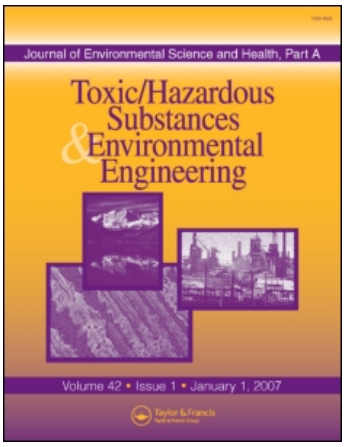

Journal of Environmental Science and Health, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597268

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Sornnarin Bangkedphol [a]; Helen E. Keenan [a]; Christine Davidson [b]; Arthit Sakultantimetha [a]; Apisit Songsasen [c]
[a] David Livingstone Centre for Sustainability, Department of Civil Engineering, University of Strathclyde, Glasgow, Scotland, UK [b] Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, Scotland, UK [c] Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Kasetsart University, Bangkok, Thailand

Online Publication Date: 01 December 2008

To cite this Article Bangkedphol, Sornnarin, Keenan, Helen E., Davidson, Christine, Sakultantimetha, Arthit and Songsasen, Apisit(2008)'Development of a low-cost method of analysis for the qualitative and quantitative analysis of butyltins in environmental samples',Journal of Environmental Science and Health, Part A,43:14,1744 — 1751

To link to this Article: DOI: 10.1080/10934520802330453

URL: http://dx.doi.org/10.1080/10934520802330453

Journal of Environmental Science and Health Part A (2008) **43**, 1744–1751

ISSN: 1093-4529 (Print); 1532-4117 (Online)
DOI: 10.1080/10934520802330453

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Development of a low-cost method of analysis for the qualitative and quantitative analysis of butyltins in environmental samples

SORNNARIN BANGKEDPHOL[1], HELEN E. KEENAN[1], CHRISTINE DAVIDSON[2], ARTHIT SAKULTANTIMETHA[1] and APISIT SONGSASEN[3]

[1]*David Livingstone Centre for Sustainability, Department of Civil Engineering, University of Strathclyde, Glasgow, Scotland, UK*
[2]*Department of Pure and Applied Chemistry, University of Strathclyde Glasgow, Scotland, UK*
[3]*Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Kasetsart University, Bangkok, Thailand*

Most analytical methods for butyltins are based on high resolution techniques with complicated sample preparation. For this study, a simple application of an analytical method was developed using High Performance Liquid Chromatography (HPLC) with UV detection. The developed method was studied to determine tributyltin (TBT), dibutyltin (DBT) and monobutyltin (MBT) in sediment and water samples. The separation was performed in isocratic mode on an ultra cyanopropyl column with a mobile phase of hexane containing 5% THF and 0.03% acetic acid. This method was confirmed using standard GC/MS techniques and verified by statistical paired *t*-test method. Under the experimental conditions used, the limit of detection (LOD) of TBT and DBT were 0.70 and 0.50 μg/mL, respectively. The optimised extraction method for butyltins in water and sediment samples involved using hexane containing 0.05–0.5% tropolone and 0.2% sodium chloride in water at pH 1.7. The quantitative extraction of butyltin compounds in a certified reference material (BCR-646) and naturally contaminated samples was achieved with recoveries ranging from 95 to 108% and at %RSD 0.02–1.00%. This HPLC method and optimum extraction conditions were used to determine the contamination level of butyltins in environmental samples collected from the Forth and Clyde canal, Scotland, UK. The values obtained severely exceeded the Environmental Quality Standard (EQS) values. Although high resolution methods are utilised extensively for this type of research, the developed method is cheaper in both terms of equipment and running costs, faster in analysis time and has comparable detection limits to the alternative methods. This is advantageous not just as a confirmatory technique but also to enable further research in this field.

Keywords: Tributyltin, dibutyltin, monobutyltin, butyltins, normal phase HPLC, Forth and Clyde canal, EQS values.

Introduction

Tributyltin compound is one of the most toxic anthropogenic compounds introduced into the environment. It has been widely used mainly as antifouling paints and wood preservatives due to its biocidal property.[1,2] The production of TBT increased significantly in the 1950s which raised the level of tributyltin in the environment. Due to the persistent nature and bioaccumulative potential TBT has been classified as a Persistent Organic Pollutant (POP), which also has a high toxicity towards organisms.[3] The usage of tributyltin and its derivatives has drawn concern about the potential damage to organisms and mammals in ecosystems. TBT levels found in water and sediment from contaminated sites are at concentration levels that may have adverse physiological effects on both organisms and mammals. The concentration of TBT and its degradation products such as dibutyltin (DBT) and monobutyltin (MBT), found in waters and sediments is a matter of growing environmental concern with many areas requiring costly remediation. DBT and MBT are only present as degradation products of TBT and are not as toxic as the parent compound. They are useful as indicators to degradation studies.

There are many methods to determine the contamination level of organotins in environmental samples. The main separation techniques involve chromatography systems (GC or HPLC) coupled with high sensitivity detection systems. Methods for the extraction and analysis of butyltins include: sonication extraction with HCl in methanol followed by derivatized and determined with GC-quartz furnace

Address correspondence to David Livingstone Centre for Sustainability, Department of Civil Engineering, University of Strathclyde, Glasgow, Scotland, UK, G1 1QE; E-mail: sornnarin.bangkedphol@strath.ac.uk
Received May 15, 2008.

atomic absorption spectrometry (QF-ASS).[4] Extraction with tropolone and *n*-hexane followed by Grignard derivatization and determination with GC–flame photometric detection (FPD).[1,5–9] However this method is increasingly replaced by the less time consuming in situ ethylation with sodium tetraethylborate ($NaBEt_4$) and using sonication technique followed by GC–FPD, GC–atomic emission detection (AED) or GC–inductively coupled plasma mass spectrometry (ICPMS).[10–12] Recently, solid-phase micro extraction (SPME) developed by Arthur and Pawliszyn[13] in combination with GC–ICPMS was applied for the analysis of $NaBEt_4$ derivatized volatile[12,14] and semi-volatile[15] butyltins in environmental samples. Moreover, the extraction method of derivatized analyses were usually concentrated to the levels necessary for detection by headspace solid-phase micro extraction (HS-SPME),[12,16–18] purge-and-trap (PT),[20] headspace single-drop micro extraction (HDME) or liquid-phase micro-extraction (LPME),[21,22] based on the same principle as SPME but with a much higher volumes of extracting phase (polydimethylsiloxane-PDMS) was applied for the determination of butyltins in environmental samples after in situ derivatization with $NaBEt_4$. In addition, the general extraction method for water samples was solid phase extraction (SPE). The ODS(C-18) cartridges were used to extract butyltin compound from water samples.[23,24]

Tripropyltin (TPT) and tricyclohexyltin (TCyT) are the most frequently used internal standards for the analysis of butyltin compounds in environmental samples.[12,25] It remains, however, questionable whether those compounds behave exactly the same as the target analytes and correct for all matrix interferences. More recently, isotopes labeled standards such as isotopically enriched TBT (Sn117, Sn118 or Sn119) were introduced resulting in more reliable and accurate results [21] for ICP/MS detection. For the analysis using HPLC method, there were a few reports using HPLC reverse phase system to separate TBT, DBT and MBT with post-column reaction by fluorescent detector.[26] Moreover, some normal phase HPLC was used to determine the amount of butyltins in sample using GF-AAS as the detection system.[27]

The methods mentioned above consist of complicated sample preparation steps which are time consuming and increases the cost of analysis. It also requires high resolution detection which might not be available in some laboratories. Therefore, this work is advantageous as it presents an improved HPLC system with normal phase using simple UV/Vis detection to provide qualitative and quantitative analysis. This method omits pre-column, post-column and derivatisation steps. However, previous studies using the same NPHPLC and UV methodology are available in the literature. The disadvantages of the reported methods are that they only measure TBT and not the degradation products that limit the use of the methodology.[28] MBT was not investigated even though separation of TBT and DBT were studied.[29] Also the conditions required iodine-chloride (ICl) on-column pretreatment which is stable for only a short period; however the main disadvantage is that this method gives only qualitative data. Therefore, the methodology described in this study is a useful and worthwhile addition to current methods of analysis for TBT and DBT, particularly due to the low cost of instrumentation. Analysis time and cost are also lower than the reported methods as derivitasion is unnecessary. This can enable more research in this field. The method described is suitable for qualitative and quantitative monitoring of contaminated sites and also for partition studies to determine environmental fate.

Materials and methods

Chemicals and instruments

All chemicals were used without additional purification. The analytical standards used were TBT chloride (96% purity), DBT chloride (98% purity) and MBT chloride (95% purity). Tetrabutyltin was used as an internal standard for GC/MS. Tropolone (98% purity) and Hexylmagnesium bromide solution (2M in diethyl ether) were obtained from Aldrich (Steinheim, Germany). All solvents were HPLC grade and obtained from Merck (Darmstadt, Germany). All of chemicals used were of analytical grade. The PerkinElmer 785A UV/VIS HPLC system (Waltham, Massachusetts, USA) was equipped with an injection loop of 20 μL volume. All tubing parts of HPLC system that come into contact with the sample were replaced by polyether ether ketone (PEEK) components. The chromatographic column used was an ultra cyano column (5 μm, 250 mm $\times$ 4.6 mm i.d., Restek, UK). The GC/MS system was a Hewlett-Packard 5980 gas chromatograph/quadrupole mass spectrometer (Ramsey, Minnesota, USA) with HP5 column (30 m $\times$ 0.25 mm i.d. $\times$ 0.25 μm). The UV/Vis spectrometer was carried on a Lambda 45 UV/Vis system Perkin Elmer (Waltham, Massachusetts, USA).

Chromatographic separation

For the HPLC separation, first the absorption wavelength of butyltins was studied by UV/Vis scanning. The λ_{max} of TBT, DBT and MBT were investigated and used as the detection wavelength of HPLC UV/Vis system. From the spectra, TBT, DBT and MBT gave a high absorption at the same wavelength at 215 nm. Therefore, normal phase was chosen as many of the solvents used by RPHPLC will also absorb this wavelength.

The separation of butyltins was adjusted by varying individual parameters, e.g., the amount of tropolone and THF, pH, polarity of mobile phase and flow rate. For the effect of tropolone and THF, various amount were added into the mobile phase, hexane. The optimum quantity of added compound was then fixed for the next variation. For the effect of acidity, the pH of the mobile phase was adjusted

with concentrate acetic acid and varied from pH 2 to 7. The optimum pH was obtained from the experimental results and then fixed for the next variation. For the polarity of mobile phase, ethanol, methanol and water were added to the hexane in order to increase the polarity. Finally, the flow rate was optimised.

For the GC/MS separation, the butyltins were derivatised with 0.5 mL 2M *n*-hexylmagnesium bromide for 30 min under inert atmosphere, 2M HCl was then added to stop the reaction. Anhydrous ammonium sulfate was added to remove moisture before the internal standard was added. A 3 μL of solution was injected into the GC/MS. The carrier gas was helium at a flow rate of 1 mL/min. The injector and detector temperatures were held at 280°C and 300°C, respectively. The column oven temperature was programmed from an initial temperature of 100°C, hold for 2 min, to a final temperature of 300°C at the rate of 15°C/min, and hold for 10 min. The peak areas and mass spectrum (Total Ion Chromatogram, TIC) were recorded. For the confirmation, the developed HPLC method was verified with the standard GC/MS method using the paired *t*-test method at 95% confidence interval.

Extraction of butyltins

For spiked water sample preparation, the stock solutions of TBT, DBT and MBT 1,000 mg/L were prepared separately in methanol. A 5 mL of each butyltin stock solution was mixed together and diluted in nanopure water to make up 5 mg/L sample solution. A 30 mL of sample solution was extracted in hexane by shaking at 350 rpm for 30 minutes 3 times with 10 mL of hexane in total. All organic phases collected from each step were mixed into one portion. The extracted solutions were determined by HPLC.

The extraction efficiency was improved by varying individual parameters, e.g., the amount of tropolone, pH and the amount of salt. For the effect of tropolone, various amount of tropolone was added into the extracting solvent, hexane. The optimised quantity of tropolone was fixed for the next variation. For the effect of acidity, pH of water samples were adjusted with concentrate HCl varied from pH 1 to 6. The suitable extraction pH was obtained. For the affect of ionic strength, up to 200 mg of sodium chloride was added into the water sample containing optimum amount of acid. The extraction efficiency was confirmed by GC/MS to obtain the optimum extraction conditions for TBT, DBT and MBT.

For sediment samples, the already optimized conditions as for water samples were adjusted by increasing the amount of tropolone. A certified reference material (CRM): BCR-646 was used to determine the extraction efficiency of butyltins in the sediment.

Sample collection

Sediment and water samples were collected from potentially polluted areas. The samples were collected in March, 2007 at Bowling Basin and Port Dundas, Glasgow, UK. In the past this was a main canal waterway between the west and east coast of Scotland. While boat activity is still present at Bowling Basin, Port Dundas has been inactive for many years and is no longer part of the canal network. Samples collected from these two sites were used to assess the persistence of butyltins in the environment. The surface layer of sediment samples were taken using a dredge sampler at approximately 4–5 m deep, and the surface water samples were collected and stored in polypropylene bottles. Samples were kept at temperatures lower than 4°C in the dark. All of the samples were extracted and analysed within 72 hours.

Results and discussion

Determination of butyltins by HPLC

The spectrum of butyltins is presented in Figure 1. From the spectra, TBT, DBT and MBT gave a high absorption at the same wavelength at 215 nm. As a result, the absorption wavelength at 215 nm was fixed for butyltins analysis.

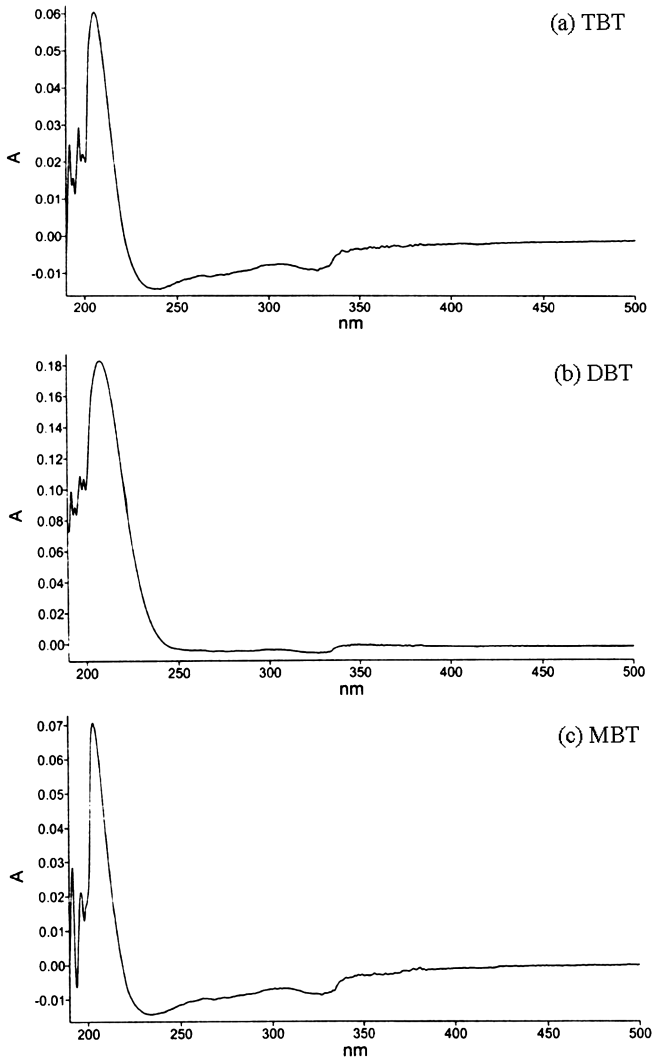

Fig. 1. The UV/Vis spectra of (a) TBT, (b) DBT and (c) MBT using hexane as reference.

For the effect of tropolone on the separation, the amount of tropolone was varied from 5 to 50 mg in 1 L of hexane at flow rate 1 mL/min. Tropolone can rapidly form a stable complex with MBT and DBT cations but not TBT, therefore, it has no effect on the elution of TBT.[27] The stoichiometric of the tropolone complex was ML_2 for MBT and ML for DBT, where M is MBT or DBT and L is tropolone. The complex formation of tropolone reduces the positive charge of butyltin compounds that can enhance the elution from the column. The results found that tropolone in the mobile phase can help to elute DBT from the column. Due to the fact that MBT has a very high positive charge, which binds very strong with cyano group in the column, tropolone does not improve the elution of MBT.

However, the mobile phase containing tropolone cannot be left overnight in contact with the column and detector as it degrades and produces a brown residue which contaminates the system. From this reason, THF was selected instead of tropolone to improve the separation as it has an oxygen donor in the molecule and similar non polarity to tropolone. The amount of THF in mobile phase was studied from 1 to 20% (v/v) at flow rate 1 mL/min. The effect of THF on the separation is shown in Figure 2a.

The results show that THF contained in the mobile phase gave the same efficiency as tropolone and can therefore be used to improve the separation. The amount of THF that is suitable for the separation is 5% in mobile phase, due to high amount of THF increase the baseline at 215 nm. However, mobile phase containing THF still cannot elute MBT from the column as shown in Figure 2a. Therefore, other parameters which have effect on separation were considered.

The addition of acid contained in the mobile phase at flow rate of 1 mL/min was studied and the results are presented in Figure 2b. The diagram shows that the mobile phase containing acid assists the elution of butyltins because the proton (H^+) can bind better with cyano-group (CN) in the column and release butyltins. pH 3 was chosen as the optimum condition. However, MBT cannot be eluted at pH 3 due to the strong interaction between MBT and the cyano-group. At pH lower than 3, MBT was eluted but gave an unsatisfactory peak shape and also the pH is over the column recommend limit (pH 2.5), which may damage the column. Moreover, the effect of polarity of mobile phase

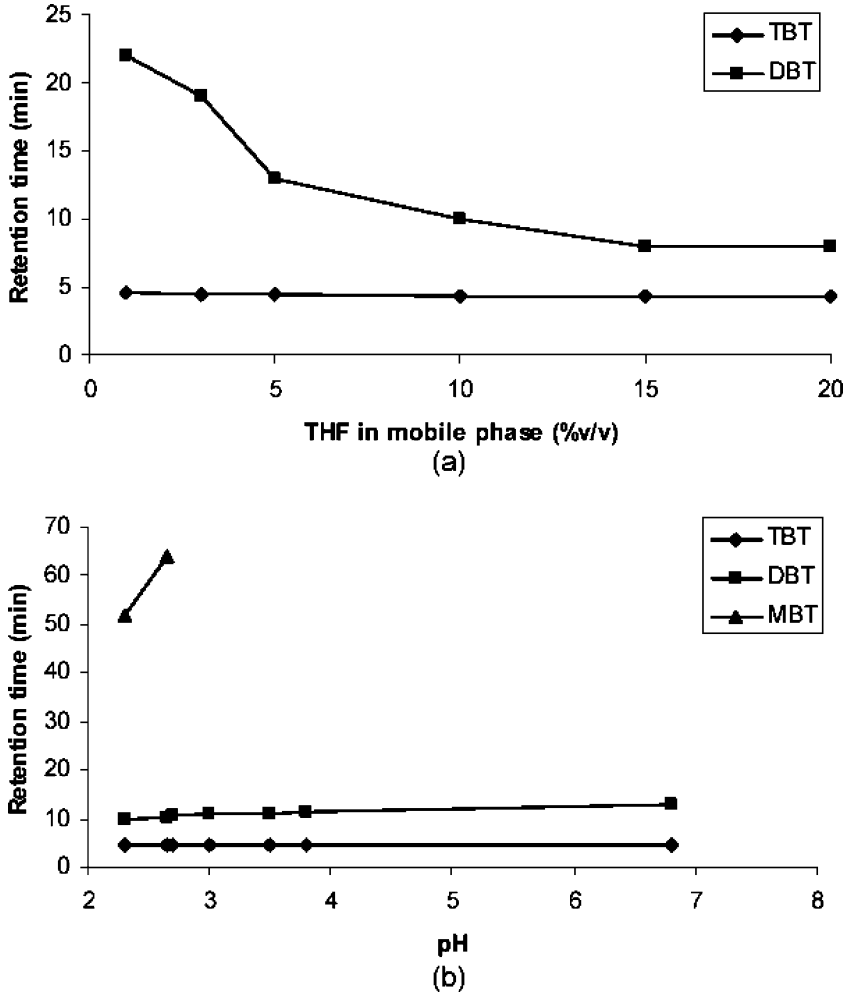

Fig. 2. The separation of butyltins (a) effect of THF (b) effect of pH.

Table 1. The regression line and detection limit HPLC and GC/MS.

	HPLC/UV-Vis		*GC/MS*	
Butyltins	*Regression line*	*LOD* ($\mu g\ mL^{-1}$)	*Regression line*	*LOD* ($\mu g\ mL^{-1}$)
TBT	$R^2 = 0.9969$, $Y = 775.77X - 307.24$	0.70	$R^2 = 0.9997$, $Y = 121106X + 22668$	1.00
DBT	$R^2 = 0.9985$, $Y = 1539.6X + 862.64$	0.50	$R^2 = 0.9994$, $Y = 120230X + 14623$	1.30
MBT	N/A	N/A	$R^2 = 0.9932$, $Y = 183376X - 41614$	2.20

was studied by adding polar solvent, e.g., 1% ethanol, 1% methanol and 4% water, respectively. From the results we found that high polarity of mobile phase increased retention time of butyltins and also the adding solvent gave very high background. Therefore, the adjustment of polarity cannot improve the separation under the stated conditions.

The flow rate of mobile phase was varied from 0.05 to 1 mL/min. The optimum flow rate was found to be 0.8 mL/min. From the optimization steps, the separation was performed in isocratic mode at 0.8 mL/min on cyanopropyl column with a mobile phase of hexane containing 5% THF and 0.03% acetic acid.

This developed HPLC technique was verified with the standard GC/MS method using paired *t*-test method at 95% confidence limit. The 10 samples at the same concentration of TBT (5 mg/L) were determined by both techniques. The calculation showed that the *t*-statistic value (0.514) is less than the *t*-distribution (2.26). Therefore, the analytical results of TBT in the samples have no significantly differences between HPLC and GC/MS. Moreover, the validation result of DBT between the two techniques was successfully proved. The regression line and detection limit of both technique are presented in Table 1.

The comparison table shows that the detection limit of the developed system is slightly better than GC/MS system. This developed HPLC method was then used to determine the contamination levels of TBT and DBT in the samples.

Extraction of butyltins

The extraction results of TBT and DBT in spiked samples using hexane as the extraction solvent show good reproducibility. The extraction gave 79.47% and 12.33% recovery for TBT and DBT, respectively. As a result of the poor DBT recovery, tropolone was added to improve the extraction. The results are presented in Figure 3a.

From the results, tropolone enhances the extraction efficiency of both compounds. The complex formation of butyltins-tropolone could reduce positive charge and water solubility of butyltin compounds. This leads to the preference of butyltins for the organic phase, which successfully increased the recoveries of DBT in the water sample from 15.41% to the highest recoveries of 100.09%. Although tropolone does not form a complex with tributyltin, the recoveries slightly increased from 80.26 to 88.31%. Tropolone may form an ion-dipole interaction with TBT, which can increase the mobility of TBT into hexane. From Figure 3a, 0.05% of tropolone in hexane was found to be the optimum minimum concentration for extraction.

The effect of pH of the water samples on extraction was studied and the results are presented in Figure 3b. The pH below 1.70 improved the recovery for both TBT and DBT compared to the higher pH. The addition of acid also preserved the sample by preventing hydrolysis and keeping the compounds in the cationic form. However under conditions of extremely low pH, the acid may break tin-carbon bonds and reduce the actual amount of butyltin compounds. Therefore, the pH of the samples should be carefully controlled.

Sodium chloride increases the ionic strength of water and causes "salting out" effect, which force butyltin compounds to transfer into organic phase.[30] From the results shown in Figure 3c, gradually improvement of extraction was found after addition of sodium salt. At 0.2% NaCl in water sample, the optimum condition was obtained. The recoveries were increased from 85.06% to 98.11% for TBT and from 92.22% to 98.99% for DBT.

Consequently, the optimum conditions for the extraction of water sample had the addition of 0.2% NaCl at pH 1.7, extracted by hexane containing 0.05% tropolone. Moreover, these extraction conditions were proved by GC/MS to confirm the efficiency on TBT, DBT and MBT in water samples as shown in Figure 4. Even the extraction procedure for MBT in water samples has not been proved in

Table 2. Contamination levels of butyltin compounds in samples using developed HPLC and optimised extraction method.

	Sediment ($\mu g\ kg^{-1}$) ± *RSD*		*Water* ($\mu g\ L^{-1}$) ± *RSD*	
Sampling site	*TBT*	*DBT*	*TBT*	*DBT*
Bowling Basin	162.31 ± 0.13 (35,284)*	BDL	0.85 ± 4.81 (4,250)*	1.16 ± 4.93
Port Dundas	148.89 ± 0.51 (32,367)*	107.84 ± 0.88	0.17 ± 1.72 (850)*	0.19 ± 2.16
				0.19 ± 2.16

BDL: Below detection limit of determination method employed the conditions.

*Number of times higher than EQS values.

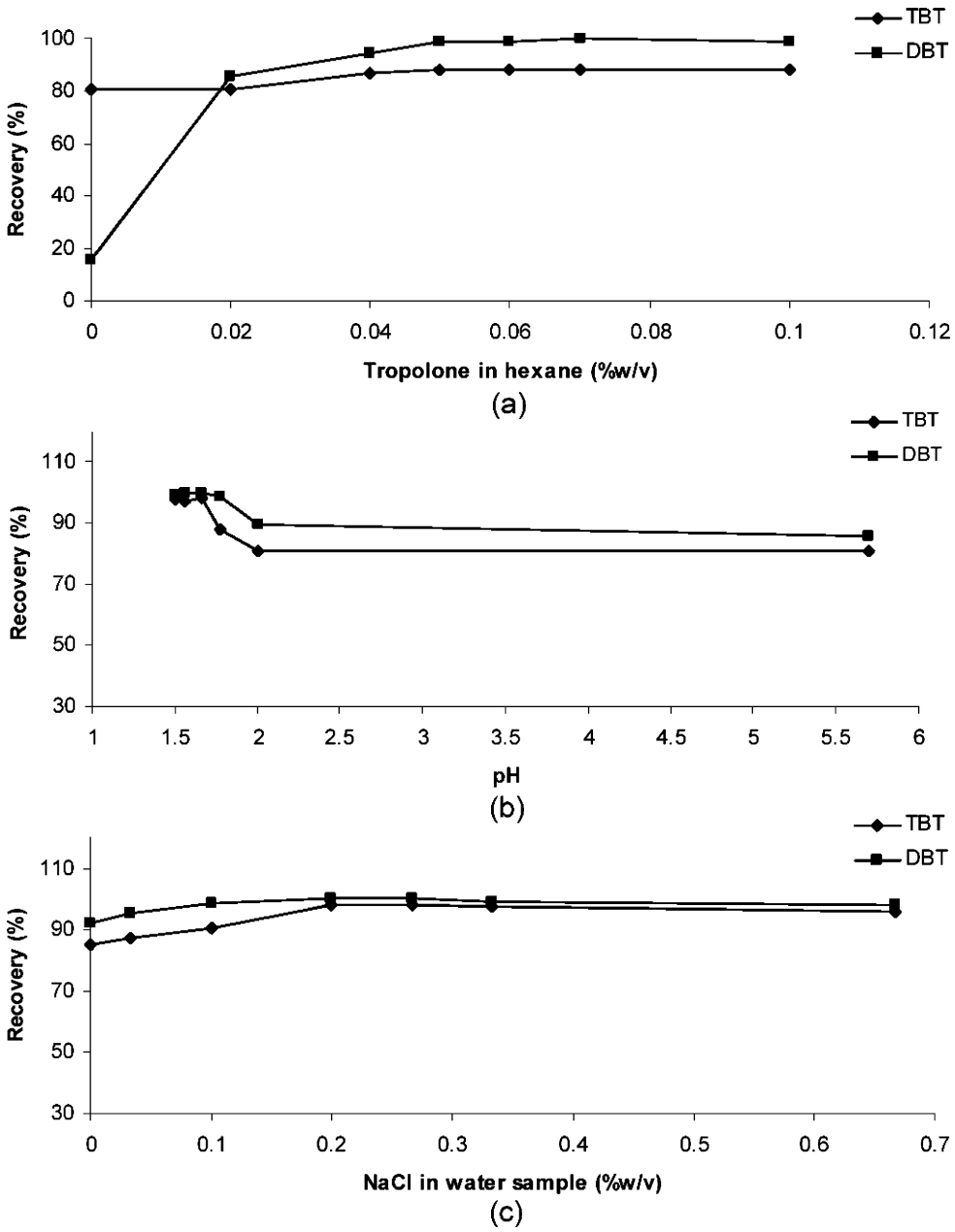

Fig. 3. The recoveries of TBT and DBT (a) at different concentration of tropolone in hexane (b) at various pH of water sample (c) at different amount of sodium chloride in water samples.

the optimization step by HPLC however the results imply the applicability of the extraction method to MBT. For sediment samples, the optimised conditions for water extraction were slightly adapted. The amount of tropolone in hexane was increased to 0.5 %w/v due to the more complicated matrix of sediment. The certified reference material (CRM): BCR-646 was analysed using the optimum conditions and the results are shown in Figure 4.

The contamination of butyltins in the samples collected from Bowling basin and Port Dundas in Glasgow are shown in Table 2. From the comparison of the contamination level of TBT to the EQS values; 0.0046 μg/kg for freshwater and marine sediment and 0.0002 μg/L for pelagic community, the contamination levels of TBT in both sampling sites are significant higher than the EQS values.[31] This means that the contaminated TBT can adversely affect the ecosystem and living organisms present in the environment. The accumulation detected also raises a possibility of biomagnification to the top of food chain. Moreover, Port Dundas where there has been no activity for many years is still highly contaminated, which confirms that butyltins are highly persistent organic pollutant (POPs).

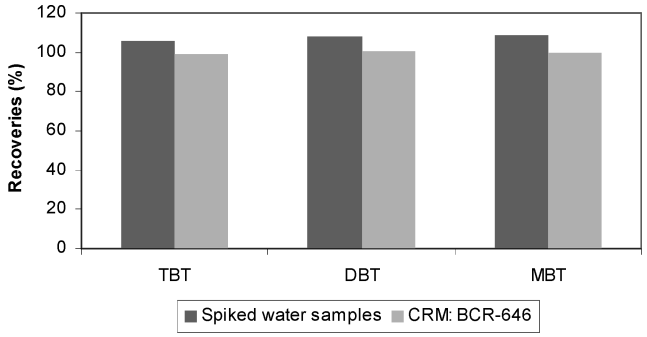

Fig. 4. The recoveries of butyltins using GC/MS from water samples and CRM: BCR-646.

Conclusion

For the effective monitoring of butyltin compounds in environment, it was necessary to establish an economic and simple analytical method to determine levels which included an appropriate extraction method. This study developed a normal phase HPLC with UV/Vis detector and also optimised extraction conditions for water and sediment samples. The advantages of the developed method are low cost instrumentation; low running cost; time and cost saving as no derivatisation is necessary, and overall technical operation requirements are lower for HPLC as opposed to GC/MS.

This opens the field for further research. The method developed gives good detection limits similar to GC/MS and is suitable for a range of environmental samples and remediation/degradation studies which are mainly concerned with contaminated water and sediments.

Acknowledgments

This work was valuable supported by Center of Excellence for Innovation in Chemistry (PERCH-CIC), Kasetsart University, Bangkok, Thailand and Thames Restek UK Ltd.

References

[1] Hoang, T.V.; Michel, A.; Guyot, A. Polyvinylchloride stabilisation with organotin compounds—Part III: Effect of lewis acidity and co-ordination of organotin chlorides upon their catalytic activity towards dehydrochlorination. Polym. Degrad. Stabil. **1982**, *4*, 213–222.

[2] Rudel, H. Case study: bioavailability of tin and tin compounds. Ecotoxicol. Environ. Saf. **2003**, *56*, 180–189.

[3] Antizar-Ladislao, B. Environmental levels, toxicity and human exposure to tributyltin (TBT)-contaminated marine environment. A review. Environ. Inter. **2008**, *34*, 292–308.

[4] Bowles, K.C.; Tiltman, M.D.; Apte, S.C.; Hales, L.T.; Kalman, J. Determination of butyltins in environmental samples using sodium tetraethylborate derivatization: characterization and minimization of interferences. Anal. Chim. Acta **2004**, *509*, 127–135.

[5] Caricchia, A.M.; Chiavarini, S.; Cremisini, C.; Morabito, R.; Scerbo, R. Influence of storage conditions on the determination of organotin in mussels. Anal. Chim. Acta **1994**, *286*, 329–334.

[6] Fent, K.; Hunn, J. Phenyltins in water, sediment, and biota of freshwater marinas. Environ. Sci. Technol. **1991**, *25*, 956–963.

[7] Gomez-Ariza, J.L.; Morales, E.; Ruiz-Benitez, M. Simultaneous speciation of butyltin and phenyltin compounds in the waters of Southwest Spain. Analyst. **1992**, *117*, 641–644.

[8] Harino, H.; Fukushima, M.; Tanaka, M. Simultaneous determination of butyltin and phenyltin compounds in the aquatic environment by gas chromatography. Anal. Chim. Acta **1992**, *264*, 91–96.

[9] Muller, M.D. Comprehensive trace level determination of organotin compounds in environmental samples using high-resolution gas chromatography with flame photometric detection. Anal. Chem. **1987**, *59*, 617–623.

[10] Ceulemans, M.; Witte, C.; Lobinski, R.; Adams, F.C. Simplified sample preparation for GC speciation analysis of organotin in marine biomaterials. Appl. Organomet. Chem. **1994**, *8*, 451–461.

[11] Lobinska, J.S.; Ceulemans, M.; Lobinski, R.; Adams, F.C. Flow-injection sample preparation for organotin speciation analysis of water by capillary gas chromatography-microwave-induced plasma atomic emission spectrometry. Anal. Chim. Acta **1993**, *278*, 99–113.

[12] Moens, L; Smaele, T.D.; Dams, R.; Broeck, P.V.D.; Sandra, P. Sensitive, Simultaneous determination of organomercury, -lead, and -tin compounds with headspace solid phase microextraction capillary gas chromatography combined with inductively coupled plasma mass spectrometry. Anal. Chem. **1997**, *69*, 1604–1611.

[13] Arthur, C.L.; Pawliszyn, J. Solid phase microextraction with thermal desorption using fused silica optical fibers. J. Anal. Chem. **1990**, *62*, 2145–2148.

[14] Centineo, G.; Gonzalez, E.B.; Sanz-Medel, A. Multielemental speciation analysis of organometallic compounds of mercury, lead and tin in natural water samples by headspace-solid phase microextraction followed b gas chromatography-mass spectrometry. J. Chromatogr. A **2004**, *1034*, 191–197.

[15] Vercauteren, J.; Peres, C.; Devos, C.; Sandra, P.; Vanhaecke, F.; Moens, L. Headspace solid-phase microextraction-capillary gas chromatography-ICP mass spectrometry for the determination of the organotin pesticide fentin in environmental samples. J. Anal. At. Spectrom. **2000**, *6*, 651–656.

[16] Jiang, G.; Liu, J.; Yang, K. Speciation analysis of butyltin compounds in Chinese seawater by capillary gas chromatography with flame photometric detection using in-situ hydride derivatization followed by headspace solid-phase microextraction. Anal. Chim. Acta **2000**, *421*, 67–74.

[17] Le Gae, M.; Lespes, G.; Potin-Gautier, M. Rapid determination of organotin compounds by headspace solid-phase microextraction. J. Chromatogr. A **2003**, *999*, 123–134.

[18] Botana, J.C.; Perero, I.R.; Torrijos, R.C. Rapid determination of butyltin species in water samples by multicapillary gas chromatography with atomic emission detection following headspace solid-phase microextraction. J. Chromatogr. A **2002**, *963*, 195–203.

[19] Reuther, R.; Jaeger, L.; Allard, B. Determination of organometallic forms of mercury, tin and lead by in situ derivatization, trapping and gas chromatography — atomic emission detection. Anal. Chim. Acta **1999**, *394*, 259–269.

[20] Colombini, V.; Bancon-Montigny, C.; Yang, L.; Maxwell, P.; Sturgeon, R.E.; Mester, Z. Headspace single-drop microextraction for the detection of organotin compounds. Talanta **2004**, *63*, 555–560.

[21] Shioji, H.; Tsunoi, S.; Harino, H.; Tanaka, M. Liquid-phase microextraction of tributyltin and triphenyltin coupled with gas chromatography-tandem mass spectrometry comparison between 4-fluorophenyl and ethyl derivatization. J. Chromatogr. A **2004**, *1048*, 81–88.

[22] Gomes, R.L.; Scrimshaw, M.D.; Lester, J.N. Determination of endocrine disrupters in sewage treatment and receiving waters. Anal. Chem. **2003**, *22*, 697–706.

[23] Serra, H.; Nogueira, J.M.F. Organotin specification in environmental matrices by automated on-line hydride generation-programmed temperature vaporization-capillary gas chromatography-mass spectrometry detection. J. Chromatogr. A **2005**, *1094*, 130–137.
[24] Vercauteren, J.; Peres, C.; Devos, C.; Sandra, P.; Vanhaecke, F.; Moens, L. Stir bar sorptive extraction for the determination of ppq-level traces of organotin compounds in environmental samples with thermal desorption-capillary gas chromatography-ICP mass spectrometry. Anal. Chem. **2001**, *73*, 1509–1514.
[25] Ebdon, L.; Gardia-Alonso, J.I. Determination of tributyltin ions in estuarine waters by high-performance liquid chromatography with fluorimetric detection using morin in a micellar solution. Analyst **1987**, *112*(11), 1551–1554.
[26] Astruc, A.; Astruc, M.; Pinel, R.; Potin-Gautier, M. Specifiation of butyltin compounds by on-line HPLC-ETAA of tropolone complexes in environmental samples. Appl. Organomet. Chem. **1992**, *6*, 39–47.
[27] Wang, X.; Ding, L.; Zhang, H.; Chenga, J.; Yu, A.; Zhang, H.; Liub, L.; Liu, Z.; Li, Y. Development of an analytical method for organotin compounds in fortified flour samples using microwave-assisted extraction and normal-phase HPLC with UV detection. J. Chromatogr. B **2006**, *843*, 268–274.
[28] Praet, A.; Dewaele, C.; Verdonck, L.; van der Kelen, G.P. Liquid chromatography of organotin compounds in cyanopropyl silica gel. J. Chromatogr. A **1990**, *507*, 427–437.
[29] Rydberg, J.; Cox, M.; Musikas, C.; Choppin, G.R. *Solvent extraction principles and practice*; Marcel Dekker, Inc.: New York, NY, 2004.
[30] Water Framework Directive. Environmental Quality Standards (EQS) substance data sheet: Tributyltin compounds (TBT-ion). In *Common Implementation Strategy for the Water Framework Directive*, 2005.