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Sub-ppt determination of butyltins, methylmercury and inorganic mercury in natural waters by dynamic headspace in-tube extraction and GC-ICPMS detection†

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A sensitive and accurate method is developed for the simultaneous ultra-trace determination of tributyltin (TBT), dibutyltin (DBT), monobutyltin (MBT), methylmercury (MeHg) and inorganic mercury (iHg) in waters including seawater by dynamic headspace in-tube extraction (dHS-ITEX) and GC-ICPMS detection. Quantitation of TBT, DBT, iHg and MeHg was achieved by isotope dilution mass spectrometry using ^{117}Sn-enriched TBT and DBT, ^{201}Hg-enriched iHg and enriched Me^{198}Hg (NRC CRM EMMS-1), respectively, wherein analyte mass fractions in enriched spikes were determined by reverse isotope dilution at the same time using natural abundance TBT, DBT, iHg and MeHg primary standards by exactly matching the analyte and enriched spikes. Quantitation of MBT was realized by standard addition calibration with ^{117}Sn-enriched DBT serving as the internal standard. The proposed method achieved detection limits of 0.06, 0.08 and 1.1 pg g^{-1} (as Sn) for TBT, DBT and MBT and 0.08 and 0.4 pg g^{-1} (as Hg) for MeHg and iHg, respectively. Validation of the proposed method was demonstrated by quantitative spike recoveries of 94–105% at 5 to 50 pg g^{-1} levels achieved in drinking water, river water and seawater, demonstrating the accuracy of the method. The obtained detection limits are sufficiently low to perform measurements in support of the Water Framework Directive. The developed method was applied for the determination of butyltins, iHg and MeHg in drinking water (AQUA-1), river water (SLRS-6) and seawater (CASS-6 and NASS-7) samples. Values of 0.124 ± 0.041 and 0.157 ± 0.060 pg g^{-1} (1SD, n = 4) for MeHg in CASS-6 and NASS-7 and values of 1.74 ± 0.61, 22.15 ± 0.13, and 31.42 ± 0.30 pg g^{-1} (1SD, n = 4) for iHg in SLRS-6, CASS-6 and NASS-7 were obtained, respectively. A value of 2.27 ± 0.45 pg g^{-1} as Sn for MBT was detected in NASS-7 seawater, whereas other butyltins were below the detection limits in the waters.

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1. Introduction

The wide usage of tributyltin (TBT) for polyvinyl chloride (PVC) stabilization, antifouling paints and biocides during the last century has led to widespread distribution of TBT and its degradation by-products in the aquatic environment.[1,2] Among the butyltins, TBT is the most toxic and its severe effects on aquatic organisms[3,4] and mammals[5] have been observed even at low parts-per-trillion levels. Polluted waters and marine organisms provide a potential source of TBT uptake for mammals and humans. The high bioaccumulation potential and toxicity of TBT have led to the global ban of TBT based antifouling paint on large vessels in 2008 in order to control pollution levels in the aquatic environment.

Similarly, mercury is another persistent environmental contaminant.[6] Among ionic Hg species, methylmercury (MeHg) is the most toxic form present in the environment which is known to be bio-accumulative in the aquatic food chain and could provide a major route of exposure for humans to mercury through consumption of marine food products.[7–9] As a result, efforts in the monitoring of TBT and MeHg in natural waters have increased significantly. In 2000 the European Union (EU)'s European Water Framework Directive listed TBT, Hg and related compounds as priority pollutants in surface water. In 2008, the EU legislation established a value of 0.2 ng L^{-1} for TBT and 50 ng L^{-1} for Hg and related compounds as the maximum allowable concentrations in surface water samples.[10–12]

Quantitation of TBT (as well as DBT and MBT) and MeHg at low parts-per-trillion (ppt) levels in natural waters is a very challenging task. Currently, the most common analytical

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methods used for the quantification of TBT[13–26] and MeHg[27–33] in water samples comprise extraction and pre-concentration steps before separation and detection, as shown in Table 1.

GC-ICPMS is usually preferred for the determination of butyltins and MeHg due to the high resolution of GC separation with high sensitivity, low DLs and the commercial availability of this hyphenated system. With mass spectrometric detection, compound/species specific isotope dilution (ID) can be applied which generally provides better accuracy and precision than other calibration techniques since a ratio rather than an absolute intensity measurement is used for the quantitation of the analyte mass fraction.[16,18,21,36–38] In addition, once isotopic equilibrium between the analyte and the enriched spike is achieved, matrix effects and subsequent minor losses during sample preparation (such as non-quantitative derivatization) are well compensated for and have no impact on the final results.

However, these organometallic analytes are not volatile in their native forms and require derivatization. Conversion of TBT, DBT, MBT, MeHg, and iHg can be achieved by means of aqueous tetraalkylborates (R_4B^-) which can convert these analytes into the corresponding R_4Sn and R_2Hg. Such derivatives are volatile and can be sampled from the vial headspace allowing for a first order separation from the matrix with several pre-concentration options. Common headspace sampling and pre-concentration methods employed for butyltins and MeHg include single drop gas–liquid extraction (SDME);[39] the purge and trap technique for the speciation of trace organotin and organosulfur compounds in a human urine standard reference material (SRM)[40] and solid phase microextraction (SPME).[9,41,42] In recent years, in order to overcome some SPME fiber related drawbacks (*e.g.*, fiber fragility and limited capacity), in-tube extraction (ITEX) has been developed as a novel solvent-free and automated dynamic headspace extraction technique.[43,44]

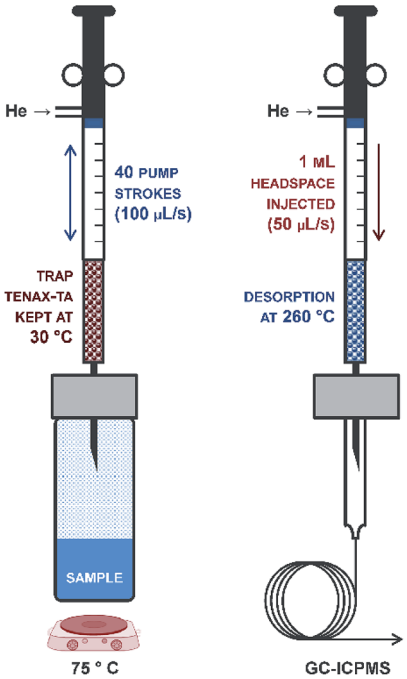

Fig. 1 Schematic of the ITEX sampling procedure. The reaction vial was incubated for 10 min at 75 °C promoting the partitioning of the analytes to the gas phase. The headspace containing the derivatives (R_2Hg and R_4Sn) was pumped through the Tenax-TA trap. Forty strokes of the plunger at a flow rate of 100 µL s^{-1} were adopted for pre-concentration (10 min process), and subsequently the analytes were thermally desorbed into the GC inlet by pumping 1 mL volume gas through the trap at 50 µL s^{-1} while it was heated at 260 °C. Finally, the trap was cleaned with a stream of He in order to avoid memory effects.

As shown in Fig. 1, the headspace of the reaction vial is pumped several times through a sorbent bed maintained at low temperature in order to favour the adsorption of the analytes on

Table 1 Summary of BT and MeHg measurements in waters[a,c]

Sample	Analyte	Method	Sample size (mL)	DLs (ng L^{-1})	Ref.
Seawater	TBT	LC-APCI-MS	5	35 000	17
Tap water and bottled water	MeHg and iHg	LC-CV-AFS	4[b]	15 and 2	29
River water and coastal seawater	MeHg, iHg, MBT, DBT, and TBT	HS-SPME-GCMS	5	3.1, 2.3, 1.4, 7.0, and 16.8	27
River water and seawater	MeHg, iHg, MBT, DBT, and TBT	HS-SPME-GCMS/MS	5	20, 27, 4, 33, and 9	34
Harbor water and waste water	TBT	SBSE-TD- GCMS/MS	52.5	0.011	19
Seawater	MBT, DBT, and TBT	HS-SPME-GC-QQQ-MS	10	0.29, 0.44, and 0.45	23
Whole water	TBT	LLE-ID-GC-ICPMS	500–1000[b]	NA	24
Coastal seawater	MBT, DBT, and TBT	LLE-ID-GC-ICPMS	100	0.04, 0.09, and 0.27	14
Seawater, river water and Antarctic snow	MeHg	Purge-and-trap-ID-GC-ICPMS	50	0.03	35
Drinking water, river water and seawater	MeHg, iHg, MBT, DBT, and TBT	ID dHS-ITEX GC-ICPMS	8	0.08, 0.4, 1.1, 0.08, and 0.06	This work

[a] APCI-MS: atmospheric pressure chemical ionization mass spectrometry; CV-AFS: cold vapor atomic fluorescence spectrometry; TD: thermal desorption; QQQ-MS: triple quadrupole mass spectrometry; LLE-liquid liquid extraction. [b] With preconcentration. [c] NA – not available.

the trap, resulting in a significant pre-concentration. In the second step the analytes are thermally desorbed into the gas chromatograph. Currently, applications of ITEX have been reported primarily for the determination of various volatile organic compounds.[43,45,46]

The aim of this study was to develop a method for the simultaneous determination of butyltins, iHg and MeHg in natural waters including seawater using dynamic headspace in-tube extraction (dHS-ITEX) and double isotope dilution GC-ICPMS.

2. Experimental section

2.1 Instrumentation

A 5975C GC-MS and 7500 ICPMS from Agilent Technologies (Mississauga, ON, Canada) were used for the identification and quantitation of derivatized TBT, DBT, MBT, iHg and MeHg. The dynamic in-tube extraction system is automated with a PAL RSI 85 autosampler (CTC Analytics, Switzerland). The butyltin and mercury derivatives were separated on a Phenomenex (Aschaffenburg, Germany) Zebron ZB-5MS GC column (5% diphenyl, 95% polydimethylsiloxane, 30 m × 0.25 mm × 0.25 μm). A commercial heated GC transfer line (Agilent Technologies, Mississauga, ON, Canada) for transferring the GC gas stream to the ICPMS was used. ICPMS optimization was carried out by monitoring the signal of 1% xenon in argon sample gas for tuning. Typical operational conditions for GC, ICPMS and EIMS are outlined in Table S1 (ESI).† Analyte isotopes ^{118}Sn, ^{117}Sn, ^{202}Hg, ^{201}Hg and ^{198}Hg were monitored by ICPMS. A mass range from m/z 30 to 600 Da was recorded in full-scan mode in GCMS measurements.

Samples were prepared in 20 mL magnetic screw cap headspace vials with silicone/PTFE septa. A standard trap material, Tenax TA (80/100 mesh, Agilent Technologies, Mississauga, ON, Canada), was used for the dynamic headspace in-tube extraction. The extraction performance of seven other trap materials, including Carbopack C (80/100 mesh), Carboxen 1000 (60/80 mesh), Carbosieve S III (80/100 mesh), Tenax TA (80/100 mesh, 2/3 bottom)/Carbosieve S III (60/80 mesh, 1/3 top), Carbopack C (2/3 bottom)/Carbosieve S III (1/3 top), Molecular Sieve 5A (80/100 mesh) and Tenax GR (2/3 bottom)/Carbosieve S III (1/3 top) was also investigated. See Table S2 (ESI)† for more detailed information on these trap materials.

2.2 Reagents and solutions

Nitric acid was purified in-house prior to use by sub-boiling distillation of reagent grade feedstock in a quartz still. HPLC grade methanol and isooctane were purchased from Fisher Scientific (Nepean, ON, Canada). High purity de-ionized water (DIW) was obtained from a NanoPure mixed bed ion exchange system fed with reverse osmosis domestic feed water (Barnstead/Thermolyne Corp, Dubuque, IA, USA). A 0.01 g mL^{-1} solution of sodium tetrapropylborate was prepared by dissolving $NaBPr_4$ (Synthese Nord GmbH, Rotenburg, Germany) in DIW. Sodium acetate buffer (1 M, pH 5.0) was prepared by dissolving appropriate amounts of NaAc (ACS grade, Fisher Scientific, Asheville, NC, USA) in water and adjusting the pH with glacial acetic acid (trace metal grade, Fisher Scientific, Asheville, NC, USA).

Natural abundance high purity methylmercury chloride, butyltin trichloride, dibutyltin dichloride and tributyltin chloride were purchased from Sigma Aldrich Canada Ltd. (Oakville, ON, Canada). Stock solutions of MeHg (2688.46 μg g^{-1} as Hg), MBT (198.03 μg g^{-1} as Sn), DBT (120.00 μg g^{-1} as Sn) and TBT (274.77 μg g^{-1} as Sn) were gravimetrically and separately prepared in methanol. A mixed standard solution of MeHg, MBT, DBT and TBT was prepared with methanol containing approximately 20 μg g^{-1} (as metal) of each individual compound. The natural abundance stock solution of iHg SRM 3133 (10 004 ± 40 μg g^{-1}, 95% confidence interval) was purchased from the National Institute of Standards and Technology (Gaithersburg, MA, USA). A standard solution of iHg (9.9996 μg g^{-1}) was prepared in 5% (v/v) HNO_3 by serial dilution of NIST SRM 3133. Working solutions were gravimetrically prepared daily from the MeHg, MBT, DBT, and TBT mixed standard solution by first dilution in methanol (tens to hundreds of ng g^{-1}) and then dilution in 0.2% (v/v) HNO_3 to 1–10 ng g^{-1}. Similarly, the iHg working standard solution was stepwise diluted to 20 ng g^{-1} in 0.2% (v/v) HNO_3.

An enriched ^{201}Hg isotope was purchased from Oak Ridge National Laboratory (USA) in metallic form. A 300 mg g^{-1} stock spike solution was prepared in 5% HNO_3. An enriched ^{201}Hg spike solution (~3.086 μg g^{-1}) was diluted in 5% (v/v) HNO_3. A Me^{198}Hg isotopically enriched solution at a nominal concentration of 33.7 ng g^{-1} in methanol was prepared from NRC CRM EMMS-1. ^{117}Sn-enriched DBT and TBT spike solutions (~220 ng g^{-1} as Sn) were prepared in methanol from stocks (~90 μg g^{-1} as Sn) obtained by courtesy of the Laboratory of Government Chemistry (LGC, Teddington, UK). Mass fractions of the Me^{198}Hg, ^{201}Hg, and ^{117}Sn-enriched DBT and TBT were determined by a reverse dilution method using natural abundance primary standards. All standards and spikes except iHg and enriched ^{201}Hg were kept refrigerated (4 °C) until use.

Drinking water CRM AQUA-1, river water SLRS-6, and seawater CASS-6 and NASS-7 from the National Research Council Canada (NRCC, Ottawa, Canada) were used as test samples.

2.3 Sample preparation and analysis

Glass containers were used for storing solutions throughout this work and plasticware was avoided.[47] All glassware was soaked in 10% (v/v) HNO_3 and 10% (v/v) HCl solution overnight, rinsed thoroughly with DIW and dried in an oven at 105 °C prior to use.

For the determination of TBT, DBT, MeHg and iHg using the dynamic headspace in-tube extraction sampling, 8 g water samples were weighed into 20 mL vials. Samples were spiked with a 0.15 g mixture of ^{198}MeHg (~40 pg g^{-1} as Hg), ^{201}Hg (180–660 pg g^{-1} as Hg), ^{117}DBT and ^{117}TBT (~40 pg g^{-1} as Sn) at appropriate concentrations to result in ratios of ^{202}Hg/^{198}Hg, ^{118}Sn/^{117}Sn and ^{202}Hg/^{201}Hg near 1. Four replicate reverse isotope dilution (RID) samples were gravimetrically prepared to

calibrate the concentrations of ^{198}MeHg, ^{117}DBT, ^{117}TBT and ^{201}Hg by mixing 0.15 g of the above enriched spike solution and 0.15 g of the natural abundance MeHg (240 pg g^{-1} as Hg), iHg (1–4 ng g^{-1} as Hg), DBT and TBT (240 pg g^{-1} as Sn) standard solution, and then diluting with 8 mL of DIW. Such blends were buffered with 1 mL of 1 mol L^{-1} NaAc buffer solution and then 1 mL of 1% (m/v) $NaBPr_4$ was added; the vial was sealed with a magnetic screw cap and subsequently transported to the agitation station (PAL RSI 85 autosampler) rotating at 500 rpm in a circular manner, where the samples were incubated for 10 min at 75 °C before the dynamic headspace in-tube extraction started. The headspace was forced through the trap following 40 extraction strokes; the collected analytes were thermo-desorbed from the sorbent trap and carried to the GC injector for ICPMS analysis. Isotopes of ^{198}Hg, ^{201}Hg, ^{202}Hg, ^{117}Sn and ^{118}Sn were monitored during each run by remote triggering the data acquisition on the Agilent 7500 in advance. The collected data were further processed by Agilent Masshunter software to yield peak areas, and the corresponding ^{202}Hg/^{198}Hg (for MeHg), ^{118}Sn/^{117}Sn (for TBT and DBT) and ^{202}Hg/^{201}Hg (for iHg) ratios from which the analyte concentrations in the samples were calculated.

For the determination of MBT by standard addition with ^{117}DBT as the internal standard, two additional 8 g subsamples of each water CRM were weighed into pre-cleaned 20 mL vials and the same amount of the enriched spike mixture used in ID above was added to each vial. 0.15 g of 440 pg g^{-1} and 850 pg g^{-1} MBT were added to obtain an approximately 1.5- and 3.0-fold increase of MBT, respectively. The rest of the sample preparation and analysis was the same as described above. The standard addition calibration curve for MBT for the quantitation of MBT was achieved based on the ^{118}Sn/^{117}Sn ratios obtained from the peak area of ^{118}Sn from MBT divided by the peak area of ^{117}Sn from ^{117}Sn-enriched DBT.

Liquid injection was also performed to confirm the identity of propylated MeHg, MBT, DBT and TBT (Section 3.1), as well as to determine the extraction efficiencies of these analytes by the dynamic headspace in-tube extraction (Section 3.4). For liquid–liquid extraction sampling, 1 mL of standard solution, 7 mL of 1 mol L^{-1} NaAc buffer, 1 mL of 1% (m/v) $NaBPr_4$ and 1 mL of isooctane were added, and after 10 min of manual shaking, the organic layer was transferred to a glass vial for GC-MS or GC-ICPMS analysis.

3. Results and discussion

3.1 GC-ICPMS characterization

Initially, individual MeHg, iHg, MBT, DBT and TBT standards were derivatized with $NaBPr_4$ and measured by GC-ICPMS following the dynamic headspace in-tube extraction to confirm their relative retention. A chromatogram of 5 pg g^{-1} mixed standard solution is presented in Fig. 2. The ZB-5MS column gave baseline resolution for the studied analytes. It is also noticeable in Fig. 2 that two small satellite peaks appeared close to the two main MBT and DBT peaks at 7.40 min and 7.70 min, respectively.

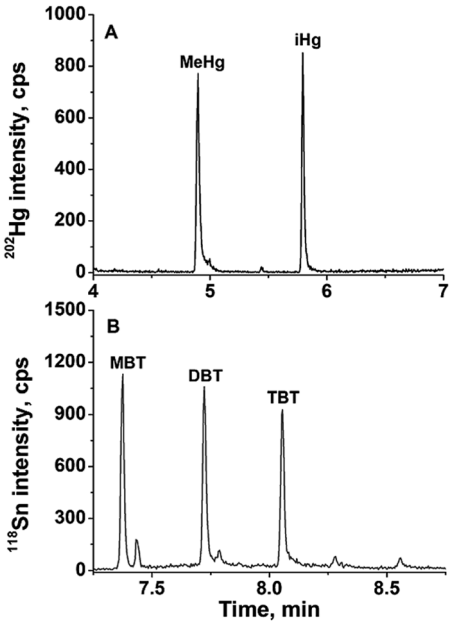

Fig. 2 Simultaneous detection of MeHg, iHg, MBT, DBT and TBT with the dynamic headspace in-tube extraction GC-ICPMS system; ICPMS chromatograms of isotopes (A) ^{202}Hg and (B) ^{118}Sn.

To further elucidate the identity of these satellite peaks, GCMS analysis was carried out. Individual MBT, DBT and TBT standard solutions were derivatized with $NaBPr_4$ and $NaBEt_4$, respectively, and then extracted into isooctane for EIMS detection. Chromatograms were acquired in full scan mode (m/z 30–600 Da) and are presented in Fig. S1–S3 (ESI).† By comparing retention times and full scan mass spectra, a conclusion can be drawn that the satellite peaks correspond to the ethyl-derivatives of these analytes. The $NaBPr_4$ used for derivatization likely contained trace levels of $NaBEt_nPr_{4-n}$ (n = 1–4). Despite the fact that $NaBEt_4$ would be a cleaner reagent for this derivatization, $NaBPr_4$ was chosen because it was significantly safer to handle and more stable in aqueous solution, and the resulting ethyl-byproducts could be efficiently separated by gas chromatography.

3.2 Sorbent trap selection

Prior to a succession of parameter optimization, the extraction performance of eight commercially available sorbent traps (detailed information on the sorbent traps is summarized in Table S2†) was evaluated. A mixed standard containing 10 ng g^{-1} of MeHg, MBT, DBT and TBT was analyzed using 5 min incubation, and 15 extraction strokes with 1250 μL extraction volume at 100 μL s^{-1} flow rate. The peak areas of ^{202}Hg and ^{118}Sn obtained with all sorbent traps are presented in Fig. 3. Tenax TA, the mixed bed trap containing 2/3 Tenax TA at the bottom and 1/3 Carbosieve S III on the top and the mixed trap comprising 2/3 Tenax GR at the bottom and 1/3 Carbosieve S III on the top were more effective for MeHg. No significant difference in the enrichment performances of all eight traps for MBT, DBT and TBT was observed. Therefore, the Tenax TA was selected for all subsequent experiments.

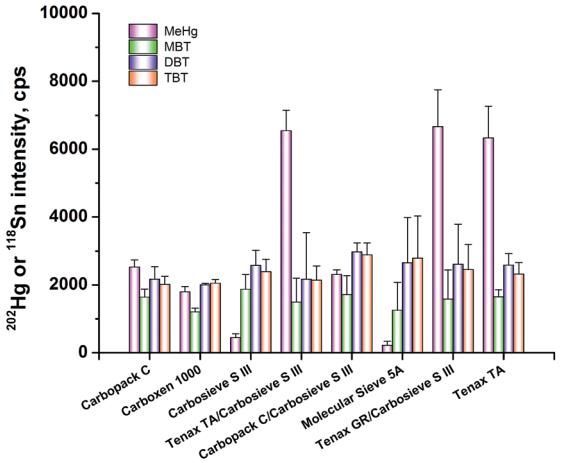

Fig. 3 Comparison of the extraction performances of eight commercial traps for 10 ng g^{-1} natural standard solutions of MeHg, MBT, DBT and TBT.

3.3 Optimization of dynamic headspace in-tube extraction

Several basic parameters affecting the extraction process were optimized, including the extraction and desorption flow rate, the extraction volume and the sampling volume. Although the multivariate optimization approach could significantly reduce the total experiments needed, it is impossible to complete all experiments within a day since each experiment could take approximately 40 minutes. Thus the traditional optimization approach was employed to optimize each parameter. The trap temperature was set at the lowest value (30 °C) to favor analyte adsorption. The effect of the extraction gas volume from 500–1300 μL and the injection/desorption gas volume from 100–1000 μL on peak areas of a 10 ng g^{-1} natural standard solution of MeHg, MBT, DBT and TBT was investigated (Fig. 4A). Larger gas volumes were found to be more favorable in terms of extracted amounts, and thus, 1250 and 1000 μL were selected as the extraction and injection gas volume, respectively, for all subsequent experiments. Higher desorption flow rates above 100 μL s^{-1} led to a decrease in peak areas, presumably caused by inefficient desorption at high flow rates. Similarly, peak areas also decreased as extraction flow rates increased. However, it was found that at the same total run time, 40 extraction strokes at 100 μL s^{-1} extraction flow rate after 10 min of incubation resulted in considerably higher yields than 20 extraction strokes at 50 μL s^{-1}, indicating that the extraction flow rate was not as important as the number of strokes, similar to previous reports for volatile organic compounds.[46] 100 μL s^{-1} and 50 μL s^{-1} were selected for the extraction flow rate and desorption flow rate, respectively, for all subsequent experiments considering both the extraction efficiency and the total run time.

Dynamic headspace in-tube extraction can be affected by several other factors, such as incubation temperature, incubation time and pH of the solution, which were thus studied in detail. Note that the extraction temperature was maintained the same as the incubation temperature. As presented in Fig. 4C, the extraction yields of the four analytes increased as the incubation temperature increased from 30 up to 90 °C which is expected for these semivolatile analytes. An incubation temperature of 75 °C was chosen to ensure efficient partitioning to the headspace and minimize problems associated with a faster degradation of the alkylating reagent. As shown in Fig. 4B, extraction efficiencies were on the rise for all species as the incubation time increased from 2 to 20 min. Considering both the total runtime and the fact that partitioning continued during the multiple extraction strokes, 10 min was selected to achieve time efficient analyte enrichment and desirable sensitivity. Similar to previous studies,[48,49] 1.0 M NaAc–HAc buffer at pH 5.0 was optimal and thus was used throughout this study. As demonstrated in Fig. 4D, a higher number of extraction strokes led to higher extraction yields, and the system did not reach equilibrium even after 60 strokes. 40 strokes following 10 min of incubation were selected, considering both the extraction yield and total run time.

Based on the above investigation, the final dynamic headspace in-tube extraction process employed sample incubation in a 75 °C heated agitator for 10 min, 1250 μL extraction volume and 100 μL s^{-1} extraction flow rate, and a desorption volume of 1000 μL and a desorption flow rate of 50 μL s^{-1} for the final analysis of water samples.

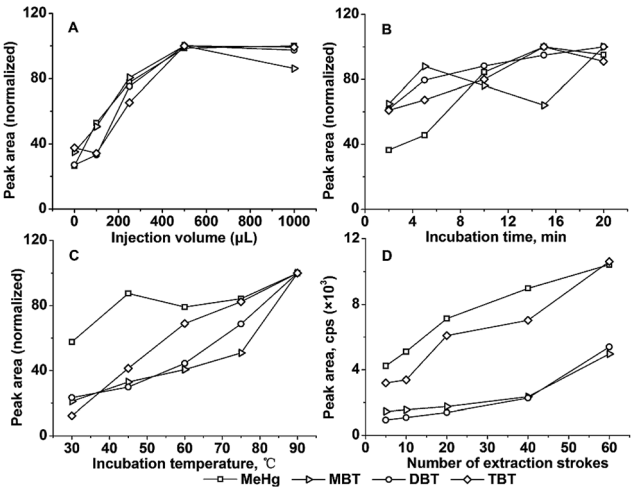

Fig. 4 Influence of extraction parameters on the peak areas obtained for MeHg, MBT, DBT and TBT: (A) injection volume; (B) incubation time; (C) incubation temperature; and (D) number of extraction strokes.

3.4 Detection limits and extraction efficiency

The detection limits, calculated as the concentration of analytes yielding a signal equal to three times the standard deviation of the blank, were determined based on the ID (TBT, DBT, MeHg and iHg) and standard addition (MBT) to be 0.06, 0.08, 1.1, 0.08 and 0.4 pg g^{-1} for TBT, DBT, MBT, MeHg and iHg, respectively. It was also of interest to estimate the extraction efficiency of these compounds with the sorbent trap using the developed methodology. The intensities measured for a 10 ng g^{-1} standard solution by the dynamic headspace in-tube extraction method were compared with those from the injection of propylated

Table 2 Determination of TBT, DBT, MBT, MeHg and iHg in natural waters (1SD, $n = 4$)[a]

Sample	Analyte	Measured (pg g^{-1} as metal)	Spike level (pg g^{-1} as metal)	Recovery (%)
AQUA-1, drinking water	MeHg	<0.08	5.114	96.1 ± 4.5
	iHg	<0.4	24.612	95.0 ± 1.4
	MBT	<1.1	5.545	117.2 ± 3.9
	DBT	<0.08	5.388	99.8 ± 1.2
	TBT	<0.06	4.984	99.9 ± 2.8
SLRS-6, river water	MeHg	<0.08	5.070	104.0 ± 1.7
	iHg	1.74 ± 0.61	20.327	105.2 ± 1.5
	MBT	<1.1	5.472	135.7 ± 9.8
	DBT	<0.08	5.603	104.5 ± 2.2
	TBT	<0.06	4.919	96.6 ± 3.7
CASS-6, seawater	MeHg	0.124 ± 0.041	4.835	98.6 ± 4.4
	iHg	22.15 ± 0.13	52.171	93.5 ± 2.9
	MBT	<1.1	5.209	101.2 ± 51.5
	DBT	<0.08	5.334	101.7 ± 3.7
	TBT	<0.06	4.683	92.6 ± 4.7
NASS-7, seawater	MeHg	0.157 ± 0.060	5.156	98.8 ± 4.3
	iHg	31.42 ± 0.30	N.A.	N.A.
	MBT	2.27 ± 0.45	5.555	97.8 ± 5.7
	DBT	<0.08	5.688	97.8 ± 5.7
	TBT	<0.06	4.993	101.5 ± 1.8

[a] In the case of values lower than the detection limit (DL), this is expressed as <DL.

MeHg, MBT, DBT and TBT extracted in isooctane using a 100 ng mL^{-1} standard solution. Extraction efficiencies of 20.2%, 12.9%, 13.4% and 19.3% were achieved with dynamic extraction (10 min incubation, 40 extraction strokes) for MeHg, MBT, DBT and TBT, respectively, significantly higher than that of static SPME fibers, typically a few percent.[42,50]

3.5 Determination of TBT, DBT, MBT, MeHg and iHg

Exact matching species specific double isotope dilution was applied for the determination of TBT, DBT, MeHg and iHg[19] using eqn (1) whereas standard addition[51] with an internal standard of ^{117}Sn enriched DBT was applied for the quantitation of MBT using eqn (2).

$$w_x = w_z \frac{m_y}{m_x}\frac{m_z}{m'_y}\frac{A_y - B_y R_n}{B_{xz}R_n - A_{xz}}\frac{B_{xz}R'_n - A_{xz}}{A_y - B_y R'_n} \quad (1)$$

where w_x is the mass fraction of the analyte in the sample (pg g^{-1}); w_z is the mass fraction of the natural abundance standard (pg g^{-1}); m'_y is the mass of the enriched spike used to prepare the blend solution of both enriched and natural abundance standard (g); m_y is the mass of the enriched spike used to prepare the blend solution of the enriched standard and sample (g); m_x is the mass of the sample used (g); A_y is the abundance of the reference isotope (^{202}Hg or ^{118}Sn) in the enriched spike; B_y is the abundance of the spike isotope (^{198}Hg, ^{201}Hg or ^{117}Sn) in the enriched spike; A_{xz} is the abundance of the reference isotope (^{202}Hg or ^{118}Sn) in the sample or in the natural abundance standard; B_{xz} is the abundance of the spike isotope (^{198}Hg, ^{01}Hg or ^{117}Sn) in the sample or in the natural abundance standard; R_n is the mass bias corrected ^{202}Hg/^{198}Hg, ^{202}Hg/^{201}Hg; or ^{118}Sn/^{117}Sn ratio in the blend solution of the spike and the sample; and R'_n is the measured and mass bias corrected reference/spike isotopic ratio in the blend solution of the spike and the natural abundance standard.

$$\frac{m_{\text{std-}i}w_{\text{std}}}{m_{\text{s-}i}}\frac{m_{\text{xf}}}{m_x} = bR_i + a \text{ and } w_x = -a \quad (2)$$

where w_x is the mass fraction of MBT in the sample (pg g^{-1}); w_{std} is the mass fraction of MBT in the primary standard solution (pg g^{-1}); R_i is the measured intensity ratio of MBT to internal standard in a set of standard addition solutions, $i = 0$, 1, 2; $m_{\text{std-}i}$ is the mass of the natural abundance standard added to the spiked sample (g), $i = 1$, 2; $m_{\text{s-}i}$ is the mass of the aliquot of the diluted sample used to prepare the spiked sample (g), $i = 1$, 2; m_x is the mass (g) of the original sample; and m_{xf} is the final mass of the original sample after the addition of internal standard.

Possible species interconversion during sample preparation and/or long term storage has been studied extensively[35,52–55] and of course conversion could be occurring here also as described in other studies. However, the goal of this study was to simply demonstrate that detection at these ultra-trace levels in water samples is possible. As a result, no harsh sample digestion was needed and only derivatization was required, and no species interconversion was observed during the derivatization using $NaBPr_4$ in this study (Fig. S1–S3 in the ESI†), similar to that reported in the earlier study.[35] In addition, species specific isotope dilution was applied which could provide accurate results despite possible species degradation during subsequent derivatization or sample preparation. Since no certified reference water sample for these analytes was available, recovery tests were performed on the above four natural waters. TBT and DBT in water samples are below the detection limits, and thus spike recovery was conducted at the 5 ng g^{-1} level (suitable for ultra-trace level measurements) in order to have accurate and precise measurements. The recoveries of TBT, DBT, MeHg and

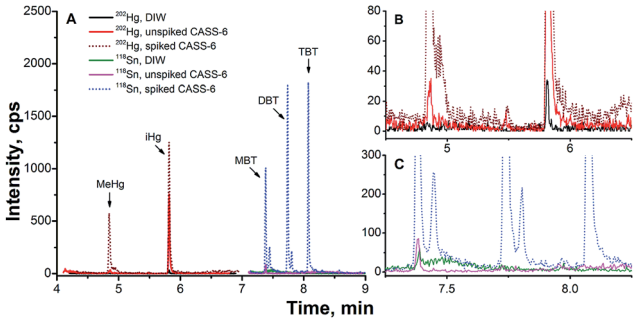

Fig. 5 GC ICPMS chromatograms of ^{202}Hg and ^{118}Sn isotopes of (A) DIW, unspiked and spiked CASS-6, spike level at 5 pg g^{-1} for MBT, DBT, TBT, MeHg and 20 pg g^{-1} for iHg; (B) and (C) are the magnified images of (A).

iHg obtained using ID dHS-ITEX GC-ICPMS are generally between 94% and 105% as shown in Table 2. Loss of MBT in the ppt level standard solution in 0.2 (v/v) HNO_3 was observed and thus resulted in poor recoveries in drinking water and river water (pH 1.6), whereas quantitative recovery was obtained for MBT in seawater samples, and the seawater matrix seems helping to retain the added MBT.

The method was applied to the determination of TBT, DBT, MBT, MeHg and iHg in four different natural water samples: drinking water (AQUA-1), river water (SLRS-6), near-shore seawater (CASS-6) and open ocean seawater (NASS-7). As shown in Fig. 5, the concentrations of the analytes of interest are low and the results are summarized in Table 2. None of the species of interest were detectable in the drinking water AQUA-1, but trace MeHg and iHg can be found in river water SLRS-6 (1.74 ± 0.61 pg g^{-1} iHg), near-shore seawater CASS-6 (0.124 ± 0.041 pg g^{-1} MeHg and 22.15 ± 0.13 pg g^{-1} iHg) and open ocean seawater NASS-7 (0.157 ± 0.006 pg g^{-1} MeHg and 31.42 ± 0.30 pg g^{-1} iHg), as well as trace MBT in open ocean seawater NASS-7 (2.27 ± 0.45 pg g^{-1} as Sn). Note that the reported values were blank corrected, assuming that the blanks are from reagents and sample preparation processes.

An information value of 0.15 pg g^{-1} for TBT is provided in CASS-6 seawater[56] which was measured by SPME ID GC-ICPMS about three years ago. However, in this study we found that TBT was below the detection limit of 0.06 ppt in CASS-6. This discrepancy will be investigated in future, but is beyond the scope of this study.

4. Conclusions

Combined with isotope dilution and GC-ICPMS detection, dynamic headspace in-tube extraction was employed for multi-elemental speciation for the first time. Owing to its ease of use and improved extraction efficiency, a simple, precise and accurate method has been developed to provide extremely low detection limits, and it is well suited to the reliable quantitation of TBT, DBT, MeHg and iHg in natural waters.

Conflicts of interest

There are no conflicts to declare.

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