



Contents lists available at ScienceDirect

# Journal of Chromatography A

journal homepage: [www.elsevier.com/locate/chroma](http://www.elsevier.com/locate/chroma)



## Retention behavior of alkyl-substituted polycyclic aromatic sulfur heterocycles in reversed-phase liquid chromatography

Walter B. Wilson<sup>a,\*</sup>, Lane C. Sander<sup>a</sup>, Miren Lopez de Alda<sup>a</sup>, Milton L. Lee<sup>b</sup>, Stephen A. Wise<sup>a</sup>

<sup>a</sup> Chemical Sciences Division, Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States

<sup>b</sup> Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT 84602, United States

### ARTICLE INFO

#### Article history:

Received 3 June 2016

Received in revised form 21 July 2016

Accepted 24 July 2016

Available online xxx

#### Keywords:

Retention indices

Reversed-phase liquid chromatography

stationary phases

Molecular descriptors

Retention behavior

Polycyclic aromatic compounds

Alkyl-substituted polycyclic aromatic sulfur heterocycles

### ABSTRACT

Retention indices for 79 alkyl-substituted polycyclic aromatic sulfur heterocycles (PASHs) were determined by using reversed-phase liquid chromatography (LC) on a monomeric and polymeric octadecylsilane (C<sub>18</sub>) stationary phase. Molecular shape parameters [length, breadth, thickness (*T*), and length-to-breadth ratio (*L/B*)] were calculated for all the compounds studied. Based on separations of isomeric methylated polycyclic aromatic hydrocarbons on polymeric C<sub>18</sub> phases, alkyl-substituted PASHs are expected to elute based on increasing *L/B* ratios. However, the correlation coefficients had a wide range of values from  $r=0.43$  to  $r=0.93$ . Several structural features besides *L/B* ratios were identified to play an important role in the separation mechanism of PASHs on polymeric C<sub>18</sub> phases. First, the location of the sulfur atom in a *bay*-like-region results in alkylated-PASHs being more retentive than non-*bay*-like-region alkylated-PASHs, and they elute later than expected based on *L/B* value. Second, the placement of the alkyl group in the *k* region of the structure resulted in a later elution than predicted by *L/B*. Third, highly nonplanar methyl-PASHs (i.e., 1-Me and 11-MeBbN12T) elute prior to the parent PASH (BbN12T).

Published by Elsevier B.V.

### 1. Introduction

Reversed-phase liquid chromatography (LC) on octadecyl (C<sub>18</sub>) stationary phases has been shown to provide excellent separations of polycyclic aromatic hydrocarbons (PAHs) [1–6] and methyl-PAHs (MePAHs) [1,2,7]. Previous studies have demonstrated that not all C<sub>18</sub> stationary phases provide the same selectivity for MePAHs [1,7]. Wise et al. showed the excellent selectivity of polymeric C<sub>18</sub> phases for separation of methyl-substituted phenanthrene (MePhe), pyrene (MePyr), fluoranthene (MeFlu), chrysene (MeChry), benzo[*a*]anthracene (MeBaA), benzo[*c*]phenanthrene (MeBcPhe) and benzo[*a*]pyrene (MeBaP) [1]. The type of the C<sub>18</sub> phase, i.e., monomeric or polymeric, played an important role in the separations of the MePAHs. Typically, monomeric C<sub>18</sub> phases are prepared by reaction of monofunctional silanes [7,8] and polymeric C<sub>18</sub> phases are prepared using trifunctional silanes in the presence of water which results in cross-linking to form silane polymers on the silica surface [8]. In general, the MePAH isomers were

better resolved on the polymeric C<sub>18</sub> phases than the monomeric C<sub>18</sub> phases, and the elution order of MePAH isomers generally followed the increase of a molecular shape parameter denoted as length-to-breadth (*L/B*) ratio.

In a later study, Wise et al. investigated the LC separations of MeChry, methylperylene (MePer), and methylpicene (MePic) on 16 commercially available C<sub>18</sub> columns [7]. Each of the columns was characterized using a standard reference material developed at the National Institute of Standard and Technology for testing the selectivity of LC columns (SRM 869b). Selectivity values for tetrabenzonaphthalene (TBN) and BaP ( $\alpha_{TBN/BaP}$ ) were used to classify the type of C<sub>18</sub> phases for PAH selectivity. Generally,  $\alpha_{TBN/BaP} \leq 1$  represent polymeric C<sub>18</sub> phases;  $\alpha_{TBN/BaP}$  in the range of 1.0–1.7 represent intermediate polymeric C<sub>18</sub> phases; and values for  $\alpha_{TBN/BaP} \geq 1.7$  represent monomeric C<sub>18</sub> phases. For the separation of MePAHs, Wise et al. [7] observed that isomers with some nonplanarity and small *L/B* values would elute prior to the parent PAH as the polymeric nature increases ( $\alpha_{TBN/BaP}$  decreases). The nonplanarity of these PAHs, which has since been characterized using a molecular shape parameter denoted as the thickness (*T*), is due to the presence of the methyl group in the *bay*-region of the PAH structure. Several publications have summarized the

\* Corresponding author.

E-mail address: [walter.wilson@nist.gov](mailto:walter.wilson@nist.gov) (W.B. Wilson).

correlation between LC retention of PAHs and MePAHs on polymeric C<sub>18</sub> phases with molecular shape parameters ( $L/B$  and  $T$ ) [2,4]. While the focus of this study was to evaluate only molecular shape parameters, quantitative structure-retention relationship (QSRR) technique has been shown to be useful for predicting the GC retention behavior of saturated S-heterocyclic compounds on standard nonpolar polydimethylsiloxane siloxane stationary phases [9].

In the current study, we investigate the LC separation of alkyl-substituted polycyclic aromatic sulfur heterocycles (PASHs), (see Fig. 1) on both monomeric and polymeric C<sub>18</sub> stationary phases. In past decades, PASHs have received far less attention than PAHs despite their carcinogenic and mutagenic potential [9,10] and their presence in air particulate matter [11,12], sediments [13–15], coal liquids [16], diesel [15], heavy oil [17–21], crude oil [15,18,22–31], shale oil [16,22,32,33], coal tar [22,23,29,34–36], mussels [13,14], and fish [13,14]. In a previous study [37], we reported LC retention indices for 70 PASHs on both monomeric and polymeric C<sub>18</sub> phases. In this study, LC retention indices were determined for 79 alkyl-substituted PASHs, and the correlation of retention on the polymeric C<sub>18</sub> phase and PASH geometry ( $L/B$  and  $T$ ) was investigated. Only two previous publications have reported the reversed-phase LC retention behavior of isomeric PASHs [2,38], and there are no previous reports of LC retention index data for alkyl-substituted PASH.

## 2. Material and methods

### 2.1. Chemicals

The following PAHs and PASHs were purchased from commercial sources with high purity (>95%): dibenzothiophene (DBT) (Acros Organics, Springfield, NJ); 1-, 2-, and 4-MeDBT, 2,8-DiMeDBT, 1,4,7-, 3,4,7-, 2,3,7-, 2,3,8-, 2,4,7-, 2,4,8-, 2,4,6-, and 1,3,7-TriMeDBT (Astec, Munster, Germany); 2-EtDBT, 3-EtDBT, and 4-EtDBT (Chiron AS, Trondheim, Norway); and BbN12T, BbN21T, BbN23T, benzo[*a*]anthracene (BaA), benzo[*b*]chrysene (BcC), and dibenzo[*a,h*]pyrene (DBaHP) (BCR, Brussels, Belgium); naphthalene (Nap) and phenanthrene (Phe) (Fluka, Buchs, Switzerland). The remaining alkyl-substituted PASHs were synthesized in the laboratories of M.L.L. at Brigham Young University (Provo, UT). Standard Reference Material (SRM) 869b, "Column Selectivity Test Mixture for Liquid Chromatography" was obtained from the Office of Standard Reference Materials at the National Institute of Standards and Technology (Gaithersburg, MD, USA). HPLC grade acetonitrile was purchased from Fisher Scientific (Pittsburgh, PA, USA).

### 2.2. Molecular descriptor calculations

The molecular modeling programs and procedure for calculating the molecular shape parameters have been described in detail previously [2,39]. Briefly, ChemDraw 3D software (PerkinElmer, Waltham, MA, USA) was used to draw the molecular structures of PASHs and converted into the mol file formats. Commercial molecular modeling programs (PC-Model and MMX, Serena Software, Bloomington, IN, USA) and algorithms were used for calculations of the molecular descriptors [length ( $L$ ), breadth ( $B$ ), thickness ( $T$ ) and length-to-breadth ratio ( $L/B$ )].

### 2.3. Liquid chromatographic retention data

LC retention index values ( $\log I$ ) were calculated according to Eq. (1) with the following index markers: (2) Nap, (3) Phe, (4) BaA, (5) BbC, and (6) DBaHP [3].

$$\log I = \frac{\log R_x - \log R_n}{\log R_{n+1} - \log R_n} \quad (1)$$

where  $R$  is the corrected retention volume,  $x$  represents the solute, and  $n$  and  $n + 1$  represent the lower and higher eluting PAH standards. Previous studies have investigated the retention behavior of PAHs on C<sub>18</sub> stationary phase using  $\log I$  values as their basis for retention indices [2,38]. The  $\log I$  values are based on three measurements obtained from reference standards. The precision (standard deviation) of the  $\log I$  values was equal to or less than  $\pm 0.02 \log I$  units. Baseline resolution of two components is achieved with a difference of  $\sim 0.06 \log I$  units on both the monomeric and polymeric C<sub>18</sub> phase.

### 2.4. Instrumentation and chromatographic conditions

LC retention measurements were recorded using the same instrumentation described in a companion publication on LC separation of parent PASHs [37]. Separations were performed on monomeric (Agilent 5) and polymeric (Zorbax Eclipse PAH) C<sub>18</sub> columns purchased from Agilent (Avondale, PA) with the following characteristics: 25 cm length, 4.6 mm diameter, and 5  $\mu$ m average particle diameters. Table 1 lists the optimal separation and detection conditions for each isomer set. PASHs were detected using selected wavelengths that correspond to a compromise among the maximum absorbance wavelengths obtained from UV-vis spectroscopic analysis of pure standards. Except for MeTeP112T isomers, LC retention index data were obtained under isocratic conditions with 85/15 (v/v) acetonitrile-water as the mobile phase with a flow-rate of 1.0 mL/min. LC retention index data were obtained for the MeTeP112T using the conditions listed in Table 1.

## 3. Results and discussion

Previous studies have shown that the retention behavior of methyl-substituted PAH isomers to be significantly different on monomeric and polymeric C<sub>18</sub> phases [1,2,7]. In the present study, two commercially available C<sub>18</sub> columns were selected and used to investigate the selectivity of 10 isomeric sets of alkyl-substituted PASHs. Previous studies from Sander and Wise [7,40] have demonstrated the use of  $\alpha_{TBN/BaP}$  values to classify the C<sub>18</sub> phases for PAH separations. The  $\alpha_{TBN/BaP}$  values for the monomeric and polymeric C<sub>18</sub> phases used in this study are 1.97 and 0.49, respectively.

The molecular structures of the seven parent PASHs investigated in this study are shown in Fig. 1 with the numbering of the positions available for substitution. The molecular shape parameters ( $L$ ,  $B$ ,  $T$ , and  $L/B$  ratio) and retention indices (monomeric and polymeric C<sub>18</sub>) for the alkyl-substituted PASHs are summarized in Tables 2 and 3. Table 4 summarizes the regression calculations for the correlation of LC retention on the polymeric C<sub>18</sub> phase with  $L/B$  ratio. The polymeric C<sub>18</sub> phase was the only phase to demonstrate a good correlation and will be discussed in detail. Previous studies have used correlation coefficients ( $r$ ) as a parameter for measuring the linear correlations for the retention of MePAHs on polymeric C<sub>18</sub> phases and  $L/B$  [2,7]. The correlation coefficient demonstrates a more significant linear trend when close to 1. Instances where the correlation coefficient is not close to 1, the calculation of a  $t$ -test value is determine using Eq. (2) for accessing if the correlation coefficient represents a significant linear trend [41]:

$$t_{exp} = \frac{|r|\sqrt{n-2}}{\sqrt{1-r^2}} \quad (2)$$

where  $n$  is the number of data points. The calculated  $t_{exp}$  value is compared to the  $t_{crit}$  value at the desired significance level based on the degrees of freedom ( $n - 2$ ). A significant correlation does exist for the correlation coefficient if the  $t_{exp}$  is greater than the  $t_{crit}$ . These concepts will be applied in the following sections for discussing the correlations between the MePASHs retention on the

Download English Version:

<https://daneshyari.com/en/article/7609905>

Download Persian Version:

<https://daneshyari.com/article/7609905>

[Daneshyari.com](https://daneshyari.com)