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## Evaluation of ionic liquid gas chromatography stationary phases for the separation of polychlorinated biphenyls

M. Ros, J. Escobar-Arnanz, M.L. Sanz, L. Ramos\*

Department of Instrumental Analysis and Environmental Chemistry, IQOG-CSIC, Juan de la Cierva, 3, 28006 Madrid, Spain

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### ABSTRACT

The feasibility of six ionic liquid- (IL-) based stationary phases for the analysis of environmentally important polychlorinated biphenyls (PCBs) by gas chromatography combined with either electron capture micro-detector (GC-micro-ECD) or quadrupole mass spectrometry (GC-MS, for confirmation) have been evaluated. These IL-based columns showed a separation mechanism different from that observed for other commercial phases, such a low bleed high temperature 8% phenyl (equiv.) polycarborane-siloxane suggested shape-selective phase for non-*ortho* and mono-*ortho*-CBs, HT-8, or a polar poly(ethylene glycol), resulting in a different elution order of the 69 investigated PCBs. However, no all phases provided equality satisfactory resolutions for the most environmentally relevant congeners, the 12 toxic and the 7 priority PCBs. From this point of view, the best results were obtained with the SLB-IL76 and SLB-IL59 phases, which showed a number of coelutions for these specific congeners only slightly higher to that observed on HT-8. Interestingly, the SLB-IL59 phase was the only one among the evaluated phases allowing a complete resolution of the most toxic non-*ortho* substituted congeners # 77, 126 and 169 from all other PCBs investigated. SLB-IL76 and SLB-IL59 also demonstrated a superior chromatographic performance concerning peak symmetry, retention time stability and column bleeding, compared to the other four IL-based columns evaluated. Altogether, results obtained for the analysis of pure standards illustrated the potential of, in particular, SLB-IL 59 as an alternative phase for confirmation of the identity of PCBs typically detected in environmental matrices that coeluted on conventional non-polar phases in use for this type of determination. However, the long-term stability and quantitative behaviour of these stationary phases during the analysis of real samples still need to be addressed.

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### 1. Introduction

Polychlorinated biphenyls (PCBs) are recognized as worldwide distributed contaminants. Their persistence, bioaccumulation capability, high toxicity of some of the congeners [1] and their potential for long-distance transport made this family of pollutants to be part of the so-called dirty dozen of the Stockholm convention on persistent organic pollutants (POPs) already in 2001 [2]. PCBs have been analysed since the 1970s, but congener-specific analysis was only possible by the introduction of capillary columns for gas chromatography (GC) [3]. Despite the high resolution offered by these modern columns, the complexity of the mixture (209 possible congeners with very similar chemical and physical properties) hinders the simultaneous unambiguous determination of all isomers with a single GC column, even if a selective detector such as

mass spectrometer (MS) in the selective ion monitoring (SIM) mode was used. Thereby, in practice, the accurate determination of individual PCB congeners in real samples can only be accomplished by either parallel analysis of the extract in two GC columns with different selectivity or by means of multi-dimensional GC techniques [4,5]. Depending on the goal of the study, the nature of the specific targeted PCB congeners can vary [5]. However, most monitoring studies worldwide include the seven indicator PCBs (PCB # 28, 52, 101, 118, 138, 153 and 180) [6] and the toxic PCBs (the non-*ortho* CB # 77, 81, 126 and 169 and the mono-*ortho* CB # 105, 114, 118, 123, 156, 157, 167 and 189) [1], for which accurate determination is mandatory (congeners nos. based on Ballschmiter et al. [7]). Even for these particular congeners, coelutions occur in all commercial GC stationary phases available at present [5,8]. In consequence, research on the evaluation of novel GC phases for the chromatographic separation of this class of contaminants remains active [4,9].

The use of room temperature ionic liquids (ILs) based on imidazolium cations with trifluoromethanesulfonate anions for the

\* Corresponding author.

E-mail address: [l.ramos@iqg.csic.es](mailto:l.ramos@iqg.csic.es) (L. Ramos).

development of stationary GC phases with high thermal stability (up to 260 °C) was first reported by Anderson and Armstrong [10]. The two new ionic liquids proposed by the authors in this pioneer study of 2003, (1-benzyl-3-methylimidazolium trifluoromethanesulfonate and 1-(4-methoxyphenyl)-3-methylimidazolium trifluoromethanesulfonate), provided symmetrical peak shapes for both polar and non-polar analytes due to their dual nature retention selectivity [10]. In a follow-up study, cross-linking by free radical reactions of a new class of IL monomers composed of vinylimidazole was proposed to obtain coating materials with improved thermal stability (up to 350 °C) [11]. Thereafter, different methodologies for mixing ILs with polysiloxane-based commercial stationary phases [12,13] or to bond ILs to polysiloxanes [14] were assayed, and a number of tailored for purpose IL-based phases have been developed [15–17]. Only few of these studies used PCBs as test compounds [4,9]. Unfortunately, in all cases, a relatively small suite of PCB congeners, selected on the basis of their chlorination degree rather than on their environmental importance or toxicity was used. More importantly, these columns were rarely commercialised. However, the increasing general interest in IL-based stationary phases resulted in the manufacturing and commercialisation of a (still limited) number of capillary columns by a commercial firm in the late 2000s. Up to now, six stationary phases have been commercialised (see Table 1 below; SLB-IL60, launched in 2012, contains the same phase as SLB-IL59 but the former is deactivated to provide improved inertness [4]). All these stationary phases had been prepared with bis(trifluoromethylsulfonfyl)imide as anion, and only SLB-IL61 contains an equal number of bis(trifluoromethylsulfonfyl)imide and trifluoromethylsulfonate anions. Meanwhile, quaternary phosphonium (SLB-IL76, SLB-IL61 and SLB-IL59) and dialkylimidazolium (SLB-IL111, SLB-IL100 and SLB-IL82) structures have been used as cations. Despite this rather limited diversity of structures, these phases have been recognised to provide a completely different selectivity compared to other commercial stationary phases [18], which encouraged their evaluation for a number of application studies [16], including the mono- [4] and bi-dimensional [19–21] separation of individual components of complex standard mixtures of organohalogenated microcontaminants. Comparison of the results obtained with these commercial IL-based phases with those found with other widely accepted stationary phases for monodimensional GC analysis of PCBs (DB-5MS, i.e., 5% phenyl methyl polysiloxane column) was only performed by de Boer et al. [4]. These authors also confirmed a different elution pattern for the 31 investigated PCBs on the IL-based phases compared to the non-polar one [18]. Apart from this study involving monodimensional GC, only a couple of systematic studies on the separation of the 209 PCB congeners by means of comprehensive two-dimensional

gas chromatography (GC×GC) combined with either flame ionization detector (FID) [19] or time-of-flight mass spectrometry (ToF MS) [20] using commercial IL-based columns as second dimension have been reported in the literature.

The goal of this study was to evaluate the feasibility of six commercial IL-based GC stationary phases (SLB-IL series) for the unambiguous determination of priority and toxic PCBs using monodimensional GC combined with either electron capture micro-detector (micro-ECD) or quadrupole-MS (q-MS) as detector. With this aim, a test PCB mixture containing the targeted congeners, their most common interfering isomers on DB-5-type and HT-8 columns and a large majority of the PCB congeners usually detected in real environmental samples (up to 69 congeners) was prepared and analysed under essentially similar conditions in the investigated IL-base stationary phases. Results were compared with those obtained when analysing the same mixture on a widely used polar commercial stationary phase, poly(ethylene glycol), and a low bleed high temperature phase suited for the analysis PCBs, HT-8.

## 2. Materials and methods

### 2.1. Chemicals and samples

The 69 PCBs considered in this study (PCB # 18, 28, 31, 33, 45, 47, 52, 55, 66, 74, 77, 80, 81, 84, 90, 91, 95, 99, 101, 105, 110, 114, 118, 119, 122, 123, 124, 126, 128, 129, 131, 132, 135, 136, 138, 139, 141, 144, 149, 151, 153, 155, 156, 157, 158, 164, 167, 169, 170, 171, 173, 174, 175, 176, 177, 178, 180, 183, 187, 189, 190, 194, 196, 197, 199, 200, 201, 202 and 206) included the 7 priority congeners, the 12 toxic isomers, their most significant coeluting congeners on DB-5-type and the HT-8 stationary phases [5,22], and other environmentally relevant congeners (i.e., those with a weight percent contribution above 1% in Aroclor 1260 according to [23] with the only exception of PCBs 146, 158, 179 and 185 because these congeners were not available at the time of performing this study). PCB standards were acquired from Dr. Ehrenstorfer (Augsburg, Germany) and Ultra Scientific Analytical Solutions (N. Kingstown, RI, USA) and covered all chlorination degrees from tri- to nonachloro-substituted congeners (see Table 2 for detailed structure description). The deca-CB 209 was removed from the test mixture because preliminary studies demonstrated that, in all instance, this congener eluted at much longer retention times than the rest of the targeted compounds, a result that agreed with previous observations. The working standard mixture was prepared to contain 1 µg mL<sup>-1</sup> of each analyte in isooctane (Pestipur quality, from Carlo Erba, Val-de-Reuil, France).

**Table 1**  
Stationary phases tested in the study.

Column	Stationary phase	T operating range (°C) <sup>a</sup>		Polarity <sup>b</sup>
		Lowest	Highest	
SLB-IL111	1,5-Di(2,3-dimethylimidazolium)pentane bis(trifluoromethylsulfonfyl)imide	50	270	4938
SLB-IL100	1,9-Di(3-vinylimidazolium)nonane bis(trifluoromethylsulfonfyl)imide	Subambient	230	4437
SLB-IL82	1,12-Di(2,3-dimethylimidazolium)dodecane bis(trifluoromethylsulfonfyl)imide	50	270	3638
SLB-IL76	Tri(tripropylphosphoniumhexanamido)triethylamine bis(trifluoromethylsulfonfyl)imide	Subambient	270	3379
SLB-IL61	1,12-Di(tripropylphosphonium)dodecane bis(trifluoromethylsulfonfyl)imide	40	290	2710
SLB-IL59	trifluoromethylsulfonate			
SupelcoWax-10	1,12-Di(tripropylphosphonium)dodecane bis(trifluoromethylsulfonfyl)imide	Subambient	300	2624
HT-8	Poly(ethylene glycol)	35	280	2324
	8% Phenyl (equiv.) polycarborane-siloxane	Subambient	370	252 (equiv.)

<sup>a</sup> Isothermal column temperature limits as indicated by the column manufacturer.

<sup>b</sup> Sum of the first 5 McReynolds constants [17].

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