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COMPARISON OF THE SELECTIVITY OF IONIC LIQUID STATIONARY PHASES FOR THE ANALYSIS OF PAHS

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Introduction

Polyaromatic hydrocarbons (PAHs) are compounds containing two or more aromatic rings and are known for their potential carcinogenic and mutagenic properties. They are typically formed during incomplete combustion of organic matter, as industrial byproducts, and in food processing. As such, they are compounds of interest in environmental and food and beverage analysis. Many of these compounds are isomeric, and must be resolved chromatographically to be accurately quantified.

Ionic liquids (IL) are a new class of GC stationary phases that provide unique polar and highly polar selectivity with higher thermal stability compared to traditional siloxane phases with similar selectivity. Traditionally, PAHs have been evaluated by US EPA method 610 using nonpolar stationary phases operated at high temperatures. In this study, we examine the effect of selectivity of the ionic liquid stationary phases based on their chemical composition. We also examine the effects of stationary phase film thickness and column dimensions.

Materials and methods

Traditionally, capillary columns coated with a 5% phenyl or higher percentage of phenyl containing stationary phase have been used for the analysis of PAHs. These columns do not adequately resolve all of the individual PAHs isomers. Key separations between isobaric PAHs such as phenanthrene and anthracene, benzo(a)anthracene and chrysene and the benzofluoranthenes (b,k,j) are typically not achieved on all of the phenyl based columns. In this study we focused on the resolution of the 16 PAHs listed in US EPA Method 610 plus the addition of benzo (j) fluoranthene.. The list is as follows:

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1. Naphthalene
2. Acenaphthene
3. Acenaphthalene
4. Fluorene
5. Phenanthrene
6. Anthracene
7. Fluoranthene
8. Pyrene
9. Benzo(a)anthracene
10. Chrysene
11. Benzo(b)fluoranthene
12. Benzo(k)fluoranthene
13. Benzo(a)pyrene
14. Dibenzo(a,h)anthracene
15. Indenol(1,2,3-cd)pyrene
16. Benzo(ghi)pyrene

We prepared a number of capillary columns coated with a variety of ionic liquids to evaluate the effects of phase selectivity, stationary phase film thickness, carrier gas, and finally optimized the column for the analysis of PAHs.

A number of germinal dicationic phosphonium and imidazolium based ionic liquid phases were evaluated. These included SLB-IL111, SLB-IL82, SLB-IL76, SLB-IL59 along with a few prototype phases. The film thicknesses studied ranged from 0.05um to 0.2um. Helium and hydrogen were the two carrier gases evaluated. Optimization of the column dimensions included preparing a shorter column with a narrower column internal diameter and optimizing the stationary phase film thickness to the same phase ratio of the larger bore column.

Typical analysis conditions were as follows:

column: 30 m x 0.25 mm I.D., 0.20 μ m df (various ionic liquid phases)
oven: 150 °C (0), 20 °C/min to 300 °C, 300 °C (hold)
det.: MSD, full scan, 45-500 m/z, 300 °C interface
carrier gas: He or H₂, 1 mL/min, constant flow
injection: 250 °C, 1 μ L splitless (1 min)
liner: 4 mm I.D. FocusLiner™ with taper

sample: EPA 610 PAH mix +Benzo(j)fluoranthene, diluted to 100 ppm in methylene chloride

Results and discussion:

Stationary Phase Selectivity Comparisons

The ionic liquid capillary columns were coated with either an imidazolium or phosphonium dicationic stationary phase. For the imidazolium based phases, the SLB-IL111 column which is more polar than SLB-IL82 had less retention of PAHs. The polarity of the imidazolium cations results in long retention times and a loss of resolution between Benzo(a)anthracene and Chrysene.

For the phosphonium based phases, which are less polar than the imidazolium phases, we determined the SLB-IL76 to be more polar than SLB-IL59 and resulted in having increased retention of PAHs possibly due to bulky side groups of this tricationic phase. The SLB-IL59 phase provided the best resolution of all the ionic liquid phases tested for the resolution of all 17 PAHs evaluated. The 30m x 0.25mm ID x 0.20 μ m df column did provide good resolution of the PAHs but the analysis time was too long.

Film Thickness Comparisons

In order to study the effects of film thickness, 30m x 0.25mm ID SLB-IL59 columns were prepared with film thicknesses of 0.20, 0.10 and 0.05 μ m. The 17 component PAHs mix was then evaluated using the previously listed conditions. The analyses showed that as expected the thinner films provide shorter retention times for PAHs. The results for the 0.2 μ m film thickness column were retention times for benzo (ghi) pyrene greater than 60 minutes. Retention times were less than 20 minutes with the 0.05 μ m film thickness but there was less resolution of benzo(a)anthracene and chrysene and the benzofluoranthenes on the 0.05 μ m film. The 0.05 μ m film thicknesses also provided lower sample capacity than the other two film thicknesses evaluated. This was demonstrated by significant peak fronting indicating overloaded peaks. The best compromise is the 0.1 μ m film thickness for shorter analysis times and resolution and capacity.

Carrier Gas Comparison

Helium and hydrogen were the two gases evaluated for PAH analysis studies. Hydrogen provides a faster separation of PAHs compared to Helium. Dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene, and benzo(ghi)pyrene) eluted in under 40 minutes with hydrogen versus nearly 50 minutes using helium on a 30m x 0.25mm ID x 0.2 μ m df column. There was no loss in the resolution of benzo(a)anthracene/chrysene and the benzofluoranthenes. The slight reduction in analysis time was expected as hydrogen has a higher optimum carrier gas linear velocity than helium. In a temperature programmed analysis, however, one of the major factors concerning analysis time is the temperature program rate rather than the carrier gas linear velocity.

Column Dimension Optimization

We decided the use of hydrogen as a carrier gas and the optimization of the column dimensions would provide a capillary column with a fast analysis time while maintaining the resolution of the PAH isomers. The column length was decreased to 20 meters to allow a faster elution of the PAHs. Since the shorter column length provided less efficiency in terms of total plates, we reduced the internal diameter of the columns to 0.18mm. This provided the necessary efficiency to keep the resolution of the PAHs seen with the longer length column. The film thickness of the stationary phase was also adjusted to provide the same phase ratio of the previous longer length and larger ID to keep the same overall retention times. The final version of the column was optimized as a 20m x 0.18mm ID x 0.07 μ m film.

Conclusions

The separation of PAHs was demonstrated on a variety of IL phases in order to evaluate phase structure relationships and their effect on analyte retention. The most non polar IL phase tested, SLB-IL59, demonstrated unique selectivity for PAHs providing the shortest retention of heavy PAH compounds and baseline resolution of isomeric sets. Optimization of film thickness and column dimension on SLB-IL59 show that faster analyses of PAHs without a compromise in performance are possible. Carrier gas comparison shows (as expected) a faster analysis time with H₂. Optimizing column dimensions with shorter length narrow bore (<0.25mm ID) provided a faster analysis with improved resolution. Future studies to further investigate phase structure/retention relationships are ongoing for the development of new ionic liquid phases.