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Short communication

Assessment of ionic liquid stationary phases for the determination of polychlorinated biphenyls, organochlorine pesticides and polybrominated diphenyl ethers



Jacob de Boer, Daan Blok, Ana Ballesteros-Gómez*

VU University, Institute for Environmental Studies, De Boelelaan 1087, 1081 HV Amsterdam, The Netherlands

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ABSTRACT

Five ionic liquid stationary phases were tested for the gas chromatographic (GC) analysis of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs). In comparison with a non-polar DB5MS stationary phase, which is normally used in single-column GC for these compounds, all phases tested provided a different elution pattern. Mono-ortho substituted PCBs showed longer retention times, whereas di-ortho PCB congeners eluted earlier. These different patterns provide a potential for use of these columns for single-column PCB analysis, but in particular for use in comprehensive two-dimensional GC (GC \times GC). The SLB-IL111 phase showed the most striking differences in elution of PCBs compared to DB5MS. The analysis of OCPs was hindered by adsorption and on-column degradation with most of the phases tested. Additional experiments with polybrominated diphenylethers (PBDEs) also revealed serious degradation of most of the congeners. Only the SLB-IL60 column showed a better performance for OCPs, in combination with a relatively low bleeding.

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1. Introduction

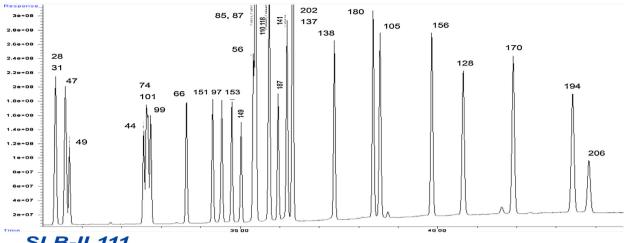
Polychlorinated biphenyls have been analyzed in many different matrices since the 1970s. The introduction of the capillary column enabled a congener-specific analysis. However, it was never possible to separate all 209 PCB congeners in one single-column GC run. Therefore, experiments were carried out with heart-cut multidimensional GC [1]. This technique was useful to separate specific pairs of PCB congeners that could not be eluted in a single-column run. The introduction of GC × GC finally offered possibilities to separate most of the 209 congeners [2]. Korytar et al. [3] showed that by using a combination of a HP-1 (100% methyl polysiloxane) and a HT-5 (5% phenyl-methyl polysiloxane or carborane) column structured chromatograms could be obtained in which the non-ortho substituted PCBs were clearly separated from the remaining PCBs. This was important because the non- and mono-ortho substituted PCBs show a dioxin-like toxicity. They are normally present at 100- or 1000-fold lower levels than the other congeners, so their separation from the bulk of the PCBs is important. In spite of this achievement, it is desirable to use more of the chromatographic plane available in $GC \times GC$, not only to further improve the PCB separation but also to enable a simultaneous determination of PCBs, organochlorine pesticides (OCPs) and a number of other contaminants classes such as polybrominated diphenylethers (PBDEs), toxaphene and chlorinated paraffins, all of which were discovered in the environment and other matrices after the PCBs. During the 1990s a few liquid crystalline columns were available. In particular the Smectic column [4] provided a very interesting PCB elution pattern. Its drawback was a considerable bleeding, which apparently could not be reduced by GC column manufacturers. Korytar et al. [3] obtained useful $GC \times GC$ chromatograms of PCBs and dioxins using 50% liquid crystalline methylpolysiloxane (LC-50) columns in the second phase, where its bleeding had minimal impact due to the short lengths (0.35-0.9 m).

Anderson and Armstrong [5] developed high-stability stationary phases based on room temperature ionic liquids based on imidazolium cations with trifluoromethanesulfonate anions. These new ionic liquids provide symmetrical peak shapes, and because of their broad range of solvation-type interactions, exhibit dualnature selectivity behavior. These phases are very interesting because they also show a high stability at relatively high temperatures, up to 230–300 °C. The ionic liquids are salts with melting points below 100 °C, which makes them suitable for application in GC. Molecular engineering offers almost endless

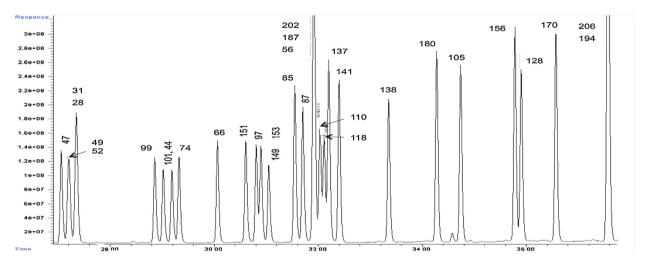
^{*} Corresponding author. Tel.: +31 205983193; fax: +31 205989553.

E-mail address: a.m.ballesterosgomez@gmail.com (A. Ballesteros-Gómez).

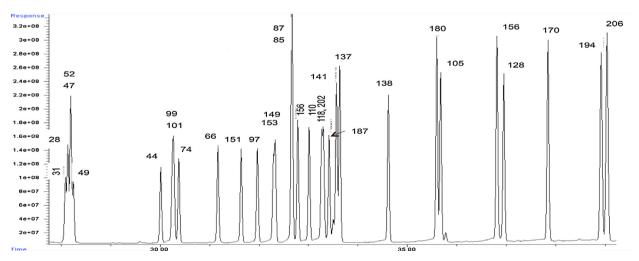
SLB-IL76



SLB-IL111



SLB-IL100



 $\textbf{Fig. 1.} \ \ \mathsf{GC} \ \mathsf{chromatograms} \ \mathsf{of} \ \mathsf{the} \ \mathsf{PCBs} \ \mathsf{mixture} \ \mathsf{in} \ \mathsf{SLB-IL100} \ \mathsf{and} \ \mathsf{SLB-IL11} \ \mathsf{columns}.$

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