



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



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## ABSTRACT

Retention indices for 70 polycyclic aromatic sulfur heterocycles (PASHs) were determined using reversed-phase liquid chromatography (LC) on a monomeric and a polymeric 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. Correlations between the retention on the polymeric C<sub>18</sub> phase and PASH geometry (*L/B* and *T*) were investigated for six specific PASH isomer groups with molecular mass (MM) 184 Da, 234 Da, 258 Da, 284 Da, 334 Da, and 384 Da. Similar to previous studies for polycyclic aromatic hydrocarbons (PAHs), PASH elution order on the polymeric C<sub>18</sub> phase was generally found to follow increasing *L/B* values. Correlation coefficients for retention vs *L/B* ranged from  $r=0.45$  (MM 184 Da) to  $r=0.89$  (MM 284 Da). In the case of smaller PASHs (MM  $\leq 258$  Da), the location of the sulfur atom in the *bay*-region of the structure resulted in later than expected elution of these isomers based on *L/B*. In the case of the larger PASHs (MM  $\geq 284$  Da), nonplanarity had a significant influence on earlier than predicted elution based on *L/B* values.

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## 1. Introduction

Polycyclic aromatic compounds (PACs) comprise a complex class of condensed multi-ring benzenoid compounds originating from a wide variety of natural and anthropogenic sources. The parent homocyclic species, which contain only carbon and hydrogen, are the familiar polycyclic aromatic hydrocarbons (PAHs). In recent decades, PAHs are one of the most studied groups of environmental contaminants because of their high carcinogenic and mutagenic potential [1–4]. However, their sulfur analogues, polycyclic aromatic sulfur heterocycles (PASHs), have received far less attention although their presence has been confirmed in air particulate matter [5,6], sediments [7–9], coal liquids [10], diesel [9], heavy oil [11], crude oil [9,11–17], shale oil [10,12,15,18], coal tar [12–15,19–21], mussels [7,8], and fish [7,8]. In addition, their carcinogenic and mutagenic potential have been reported [22,23]. PASHs exist in an even greater variety of structures compared to PAHs due to the presence of the sulfur atom. Therefore, the number of isomers and alkylated isomers can be extremely large, which increases the

difficulty to quantify individual PASH isomers in complex natural mixtures.

Reversed-phase liquid chromatography (LC) on octadecylsilane (C<sub>18</sub>) stationary phases has been shown to provide excellent separations of isomeric PAHs [24–31]. However, not all C<sub>18</sub> stationary phases provide the same selectivity for PAHs. In past decades, several studies have compared different commercial C<sub>18</sub> columns for the separation of PAHs with particular emphasis on the separation of isomeric PAHs [28,29]. These studies demonstrated that all stationary phases were C<sub>18</sub> but some provided significantly enhanced selectivity for the separation of isomeric PAHs. One of the studies focused on the importance of the synthesis of the bonded C<sub>18</sub> phase. Typically, monomeric C<sub>18</sub> phases are prepared by reaction of monofunctional silanes [24–26] 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 [24,25].

Polymeric C<sub>18</sub> phases have been demonstrated to separate PAH isomers [24,26,27,33] based on shape of the PAH solute. The relationship between the PAH shape and LC retention on polymeric C<sub>18</sub> phases was first reported by Wise et al. [24]. The shape of the PAH was defined as the length-to-breadth ratio (*L/B*) of the box drawn around the molecule that produces the maximum *L/B* value. Retention of PAH isomers was observed to increase with increas-

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ing  $L/B$  values. In later studies, the similarity of LC retention on polymeric  $C_{18}$  phases and gas chromatography (GC) retention on liquid crystalline stationary phases was demonstrated for isomeric PAHs [31–34]. In general, the nonplanar PAH isomers, as indicated by a thickness parameter ( $T$ ), elute earlier than expected based on  $L/B$  values. Farkas et al. [35] have demonstrated the usefulness of the quantitative structure-retention relationship technique (QSRR) to predict the retention indices for saturated 5-heterocyclic compounds on standard nonpolar polydimethylsiloxane siloxane stationary phases.

In the current study, the LC separation of isomeric PASHs on both a monomeric and a polymeric  $C_{18}$  stationary phase was investigated. There are few publications that have reported the reversed-phase LC separation of isomeric PASHs [36,37]. In the current study, LC retention indices were determined for 70 PASHs on both monomeric and polymeric  $C_{18}$  phases. Correlation of PASH geometry ( $L/B$  and  $T$ ) and retention on both the monomeric and polymeric  $C_{18}$  phases was investigated. The polymeric  $C_{18}$  phase was the only phase to demonstrate good correlation and will be discussed in detail. This study provides the most comprehensive investigation of reversed-phase LC retention behavior of PASH to date. A similar study for alky-substituted PASHs is published elsewhere [38].

## 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); benzo[*b*]naphtho[1,2-*b*]thiophene (BbN12T), benzo[*b*]naphtho[2,1-*b*]thiophene (BbN21T), benzo[*b*]naphtho[2,3-*b*]thiophene (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 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) were 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 descriptors calculations

Molecular shape parameter calculations have been described in detail previously [36,39]. Briefly, ChemDraw 3D software (PerkinElmer, Waltham, MA, USA) was used to draw the molecular structures of PASHs and convert them 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. UV-vis absorption spectrometry

LC detection of PASHs was achieved using selected wavelengths that corresponds to a compromise among the maximum absorbance wavelengths obtained with a commercial spectrophotometer (model Cary 100, Agilent) from measurements of pure standards. The light source was a 75 W pulsed xenon lamp with a 3000 nm  $\text{min}^{-1}$  maximum scan rate. The Czerny-Turner monochromator had an accuracy ( $\pm 0.2$  nm to 0.4 nm with <0.189 nm resolution) and reproducibility (<0.02 nm,  $N = 10$ ). The monochromator 1200 lines  $\text{mm}^{-1}$  grating (30 × 35 mm) were blazed at an

angle of 8.6° at 240 nm. Detection was made with a photomultiplier tube (P928) with wavelength range from 190 to 900 nm. Measurements were made with a standard 700  $\mu\text{L}$  quartz cuvette with 1 cm path length.

### 2.4. 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 [28].

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

$R$  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  $C_{18}$  stationary phase using  $\log I$  values as their basis for retention indices [34,35]. 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 could be achieved with a difference of  $\sim 0.06 \log I$  units on both the monomeric and polymeric  $C_{18}$  phase.

### 2.5. Instrumentation and chromatographic conditions

LC-UV analysis was performed using a liquid chromatograph (1200 series, Agilent, Avondale, PA) coupled to a UV-vis detector (UV2000, Thermo Scientific, Waltham, MS). The LC system was equipped with a gradient pump (G1311A), a degasser (G1322A) and an auto sampler (G1329A). The instrument was computer controlled using commercial software (Chromeleon, Thermo Scientific). Separations were carried out on a monomeric (Agilent 5) and polymeric (Zorbax Eclipse PAH)  $C_{18}$  columns purchased from Agilent (Avondale, PA) with the following characteristics: 25 cm length, 4.6 mm diameter, and 5  $\mu\text{m}$  average particle diameters.

Both LC columns were characterized using the Column Selectivity Test Mixture for Liquid Chromatography (SRM 869b) using selectivity ratios ( $\alpha_{\text{TBN/BaP}}$ ) of tetrabenzonaphthalene (TBN) and benzo[*a*]pyrene (BaP). The  $\alpha_{\text{TBN/BaP}}$  values were determined with a mobile phase of 85/15 (v/v) acetonitrile (ACN) – water ( $\text{H}_2\text{O}$ ) at a flow-rate of 1.5  $\text{mL min}^{-1}$ . The optimal separation and detection conditions for each isomer set are listed in Table 1. The LC retention index data ( $\log I$ ) were determined using these conditions.

## 3. Results and discussion

In previous studies, the LC retention behavior of isomeric PAHs has been shown to be significantly different on various  $C_{18}$  phases that can be classified as monomeric or polymeric [26–28]. Sander and Wise [28] previously proposed a scheme that uses an LC column test mixture (SRM 869) for determining  $\alpha_{\text{TBN/BaP}}$  values to classify the type of  $C_{18}$  phase. In general, the shape selective behavior of the stationary phase for separation of complex isomeric PAH mixtures increases with decreasing  $\alpha_{\text{TBN/BaP}}$ . Values for  $\alpha_{\text{TBN/BaP}} \geq 1.7$  represent monomeric  $C_{18}$  phases,  $\alpha_{\text{TBN/BaP}}$  in the range of 1.0–1.7 represent intermediate polymeric  $C_{18}$  phases, and values for  $\alpha_{\text{TBN/BaP}} \leq 1$  represent polymeric  $C_{18}$  phases [29].

In the present study, two commercially prepared  $C_{18}$  columns were selected and used to investigate the LC selectivity for separating isomeric PASHs. The polymeric  $C_{18}$  phase had a  $\alpha_{\text{TBN/BaP}} = 0.49$  and the monomeric  $C_{18}$  phase had a  $\alpha_{\text{TBN/BaP}}$  value of 2.05. The LC retention behavior of isomeric PASHs on the two  $C_{18}$  phases was investigated and the optimized conditions for the separations are listed in Table 1. The correlation between retention on the polymeric  $C_{18}$  phase and the molecular shape parameters ( $L$ ,  $B$ ,  $T$ , and

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