Determination of Dibutyltin in Sediments Using Isotope Dilution Liquid Chromatography-Inductively Coupled Plasma Mass Spectrometry

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A method is described for the determination of dibutyltin (DBT) in sediment by isotope dilution using liquid chromatography inductively-coupled plasma/mass spectrometry (LC-ICP/MS). To achieve the highest accuracy and precision, special attentions are paid in optimization and evaluation of overall processes of the analysis including extraction of analytes, characterization of the standards used for calibration and LC-ICP/MS conditions. An approach for characterization of natural abundance DBT standard has been developed by combining inductively-coupled plasma/optical emission spectrometry (ICP/OES) and LC-ICP/MS for the total Sn assay and the analysis of Sn species present as impurities, respectively. An excellent LC condition for separation of organotin species was found, which is suitable for simultaneous DBT and tributyltin (TBT) analysis as well as impurity analysis of DBT standards. Microwave extraction condition was also optimized for high efficiency while preventing species transformation. The present method determines the amount contents of DBT in sediments with expanded uncertainty of less than 5% and its result shows high degree of equivalence with reference values of an international inter-comparison and a certified reference material (CRM) within stated uncertainties.

Key Words : Organotin, Dibutyltin, Speciation, Isotope dilution, LC-ICP/MS

Introduction

Trace metal speciation analysis has attracted a growing interest recently as it is recognized that the toxicity and the environmental mobility of metals, as well as their availability in living systems, highly depend on their chemical forms.[1] For speciation analysis, a separation technique such as gas chromatography (GC), liquid chromatography (LC), or capillary electrophoresis (CE) is used in combination with a sensitive and selective mass spectrometer equipped with electron ionization (EI), atmospheric pressure ionization (API) or inductively-coupled plasma (ICP) sources.[2-6] In spite of extensive development of instrumental methods for separation and detection of various species, lack of methods for quantitative recovery of analytes from complex sample matrices, species transformation during sample preparation and limited availability of standards are the major limiting factors for their development as accurate and reliable analytical methods, especially for certification of reference materials.[2,7-10] As an effort to overcome these limitations, isotope dilution (ID) combined with various mass spectrometry (MS) methods has been adopted in the speciation analysis.[2,7-10] When there is a sufficient equilibrium between the endogenous analyte in the sample and the added spike, loss of analytes during sample manipulation, matrix effect and instrumental drift can be compensated by using ID analysis. However, isotope dilution mass spectrometry (IDMS) cannot completely compensate non-quantitative extraction related to insufficient equilibrium or species transformation induced by aggressive extraction conditions.[2]

Therefore, rigorous evaluation on sample preparation including extraction is required to prevent species transformation while ensuring quantitative recovery of analytes. It should be also noted that the standard materials, such as high-purity standards with natural isotopic abundance and species-specific enriched spikes, are often commercially unavailable or supplied with unspecified purity. A well-characterized standard with natural isotopic abundance makes is possible to determine the concentration of an enriched spike in the double ID analysis. This, in turn, provides means for accurate calibration of the species for quantitation. Therefore, the characterization of the natural standard used for calibration is essential to obtain accurate and reliable result using the double ID analysis

Butyltin compounds are well-known contaminants introduced in the marine environment mainly from its extensive use as an antifouling agent. For the exact evaluation of eco-toxicological impacts and the establishment of regulations for organotin compounds, accurate determination of individual organotin species is required as in the other speciation analysis. Due to its high sensitivity, wide dynamic range and the capability of multi-element detection, ICP/MS coupled with GC[11-14] or LC[9,14-16] has been used as the most common technique for organotin speciation. Although GC is known to has better resolution than LC, derivatization of organotins into volatile and thermally stable forms is generally required for GC injection. In contrast, a simple and rapid sample preparation is usually sufficient for LC-ICP/MS, provided that the LC gives enough separation for compounds containing Sn. Previous LC studies[8,9,14,16] were mostly

focused on TBT analysis and optimzed for TBT analysis, while a systematic study of Chiron *et al.*[15] for the optimization of LC condition provided an optimum LC condition for the other organotin species as well. However, analysis of other butyltin species or simultaneous analysis of butyltin species require further optimization, especially when purity analysis using LC is also considered. For purity analysis of DBT where excessive amount of DBT is injected into a column, for example, enough separation of DBT from the other organotin species is required.

In this work, a method for purity assay of the standard dibutyltin (DBT) material was developed combining ICP/ optical emission spectrometry (OES) analysis of total Sn content and LC-ICP/MS analysis of the other organotin impurities. Optimized LC condition provided an excellent separation of all butyltin species, which made the impurity analysis of DBT standard as well as the determination of DBT in sediments feasible. The sample preparation procedure including microwave (MW) extraction was also optimized for recovery without species transformation. By optimization and rigorous evaluation for the overall procedures of DBT analysis using ID LC-ICP/MS, we pursued accurate determination of DBT, which is traceable to SI unit, potentially. The ID LC-ICP/MS method was validated by use of a PACS-2 sediment CRM and a sediment sample provided for interlaboratory study, CCQM-P43.[17]

Experimental Section

Materials. The CCCQM-P43 test sediment and the PACS-2 sediment reference material were provided by the National Research Council of Canada (NRCC), which is one of the pilot laboratories of the interlaboratory study. The DBT standard synthesized from enriched ^{117}Sn for ID analysis was supplied by the other co-pilot laboratory, the Laboratory of the Government Chemist (LGC), UK, in form of methanolic solution with approximate concentration of 110 μg/g as DBTCl$_2$. DBTCl$_2$ with natural isotopic abundance was purchased from Sigma-Aldrich (Sheboygan, WI, USA) and used as calibration standard after purity assay. Tropolone, triethylamine (TEA), acetonitrile, methanol, acetic acid, tin tetrachloride, monobutyltin trichloride, and tributyltin chloride were also purchased from Sigma-Aldrich.

Sampling and Preparation of Isotope Dilution Mixtures. Although a reference value is given for the PACS-2 CRM, a preliminary experiment was necessary for the test sediment to obtain approximate amount contents of DBT, which are required in exact sampling for ID analysis. Sediment samples of about 1.0 g were weighed directly into Teflon medium-pressure MW extraction vessels having volume of 100 mL and spiked with appropriate amounts of ^{117}Sn-enriched DBT spike solution so that isotope ratio, ^{120}Sn/^{117}Sn, of DBT in sample blends to be about 0.9. The same spike solution was also used to prepare four replicates of calibration standards at three different isotope ratios (0.85, 0.90 and 0.95) around that of the sample blends by

combining appropriate portions of the solution and four independently prepared DBT standard solutions. Before and after the sediment sampling, about 0.2 g of samples from each bottles were weighed into weighing bottles to measure moisture contents of the sample. Samples in weighing bottles were dried for several hours in an oven maintained at 105 $^{\circ}$C until successive weights after drying didn't change more than 0.1%. Two procedure blanks were prepared by spiking diluted ^{117}Sn-enriched DBT solution into empty vessels. Precision balances (Mettler Toledo AT205 and AT26, Grefensee, Switzerland) were used to accurately weigh samples, spike solution and standard solutions.

Extraction and Clean-up MW extraction of organotin compounds from the sediments was performed using an ETHOS SEL MW extraction system (Milestone, Italy). Extraction vessels containing isotope-spiked sample or blank were filled with 20 mL of extraction solvent (methanol : acetic acid : tropolone = 90 : 10 : 0.03, v/v/w) and left for several hours. A reference vessel with a temperature sensor was used for temperature monitoring and control. It was also filled with almost the same amounts of sediment and solvent. The vessels including blank and reference vessels were put into the MW oven and heated to 110 $^{\circ}$C within 5 min using the MW extraction system with magnetic stirring, which were maintained at the temperature for 5 min. After sufficient cooling, the extracts were centrifuged for 10 min at 3000 rpm and filtered through 1 μm filter to remove residual particulates. The final extracts were collected in glass vials and concentrated to final volume of less than 1 mL, then, diluted to appropriate volume with methanol.

LC-ICP/MS Analysis. A LC system (Waters, Milford, MA, U.S.A.) equipped with a 626 quaternary pump and a 717 autosampler was used for separation of the organotin species. The LC system was coupled to an Elan DRC ICP/ MS (PerkinElmer Instruments, Shelton, CT, U.S.A.) using a PFA organic solvent introduction system (Elemental Scientific, Omaha, NE, U.S.A.) with a microflow PFA nebulizer and a PFA spray chamber. The whole LC eluent flow was directed into the nebulizer without splitting. The detailed conditions of LC and ICP/MS are shown in Table 1. RF power and gas flow rates, especially that of the oxygen gas, were adjusted to obtain the optimum intensities of tin ions, m/z 117 and 120, while preventing overheating of torch by excessive O$_2$ flow or carbon deposition on the interface due to insufficient O$_2$ supply. Isotope ratios were measured as peak area ratios of m/z 120 vs. m/z 117. Mass bias in the isotope ratio measurement was corrected for by several alternatives measurements of natural DBT standard solution and one of the calibration standard mixtures. Instrumental drift was also corrected for by injecting that particular calibration standard mixture before and after every 5 or 6 calibration standard mixtures or spiked sample mixtures. Four repetitive LC-ICP/ MS measurements were carried out for each sample blends and calibration standards.

Purity Assay of DBT Standard Material. Purity of DBT standard material was determined by subtracting the contribution of impurities containing Sn from the total Sn contents

Table 1. LC and ICP/MS operating conditions

LC conditions	
Column	Waters DELTA-PAK C18 (2.0×150 mm, 5 μm)
Mobile phase	$CH_3CN : H_2O : AcOH = 72 : 22 : 6$ (v/v/v) with 0.2% tropolone
Flow rate	0.2 mL/min
Injection volume	10 μL
ICP/MS conditions	
Sampler/skimmer cones	Pt
Plasma gas	20 L/min
Auxiliary gas	1.3 L/min
Nebulizer gas	0.5 L/min
Oxygen gas	50 mL/min
RF power	1100 W
Nebulizer	Microflow PFA nebulizer
Spray chamber	PFA spray chamber

in the material. The total Sn contents was obtained by ICP/OES analysis of DBT standard acid-digested in a closed vessel. The Sn-containing impurities in the material, such as inroganic Sn, MBT and TBT, were determined by LC-ICP/MS. For total Sn analysis, four of accurately weighed sub-samples of DBT standard material were transferred to 100 mL Teflon high-pressure MW digestion vessels. Then they were spiked with appropriate amount of 1000 mg/kg Y internal standard solution to reach concentrations of 100 mg/kg for Sn and 20 mg/kg for Y after diluting to 200 g with 5% HCl. After adding 1 mL of sub-boiled HNO_3 and the same volume of sub-boiled HCl into digestion vessels, DBT standard samples were subjected to MW digestion using a MLS 1200 mega MW Labstation (Milestone, Italy). Four vessels for sub-samples and two additional vessels containing procedure blanks were put together in the oven, and heated as follows: 1 min at 250 W, 1 min at 0 W, 8 min at 250 W, 5 min at 400 W and 5 min at 650 W. After digestion, the digested solutions were transferred to polyethylene bottles and diluted to 200 mL with 5% HCl. Four calibration standards were prepared by combining appropriate amounts of 1000 mg/kg Sn standard solution and the Y standard solution so that Sn/Y ratios and concentrations closely matched with those in Y-spiked DBT samples. By performing alternates measurement of peak intensity ratio of Sn/Y for four of calibration standards and four of spiked samples

using a Jobin Yvon Ultima ICP/OES (Jobin Yvon, Longju-meau, Cedex, France), total Sn in DBT standard material was determined. Amounts of Sn species other than DBT were determined by LC-ICP/MS analysis of a 100 mg/kg (as Sn) methanolic solution prepared with the DBT standard material. For one-point external calibration, methanolic solutions of $SnCl_4$, MBT and TBT with similar levels of concentration to those in the 100 mg/kg (as Sn) DBT solution were used. Result from three replicate LC-ICP/MS runs was averaged.

Results and Discussion

Dry Mass Correction. The moisture content of the sample should be determined and corrected for to obtain comparable DBT content in the sediment sample. The moisture content correction factor for the unknown sediment sample was 0.9935 with standard uncertainty of 0.0007, which is negligible compared with overall uncertainty. Corresponding values for PACS-2 CRM were 0.9904 and 0.0017, respectively.

Extraction of DBT from Sediment. The quantitative extraction of organometallic compounds from a complex matrix is very difficult because analyte should be separated from interfering matrices with adequate recovery while preventing degradation or transformation into other species during extraction process. There have been a large number of studies on the extraction of organotin compounds from various matrices.[7-8,18] Mechanical shaking, ultrasonic extraction, MW extraction and accelerated solvent extraction were used with various acidic solvent mixtures. However, critical comparison of these methods is difficult due to differences of steps involved, such as derivatization, clean-up, separation and detection methods with different precision and accuracy, and in the sample matrices. A preliminary experiment was carried out to evaluate efficiency of mechanical and MW extractions with two different extraction solvents using PACS-2 as a reference material. Results from isotope-dilution LC-ICP/MS for all four different extraction conditions were in excellent agreement with the certified value as shown in the Table 2. However, MW extraction using MeOH : AcOH : tropolone (90 : 10 : 0.03, v/v/w) was chosen as the extraction method for the present study considering short extraction time of the MW extraction and the known infuence of tropolone on the extraction of MBT

Table 2. Preliminary study of extraction methods using PACS-2 CRM

|	Extraction Method	DBT determined (μg/kg as Sn)	Reference value (μg/kg as Sn)
Mechanical extraction (12 hours in a vial)	AcOH : MeOH (3 : 1, v/v) 16 mL per 1 g sample	1.076	
	MeOH : AcOH : tropolone (90 : 10 : 0.03, v/v/w) 10 mL per 1 g sample	1.065	
Microwave extraction (temperature control as in the experimental section)	AcOH : MeOH (3 : 1, v/v) 16 mL per 1 g sample	1.096	1.09 ± 0.15
	MeOH : AcOH : tropolone (90 : 10 : 0.03, v/v/w) 10 mL per 1 g sample	1.088	
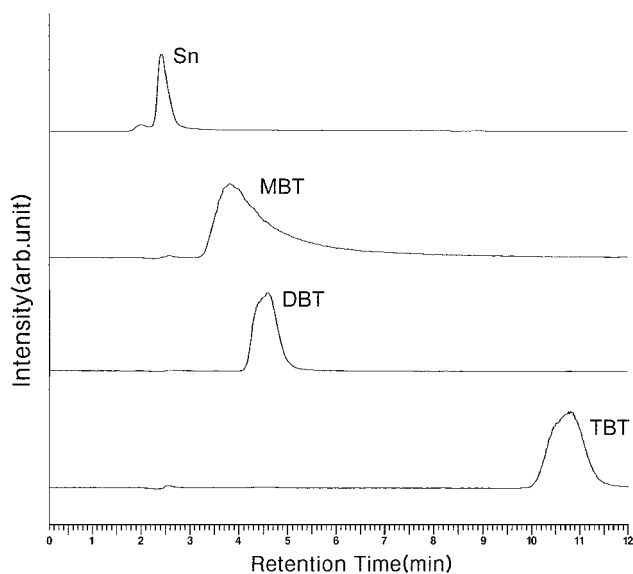
Figure 1. LC-ICP/MS chromatogram of inorganic Sn, MBT, DBT, and TBT obtained by injecting 5 μL of about 10 μM standard solutions using 0.2 mL/min of CH$_3$CN : H$_2$O : AcOH : TEA (65 : 23 : 12 : 0.0005. v/v/v/v) as an eluent in an Waters Delta-Pak C18 column (2.0 × 150 mm, 5 μm end-capped).

Figure 2. LC-ICP/MS chromatogram of inorganic Sn, MBT, DBT, and TBT obtained by injecting 5 μL of about 10 μM standard solutions using 0.2 mL/min of CH$_3$CN : H$_2$O : AcOH : Tropolone (72 : 22 : 6 : 0.2. v/v/v/w) as an eluent in an Waters Delta-Pak C18 column (2.0 × 150 mm, 5 μm end-capped).

& DBT.[2] As described in the experimental section, amount of the extraction solvent was adjusted to 20 mL (per 1 g sample) to guarantee sufficient mixing with sample as well as for convenience of subsequent sample handling.

MW extraction with temperature-control is more reliable and convenient method compared with previously used method with power-control. In the power control mode, reproducible extraction condition cannot be guaranteed if number of extraction vessel, amount of samples and solvent in the vessels do not remain almost the same. Hence, an extraction condition used in one laboratory is not compatible in other laboratories with different MW oven and vessel settings, which result in different power absorption in individual sample vessels. In the temperature-control mode, however, extraction condition is more tightly-controlled by universal parameters, temperature and time. Temperature inside sample vessels is monitored via a reference vessel containing almost the same amount of sample and solvent as in the other vessels, and it is used to control the power of MW heating. All of these parameters can be easily transferred to other laboratories.

Optimization of LC-ICP/MS. The best LC separation of TBT from the other organotin species has been achieved when 0.2 mL/min of CH$_3$CN : H$_2$O : AcOH : TEA (65 : 23 : 12 : 0.0005. v/v/v/v) is used as an eluent with a C18 reversed-phase column (2.1 × 150 mm, 3 μm particle).[19] A similar LC conditions were tested for DBT analysis with the sediment samples. However, quantitation of DBT in the presence of MBT is hampered by the excessive tailing of MBT that elutes earlier as shown in the Figure 1. Use of a C18 column without end-capping (Michrom BioResources, Magic C18) made the tailing so severer that MBT could not be observed as a separated peak and even DBT peak showed
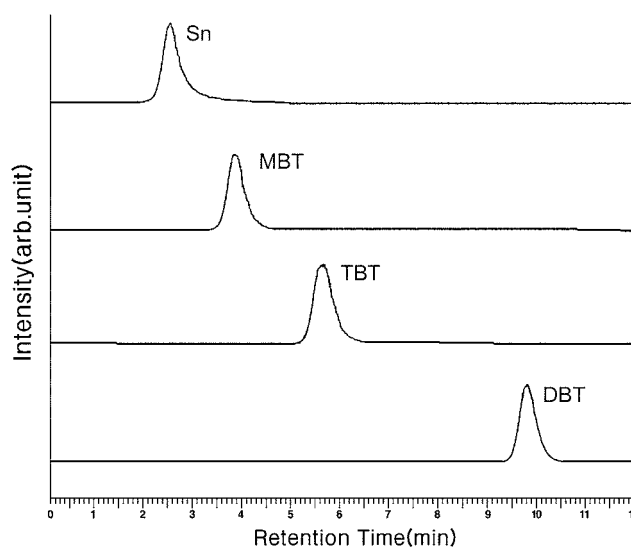
severe tailing (data not shown).

To selectively separate DBT from MBT and minimize the tailing due to non-ideal interaction of MBT ion with the column particle surfaces, tropolone was used as an additive of LC eluent[7,15] because it is known to complex with DBT and MBT. By adjusting the composition of acetonitrile, water, acetic acid, TEA and tropolone, the LC separation was optimized for DBT analysis. Although the detailed LC study of organotin species by Chiron *et al.*[15] provided a good starting point for optimization of LC condition, further adjustment of eluent composition was required to achieve enough separation of butyltin species with the column used in the present study. As shown in the Figure 2, butyltin species are separated completely when CH$_3$CN : H$_2$O : AcOH : tropolone (72 : 22 : 6 : 0.2. v/v/v/w) was used as an eluent with flow rate of 0.2 mL/min, although there is a slight tailing for inorganic tin ion. More importantly, elution of DBT is delayed farther than the other butyltin species, which makes impurity analysis of DBT standard material as well as quantitation of DBT more viable.

For LC-ICP/MS interfacing, mobile phases eluted from LC have been usually introduced into ICP using a peltier-cooled spray chamber to prevent excessive solvent load on the ICP torch. However, use of a microflow PFA nebulizer with a PFA spray chamber does allow a stable ICP/MS operation without peltier-cooling as done in the present study. Only a little bit of additional oxygen flow into the spray chamber is sufficient to maintain stable condition for an extended period. ICP/MS tune parameters were optimized while eluting DBT dissolved in the mobile phase at a flow rate of 0.2 mL/min using a syringe pump. The detection limit of DBT in the present condition was 2.7 ng DBT (as Sn) per one gram of solution (at S/N=3), which corresponds to 0.18 pmol DBT consumed.

Purity of DBT Standard. The purity of DBT standard material obtained from Aldrich was assigned as 96%. To assure the traceability to SI, however, a reliable purity assay for the material is required. For organometallic compounds, a rigorous and convenient purity assay is conceivable by taking advantage of their possession of specific metal, using a total metal content analysis combined with an LC-ICP/MS analysis of corresponding metallic species except for the primary component. Provided that each metallic species is sufficiently separated each other by LC, it can be used as a reliable purity assay method. The first example of this approach can be found in the recent article by Lu Yang *et al.*,[9] where they used an IDMS method to determine the total Sn content and hydride generation GC-MS to characterize Sn species impurities in their butyltin standards.

In the present study, MW-assisted acid digestion of the standard material followed by ICP/OES analysis using Y as an internal stanard has been carried out to determine total Sn content in the DBT standard material. It is well-known that highly element-specific and reproducible ICP/OES analysis combined with rigorous drift correction permits the determination of major inorganic constituents in solution with relative expanded uncertainty down to 0.1%.[20-21] Therefore, the content of major element can be determined accurately if quantitative recovery of the element is guaranteed.[22] The total Sn content in the standard DBT material was 0.3832 g/g (as Sn) with relative standard uncertainty of around 1% as shown in the Table 3, which includes uncertainty component due to the sample inhomogeneity.

Sn species impurities in the DBT standard material were determined using the optimized LC-ICP/MS method. TBT and MBT were found as major impurities in the analysis with much less amount of an unknown compound regarded as one of the isomeric compounds of TBT. The result of impurity assay is shown in the Table 3. The purity of DBT material was 97.3% as DBTCl$_2$.

Determination of DBT in Sediment. Although the LC-ICP/MS condition is optimized using the butyltin standards and possible interference sources are rare, one has to check any possible influence of complex matrices from a real sample to the chromatographic separation and unexpected interferences. For that purpose, organotin compounds extracted from the test sediment without spiking [117]Sn-

Table 3. Result of purity assay for DBT standard material

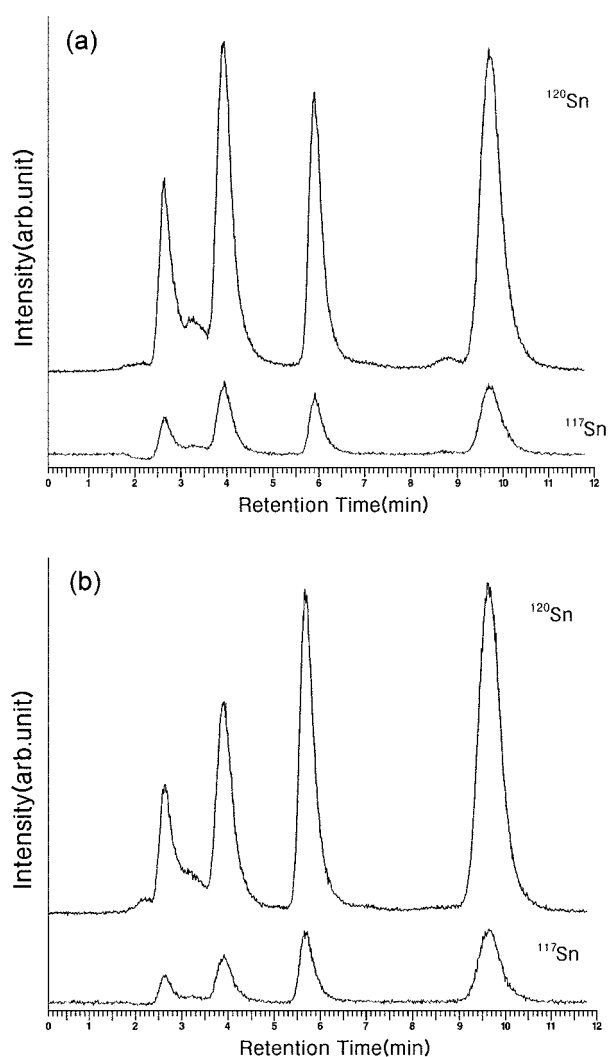|	Mass fraction of Sn (g/g)	Standard uncertainty (g/g)
Total Sn	0.3832	0.0041
Inorganic Sn	not detected	
MBT	0.0021	< 0.0001
TBT	0.0010	< 0.0001
Unknown	0.0001	< 0.0001
DBT	0.3800	0.0042
Calculated for 100% DBTCl$_2$	0.3907	

Figure 3. LC-ICP/MS chromatogram of butyltins from extract of (a) the CCQM-P43 test sediment and (b) the PACS-2 sediment.

enriched DBT were analyzed. The four organotin species identified are present with natural isotope ratios and well-separated in the chromatogram as shown in the Figure 3. The PACS-2 sediment also shows a similar profile, although the relative abundance of each species is a little bit different from that of the test sediment. The LC-ICP/MS chromatograms clearly show that the present method maintains a proper chromatographic separation for sediment samples with negligible interference from other Sn species.

An analysis of the test sediment spiked with [117]Sn-enriched DBT also shows excellent chromatographic resolution as shown in the Figure 4. The organotin species other than DBT are still in the natural isotope ratios while that of DBT has been changed to around 0.9 after spiking. This shows that the species transformation from DBT to MBT or inorganic Sn was negligible in the sample preparation process. Even if minor transformation exists, it is also compensated for in the isotope dilution analysis provided that DBT spiked in the sample achieves sufficient equilibrium with that in the sample. Transformation from
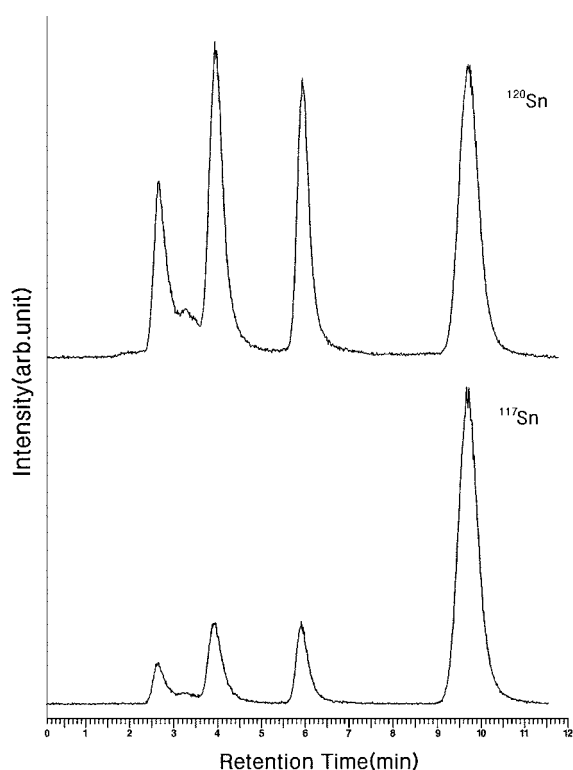
Figure 4. LC-ICP/MS chromatogram of butyltins from extract of the [117]Sn-DBT spiked test sediment.

Table 4. Data obtained for DBT in a test sediment and a certified reference material

sample	DBT determined from each aliquot (μmol/kg)	Final result (μmol/kg)	Reference value (μmol/kg)
Test sediment	1.414 1.433 1.388 1.433 1.531 1.455 1.631 1.442	1.467 ± 0.071	1.48 ± 0.11[a]
PACS-2	8.808 8.639 8.758 8.644	8.712 ± 0.220	9.18 ± 1.26

TBT to DBT also affects DBT analysis, but the isotope dilution with [117]Sn-enriched DBT spike cannot mitigate it. Multi-isotope-labeled ID analysis can be used to address the issue of species transformation wherever multi-isotope-labeled organotin standards are available.[8] Another method is the used of well-characterized CRMs. In this study, the influence of degradation reactions in the sample preparation process to the DBT analysis is shown to be negligible using the PACS-2 CRM as a control sample.

 The results of analysis for the test and PACS-2 sediments are listed in the Table 4. Our results show excellent agreements with either the median value of the international comparison or the certified value of the PACS-2 CRM within their stated uncertainties. A GC-MS for the same sample with a derivatization reaction also showed almost equivalent results to those from the present analysis.[23] The expanded uncertainties of the measurement were 4.87 and 2.53% for the test sediment and the PACS-2 sediment, respectively, which is excellent in the present status of organotin analysis.

Conclusion

 An ID LC-ICP/MS method has been established for determination of trace DBT in sediments. Use of species-specific isotope-labeled DBT as internal standard minimizes the effects of any sample loss after extraction and instrument drift. The MW extraction conditions were optimized for efficiency as well as minimum species transformation. Excellent LC conditions for separation of organotin species were found, which is best for simultaneous DBT and TBT analysis as well as impurity analysis of DBT and TBT standard materials. Most importantly, a method combining ICP/OES and LC-ICP/MS for total Sn analysis and Sn species impurity analysis, respectively, has been developed for purity assay of DBT standard material. It makes the measured concentration of DBT in the sample traceable to a gravimetrically prepared Sn primary standard solution from the Korea Research Institute of Standards and Science (KRISS). The present method determines the amount contents of DBT in sediment with relative expanded uncertainty of less than 5% and its result shows high degree of equivalence with those from the international inter-comparison, CCQM-P43 and the certified value of the PACS-2 CRM within the stated uncertainties. It is also expected that many forms of organotin species in the environmental samples can be determined accurately with the present method.

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