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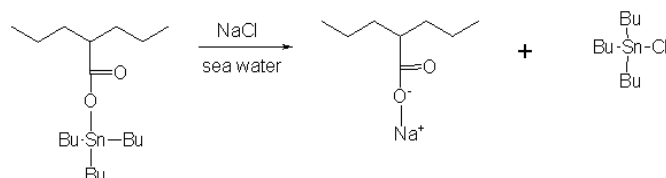
ISSN 1313-2563, Published at: <http://www.science-journals.eu>**IONIC LIQUIDS USED AS A GREEN APPROACH IN HEADSPACE SINGLE DROP MICROEXTRACTION AND GCMS DETERMINATION OF ORGANOTIN COMPOUNDS**Lora I. Georgieva<sup>1</sup>, Ivan. P. Román<sup>2</sup>, Violeta M. Stefanova<sup>1</sup>, Veselin Y. Kmetov<sup>1</sup>, Antonio Canals<sup>2</sup><sup>1</sup> Department of Analytical Chemistry and Computer Chemistry, University of Plovdiv "Paisii Hilendarski", 24 Tzar Assen, Str., 4000 Plovdiv, Bulgaria<sup>2</sup> Department of Analytical Chemistry and Food Sciences, and Institute of Materials, Faculty of Science, University of Alicante, P.O. Box 99, 03080 Alicante, Spain**Abstract**

Gas chromatography with MS detection was applied for simultaneous determination of six of the most toxic organotin compounds (OTs): monobutyltin, dibutyltin, tributyltin, monophenyltin, diphenyltin, triphenyltin. Headspace single drop microextraction (HS-SDME) in Ionic liquids (ILs) was proposed as Green alternative to the traditional one. Three different ILs ( $[C_8MIM][PF_6]$ ;  $[C_6MIM][PF_6]$ ) and  $[C_4MIM][PF_6]$ ) were evaluated as a collector phase. The first one was found as the most appropriate for a group microextraction of the tested OTs. Analytes were evaporated from the IL microdrop by means of thermal desorption. ILs possess some advantages as an extraction phase in comparison with traditionally used organic solvents. They are more stable during the analytical process and are considered as environmentally friendly compounds. Moreover HS-SDME procedure was performed in a single drop of only 5  $\mu$ l IL. The time needed for the extraction was proved to be only 20 min. Therefore the proposed method could be related to the Green chemistry methods.

**Key words:** ionic liquids, organotin compounds, headspace single drop microextraction, green chemistry.

**INTRODUCTION**

Organotin compounds (OTs) have been widely used (e.g. Butyltin-BT and Phenyltin-PhT) in the past 50 years as active components in different applications. Some of them are: antifouling paints; pesticides formulations; catalysts; additives for thermal and light stabilization in the plastic industry; fungicides; insecticides; water disinfectants; pharmaceuticals and cosmetics [1, 2]. The most extensive use of trialkyltins is as biocides in marine antifouling paints in which the active components of the antifouling paint are usually incorporated in a copolymer which induces their steady diffusion into water:



After the awareness of their significant toxicity for mammalian and aquatic organisms in the 1980s, the interest of their speciation increased rapidly. OTs can cause changes in the endocrine system such as the occurrence of imposex in gastropods, which can lead to sterilization and death of the affected organisms [1]. They might exhibit toxic effect on a broad range of non-target organisms. Their

toxicity, environmental persistence and ability to transfer along the trophic chains are dependent on the type, size and number of organic groups attached to the tin atom, so the determination of their species is of crucial importance. European Union listed them as priority pollutants. The Directive 2000/60/EC (Water Framework Directive, WFD) includes as a priority and hazardous substance the tributyltin compounds among the other substances. Moreover, the Directive 2008/105/EC establishes extent permitted of tributyl compounds (tributyl cation) in inland and other surface waters, expressed as an annual value ( $0.0002\mu\text{g/L}$ ) or as maximum allowable concentration ( $0.0015\mu\text{g/L}$ ).

This work aimed to develop a method for determination of six of the most toxic OTs: monobutyltin (MBT), dibutyltin (DBT), tributyltin (TBT), monophenyltin (MPT), diphenyltin (DPT), triphenyltin (TPT). OTs are generally detected by gas chromatography or liquid chromatography (LC) as separation method in combination with selective techniques such as mass spectrometry (MS), tandem mass spectrometry (MS-MS) or an element selective techniques as an inductively coupled plasma-mass spectrometry [3, 4]. The Gas chromatography (GC) is more widely used for OTs analysis and was applied in this work for simultaneous determination of six organotin compounds. Due to the very low content of OTs in the environment preliminary extraction and preconcentration are needed. Nowadays there is a tendency of replacing the traditional liquid-liquid extraction with microextraction techniques [5, 6].

In this work liquid-liquid microextraction was applied as a green alternative of the traditional liquid-liquid extraction.

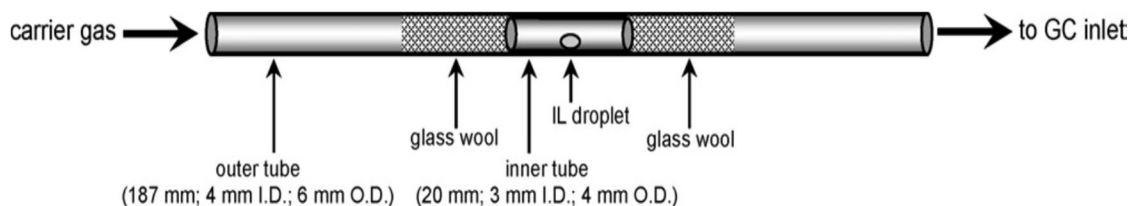
Ionic liquids are considered as more friendly to the environment than traditionally applied organic solvents so it was interesting to test their applicability as a collector phase for HS SDME procedure. One problem is that ILs are not compatible for direct introduction to GC-MS. Their use in gas chromatographic analysis could block the chromatographic column. In order to avoid this problem the efficiency of a device for thermal desorption was checked, and thermal desorption program was optimized. Procedure of cryofocusing was added for trapping the analytes before introducing them to the GC-MS[7]. Such technique has not been previously applied in the case of OTs determination.

## 2. EXPERIMENTAL:

### 2.1. Reagents and instruments

- Organotin compounds: monobutyltin (MBT), dibutyltin (DBT), tributyltin (TBT), monophenyltin (MPT), diphenyltin (DPT), triphenyltin (TPT) and sodium tetraethyl borate  $\text{NaBEt}_4$  have been obtained from Aldrich (Steinheim, Germany).
- Ionic liquids 3-Methyl-1-octylimidazolium hexafluorophosphate ( $[\text{C8MIM}][\text{PF6}]$ ); 1-Hexyl-3-methylimidazolium hexafluorophosphate ( $[\text{C6MIM}][\text{PF6}]$ ) and 1-Butyl-3-methylimidazolium hexafluorophosphate ( $[\text{C4MIM}][\text{PF6}]$ ) have been obtained from Merck (Damstadt, Germany).

A two-tubes concentrically disposed system made up of a Gerstel thermal desorption glass tube (187 mm length, 4 mm I.D., 6mm O.D.), a laboratory-cut glass Pyrex tube (20 mm length, 3 mm I.D., 4 mm O.D.) from Corning Incorporated (Corning, NY, USA) and washed glass wool from Panreac (Barcelona, Spain) were used for desorption of the compounds from the IL droplet (Fig.1).



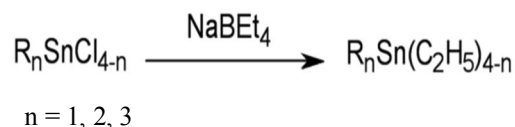
**Fig.1 Thermal desorption device**

A Gerstel TDS 2 thermodesorption system equipped with a Gerstel CIS-4 cooled injection system programmable temperature vaporization inlet from Gerstel (Mülheim an der Ruhr, Germany) was used to carry out the TD process.

An Agilent 6890N gas chromatograph coupled with an Agilent 5973 mass spectrometry detector, both from Agilent Technologies (Palo Alto, CA, USA), were employed for the analytical measurements. The column used was DB-5 (30m x 0.25 mm i.d.) film thickness 0.25 $\mu$ m. Helium was used as carrier gas.

### 2.2. Headspace microextraction procedure with in-situ derivatization by NaBEt<sub>4</sub>

In order OTs to be converted into a suitable form for GCMS analysis derivatization by sodium tetraethyl borate (NaBEt<sub>4</sub>) was performed.



In this procedure 8 ml freshly prepared working standard solution (20 ng ml<sup>-1</sup>) of each OTs analyte were placed into a vial containing a stir bar. Then 100  $\mu$ l 1% NaBEt<sub>4</sub> (freshly prepared) were added. The derivatization process was held at pH 5 with the help of acetate buffer. The needle of a microsyringe containing 5 $\mu$ l IL was passed through a valve septum. Thus, a 3-mm piece of PTFE tube was fitted to the tip of the syringe needle, and the vial finally capped with the valve stopper. Then the syringe was placed until its tip was 1 cm approximately up to the liquid surface of the sample. The plunger was then depressed and a droplet of IL was formed and exposed to the headspace of the stirring (at 1600 rpm) solution at 45  $^{\circ}$ C.

After extraction, the droplet was retracted into the syringe. Then, the cap was removed from the vial and the PTFE tube was removed from the syringe tip. Finally, the IL droplet was placed inside the commercial TD glass tube as shown in Fig. 1.

### 2.3 TD-GC-MS conditions

Thermal desorption conditions were optimized experimentally. Higher sensitivity and reproducibility have been obtained at the followed parameters: the drop was initially conditioned for 0.5 min at 25  $^{\circ}$ C, after that the temperature was increased to 240  $^{\circ}$ C with ramp of 60  $^{\circ}$ C min<sup>-1</sup> and held for 5 min (desorption time); helium flow rate was 100 mL min<sup>-1</sup>. The desorbed compounds were cryofocused in the cool injection system with liquid nitrogen at -40  $^{\circ}$ C. Then the collected fraction was rapidly heated to 250  $^{\circ}$ C with ramp of 12  $^{\circ}$ C s<sup>-1</sup>. This allowed analytes to be transferred to the GC column by the He gas. Gas chromatographic conditions for separation were set as: the GC oven temperature was set at 50  $^{\circ}$ C for 1min and was increased to 300  $^{\circ}$ C at 10  $^{\circ}$ C min<sup>-1</sup> and held for 4min.

The MS detector voltage was set at 1700V. Electron impact ionization was 70 eV ionization energy. The mass source was set at 230 °C. The measurements were carried out in selected ion monitoring (SIM) mode.

### 3. RESULTS AND DISCUSSION

The use of ionic liquids as collector phase for head space single drop microextraction showed to be a good choice for organotin compounds preconcentration. The high viscosity of the tested ILs improves the stability of the microdrop and makes the method more robust even using a 5 µl drops. On the other hand, ILs possess high boiling points and it is not possible to use them for direct injection in GC instruments. The optimized procedure for thermal desorption (2.3) and the selected device (Fig. 1) allowed good repeatability for introducing the six analytes into GC-MS instrument.

The efficiency of HS-SDME was tested by heating the sample solution (down to the head space) at different temperature: 10<sup>0</sup>, 20<sup>0</sup>, 30<sup>0</sup>, 40<sup>0</sup>, 45<sup>0</sup>, 50<sup>0</sup> and 80<sup>0</sup> C. Results obtained by 45<sup>0</sup> C showed the most sophisticated extraction yield for all compounds with exception of TPT - Fig. 2. It was observed that TPT extraction needs at least 80<sup>0</sup> C. The phenomena is due to the higher molecular mass and boiling point of triphenyltin compound. On this temperature in comparison to 45<sup>0</sup>., there is quite high loss of extraction efficiency for MPT, TBT and DPT (Fig. 2). Therefore compromise must be done depending on the analytical task needed. In order to accomplish a group extraction of the all six analytes 80<sup>0</sup> C was preferred.

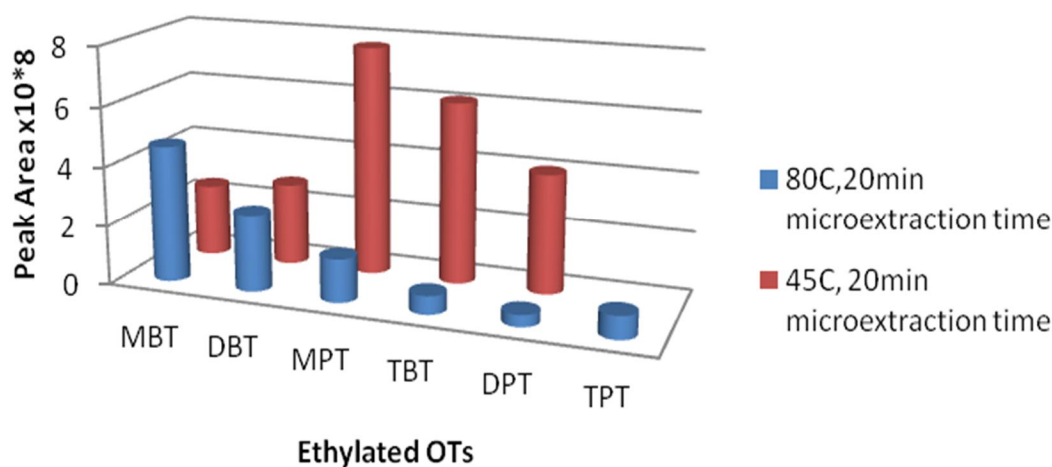


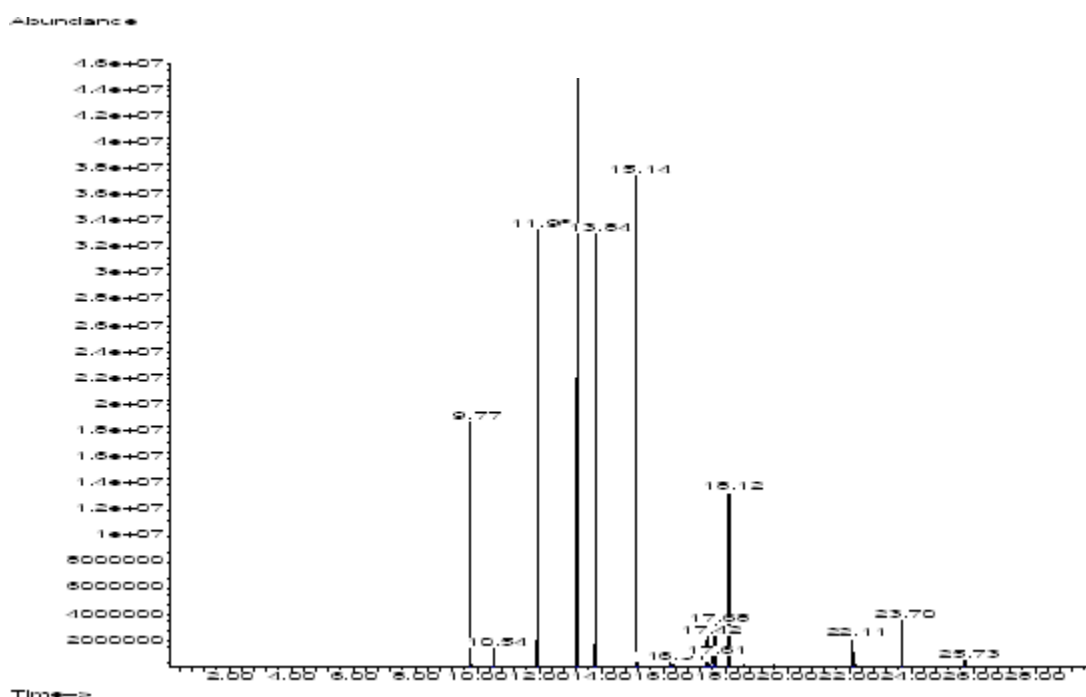
Figure 2 Extraction efficiency at 45<sup>0</sup>C and 80<sup>0</sup>C

The microextraction was tested at different time from 10 and 60 min. It was found that the treatment longer than 20 min did not lead to higher extraction efficiency for the six OTs.

The organotin compounds were chromatographically separated (Fig.3). The retention times of the ethylated organotin derivatives were determined experimentally using model solutions - Table 1.

**Table 1 Retention times of OTs derivatized by NaBEt<sub>4</sub>**

Analytes	MBT (BuSn <sup>3+</sup> )	DBT (Bu <sub>2</sub> Sn <sup>2+</sup> )	TBT (Bu <sub>3</sub> Sn <sup>+</sup> )	MPT (PhSn <sup>3+</sup> )	DPT (Ph <sub>2</sub> Sn <sup>2+</sup> )	TPT (Ph <sub>3</sub> Sn <sup>+</sup> )
Ethylated derivatives	BuSnEt <sub>3</sub>	Bu <sub>2</sub> SnEt <sub>2</sub>	Bu <sub>3</sub> SnEt	PhSnEt <sub>3</sub>	Ph <sub>2</sub> SnEt <sub>2</sub>	Ph <sub>3</sub> SnEt
Retention time, min	9.7	11.9	13.8	13.2	15.1	22.1



**Figure 3 Chromatogram of ethylated OTs**

The suitability of the Ionic liquids to be used as collector phase for HS-SDME was compared by the extraction yield obtained for the three ILs tested. Fig. 4 represents the results for 3-Methyl-1-octylimidazolium hexafluorophosphate ([C8MIM][PF<sub>6</sub>]); 1-Hexyl-3-methylimidazolium hexafluorophosphate ([C6MIM][PF<sub>6</sub>]) and 1-Butyl-3-methylimidazolium hexafluorophosphate ([C4MIM][PF<sub>6</sub>]) respectively. It was found that only 1-octylimidazolium hexafluorophosphate has the ability to extract all six OTs analytes. Moreover with an exception of MPT is gives greater extraction yields for all the rest organotin compounds tested. Therefore the [C8MIM][PF<sub>6</sub>] was appointed as the best choice for the method created.

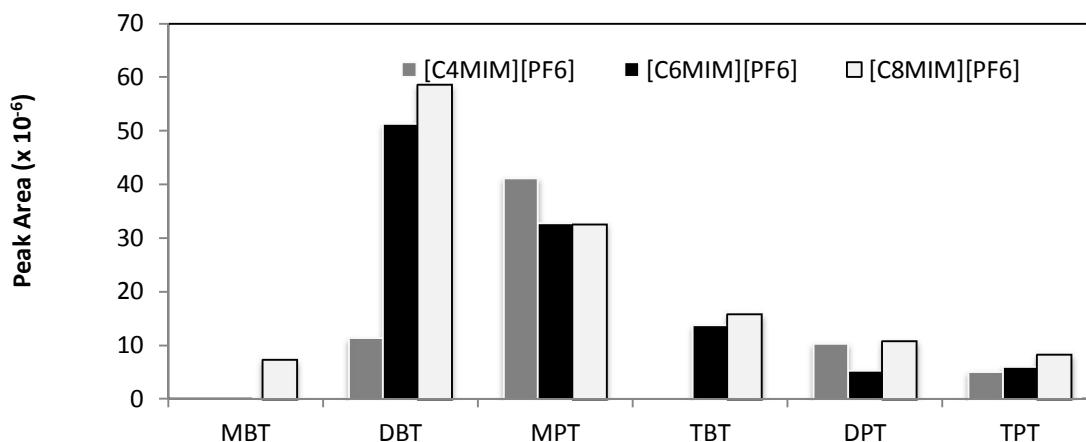


Fig. 4 Extraction yield of ethylated OTs obtained by the evaluated ILs

#### 4. CONCLUSIONS

The combination of head space microextraction with ionic liquids with GC-MS was proved to be applicable for simultaneous determination of butyl- and phenyltin compounds. Results from evaluated three ionic liquids shown that the extraction with 1-octylimidazolium hexafluorophosphate gives greater yield than the others two ILs studied. The device for thermal desorption and cryofocusing was successfully applied for introducing organotin compounds from IL into GC-MS instrument.

The small volume (5 $\mu$ l) of IL consumed, the replacement of the classical organic solvents with more environmentally friendly compounds, as well as the possibility for group extraction of six organotin compounds refers the suggested method as relevant to the Green Chemistry principles.

#### Acknowledgements

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