STRATEGIES TO COMPARE BONDED STATIONARY PHASES OF HPLC FOR THE PREPARATIVE OR SEMI-PREPARATIVE SEPARATION OF UNSATURATED POLYCYCLIC HYDROCARBONS BY GROUPS IN PRODUCTS DERIVED FROM PETROLEUM

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1. Summary

This contribution summarizes methods to compare bonded stationary phases for the compound-class HPLC separations of unsaturated polycyclic hydrocarbons and polar compounds. These strategies are based on the physical chemistry behavior of the functional group of the bonded stationary phase, behavior of the unsaturated polycyclic hydrocarbons under isocratic and gradient elution, regression analysis, retention index, resolution between adjacent groups and behavior of the bonded stationary phase in real samples.

Keywords: Bonded stationary phases, group separation, polar compounds, comparison among bonded phases, preparative or semi-preparative HPLC

2. Extended Abstract

The unsaturated polycyclic hydrocarbons are abundant in products derived from petroleum and are of particular interest because of their role in various petrochemical processes, as well as their possible carcinogenic and mutagenic properties [1,2,3,4]. The knowledge of the concentration of these compounds allows us to minimize hydrogen consumptions in fossil fuel processing. Due to the complexity of products derived from petroleum, it is required to separate the unsaturated polycyclic hydrocarbons by classes or groups before making the characterization of the components by means of instrumental methods of analysis. New preparative or semi-preparative methods in HPLC are oriented to search for bonded stationary phases to replace the typical stationary phases of silica and alumina to make separations by groups [5,6]. The market of instrumental analysis offers a great diversity of bonded stationary phases and, therefore, it is required to develop a strategy or to implement a systematic method that allows us to compare and to select an appropriate bonded stationary phase for the preparative or semi-preparative separation of the unsaturated polycyclic hydrocarbons by groups in products derived from petroleum.
 Comparison based upon columns of the same size, same solvent, regression analysis for the dependence of the *log k'* and *k'* on the number of carbon atoms, numbers of electrons pi, number of aromatic rings and number of pi bonds under isocratic and gradient elution respectively, retention index, resolution between adjacent groups and behavior of the bonded stationary phase in real samples seems to be convenient strategies to compare and to select a bonded stationary phase for many purposes. We have used these strategies to compare columns with the same solvent and packing (hexane, 25 cm of length, 4.6 mm I.D and 10 µm particle size for isocratic elution and

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hexane + methylene chloride, 15 cm length, 4.6 mm I.D and 5 µm particle size for gradient elution). Because the column size and solvents are the same, the retention properties are related to the physical chemistry behavior of the functional group bonded to the stationary phase. These comparisons based upon the interaction between the functional group bonded to the stationary phase and phenols and nitrogen model compounds, have indicated that polar-polar interaction including hydrogen bonding and acid-base interaction are the predominant separation mechanism, although effect of alkyl substitution in the polar compound is not negligible. Basic nitrogen compounds are strongly retained on $-NO_2$ and $-CN$. Phenols are strongly retained on $-NH_2$ and $(-NH_2)_2$. There are an acceptable correlation between pK_a values for basic nitrogen compounds and phenols and their capacity factors obtained on the bonded stationary phase $–NH_2$.

We have defined the resolution between adjacent groups of unsaturated polycyclic hydrocarbons under isocratic and gradient elution by means of the following expressions. In the first expression ($Log\ Ir$) is the log retention index average for a group under isocratic elution and Ir is de average of the retention index for a group under gradient elution. σ is the variance and 2σ is the peak half width at the base for each group. To calculate the resolutions with these equations, it is required to obtain values of Ir for model compound of unsaturated polycyclic hydrocarbons. In order to obtain these values it is first necessary to define values of

$$R = \frac{(Log Ir)_2 - (Log Ir)_1}{2(\sigma_1 + \sigma_2)}$$

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retention index for selected model compounds and to obtain its capacity factors on the column to be investigated. Under isocratic elution $Ir = 10^A$ where A is the number of rings of the unsaturated polycyclic hydrocarbon. Under gradient elution $Ir = A$. The following unsaturated polycyclic hydrocarbons were selected to obtain the calibration curve under gradient elution. Benzene ($Ir = 1$), naphthalene ($Ir = 2$), phenanthrene ($Ir = 3$), pyrene ($Ir = 4$), perylene ($Ir = 5$) y dibenzo[e,h]pyrene ($Ir = 6$). For isocratic elution the same compoundas would have Ir values of 10, 100, 1 000, 10 000, 100 000 and 1 000 000. Under isocratic elution a plot of $log\ k'$ of these compounds Vs Log Ir was linear for most of the columns given in Tables 1 and 2. Under gradient elution a plot of k' Vs Ir was linear for $–NH_2$, $-NO_2$ y $–CN$. Values of Ir and $log\ Ir$ for many unsaturated polycyclic hydrocarbons were calculated from these least squares lines. The resolution was calculated from the average retention index or average log retention

Table 1. Regression parameters (isocratic)

Column	Log k' Vs Log Ir		
Name	r	m	b
NH$_2$	0.9898	0.265	-0.758
CN	0.9871	0.207	-0.724
R(OH)$_2$	0.9355	0.1823	-0.6568
ROR	0.7779	0.0627	0.2065
RCN	0.9835	0.381	-1.013
-(NH$_2$)$_2$	0.9775	0.254	-0.457

Table 2. Resolution in isocratic elution

N° of ring	-NH$_2$	Si	Al	C$_{18}$	(NH$_2$)$_2$
1 to 2	1,80	0,94	0,48	0,25	1,28
2 to 3	1,37	0,37	0,38	0,14	0,76
3 to 4	0,81	0,24	0,48	0,32	0,48
4 to 5	0,88	0,50	—	1,11	0,55

index and two times its variance for each ring number group. The bonded stationary phases RCN and $-NH_2$ gave, under isocratic elution, the largest selectivity to separate unsaturated polycyclic hydrocarbons by ring number, number of carbon atoms of the ring, pi electrons of the ring and pi bonds of the ring. The bonded phase $-NH_2$ gave the largest resolution under isocratic elution. Comparison among bonded stationary phases under gradient elution has indicated that the bonded phases $–NH_2$ and $–NO_2$ are the best to separate unsaturated polycyclic hydrocarbons of four and five rings and they are also appropriate to investigate molecular parameters. Comparisons made on real samples (oil shale, diesel, light and heavy petroleum distillate) have indicated that the bonded stationary phases $–NH_2$ and $-NO_2$ are appropriated to separate unsaturated polycyclic hydrocarbons according to the ring number and therefore both bonded

stationary phases look suitable for the preparative or semi-preparative separation of unsaturated polycyclic hydrocarbons by groups in unfinished oils, lubricating oil base stock and other products. The bonded stationary phase –NO$_2$ is not suitable for the separation of weakly polar compounds from unsaturated polycyclic hydrocarbons of 5 to 6 rings.

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