

[a] The Certified values are the unweighted mean of *p* accepted sets of results.

CONCLUSIONS

The success of this certification campaign clearly illustrates the improvement achieved by the participating laboratories in the course of the interlaboratory programme. As mentioned in the other study on TBT in harbour sediment,[8] Certification of butyltins in sediment could not be achieved in 1990 due to a lack of control of some techniques, e.g. involving hydride generation. The results obtained in this campaign show that all the techniques used (including hydride generation-based methods) were at the best obtainable agreement in relation to the state-of-the-art. Recommendations were given to use standard addition procedures systematically and to check carefully the extraction recovery and the derivatization yield. Particular precautions were taken over the quality control of hydride generation in this exercise; this technique was accepted for certification, providing that all the proofs for a good QC were given.

Further efforts are needed to certify MBT in sediment. The certification of butyl- and phenyltins in both freshwater sediment and mussel materials is now contemplated within the EC Measurements and Testing Programme.

AVAILABILITY

The reference materials are available from the Measurements and Testing Programme, rue de la Loi 200, B-1049 Brussels, Belgium (Fax +32-2.2958072). Each bottle is accompanied by a certificate and a report [13] describing the work performed (preparation, homogeneity and stability studies, analytical methods used and individual results).

Acknowledgements The following laboratories participated in the interlaboratory studies on solutions and TBT-spiked sediments. The participants are gratefully acknowledged for their efforts, which guaranteed the success of this programme: CIBA–Geigy, Bensheim, Germany (H. Müller); CID–CSIC, Department of Environmental Chemistry, Barcelona, Spain (J. M. Bayona); De Monfort University, Department of Chemistry, School of Applied Sciences, Leicester, UK (P. J. Craig); Institute for Environmental Studies, Amsterdam, The Netherlands (J. Stäb); IFREMER, Nantes, France (P. Michel); Institute for Spectrochemistry, Dortmund, Germany (G. Weber); International Tin Research Institute, Uxbridge, UK (A. Samuel-Lewis); Max-Planck Institute for Chemistry, Mainz, Germany (L. Schebeck); Ministry for Agriculture, Fisheries and Food, Burnham-on-Crouch, UK (M. Waldock); Ministry for Transport and Public Works, Tidal Water Division, Haren, The Netherlands (R. Ritsema); National Technical University of Athens, Athens, Greece (M. Ochsenkühn-Petropulu); Schering AG, Bergkamen, Germany (P. Schultze); University of Antwerp, Department of Chemistry, Antwerp, Belgium (F. Adams and W. Dirkx); University of Bordeaux I, Laboratory of Molecular Photophysics and Photochemistry, Talence, France (O. F. X. Donard and F. Martin); University of Pau, Laboratory of Analytical Chemistry, Pau, France (M. Astruc and R. Pinel); University of Plymouth, Department of Environmental Sciences, Plymouth, UK (L. Ebdon).

REFERENCES

1. P. J. Craig, *Organometallic Compounds in the Environment*. Longman, London (1986).
2. R. J. Maguire, *Appl. Organomet. Chem.* **1**, 475 (1987).
3. Ph. Quevauviller, and O. F. X. Donard, in *Element Speciation in Bioinorganic Chemistry*, edited by S. Caroli, Chap. 11. Wiley, New York (1994).
4. Ph. Quevauviller, O. F. X. Donard, E. A. Maier and B. Griepink, *Mikrochim. Acta* **109**, 169 (1992).
5. Ph. Quevauviller, B. Griepink, E. A. Maier, H. Meinema and H. Muntau, in *Euroanalysis VII Int. Conf., Vienna*, 26–31 1990.
6. Ph. Quevauviller and O. F. X. Donard, *Appl. Organomet. Chem.* **4**, 353 (1990).
7. M. E. Waite, M. J. Waldock, J. E. Thain, D. J. Smith and S. M. Milton, *Mar. Environ. Res.* **32**, 89 (1992).
8. Ph. Quevauviller, M. Astruc, L. Ebdon, G. N. Kramer and B. Griepink, *Appl. Organomet. Chem.* **8**, 639–644 (1994).
9. E. A. Maier, *Trends Anal. Chem.* **10**(10), 340 (1991).
10. Ph. Quevauviller, *Analusis* **21**(2), M47 (1992).
11. B. Griepink and M. Stoeppler, in *Hazardous Metals in the Environment*, edited by M. Stoeppler, p. 517. Elsevier, Amsterdam (1992).
12. L. Ebdon, BCR Internal Report (1991).
13. Ph. Quevauviller and O. F. X. Donard, *Fresenius' J. Anal. Chem.* **339**, 6 (1991).
14. Ph. Quevauviller, M. Astruc, L. Ebdon, G. N. Kramer and B. Griepink *EUR Report*, No. 15337. CEC, Brussels (1993).
15. S. Zhang, Y. K. Chau, C. W. Li and A. S. Y. Chau, *Appl. Organomet. Chem.* **5**, 431 (1991).