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# Study of polar and nonpolar substituted benzenes and aromatic isomers on carbon-coated zirconia and alkyl bonded phases

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## Abstract

Retention factors of polar and non-polar mono- and di-substituted benzene derivatives were measured on carbon coated zirconia (C/ZrO<sub>2</sub>) and an alkyl modified silica using water–acetonitrile mobile phases. Published data on porous graphitic carbon phases (PGC) were used to facilitate comparisons between the two types of carbon media. This work showed that retention on both C/ZrO<sub>2</sub> and PGC is much more sensitive to the solute polarizability, dipolarity, and shape than on aliphatic phases. For simple disubstituted benzenes there was no general clear cut advantage in terms of chromatographic selectivity to using a carbon-based phase over a bonded phase silica; however, the selectivities towards such isomers are quite different on the two types of media. In contradistinction to their effect on alkyl bonded phase retention, addition of a dipolar substituent and weak hydrogen bond acceptor to a benzene ring almost always *increases* the solute's retention on C/ZrO<sub>2</sub> and PGC. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Stationary phases, LC; Carbon-coated zirconia; Porous graphitic carbon; Benzene

## 1. Introduction

The retention behavior of carbon-based liquid chromatographic stationary phases has been of interest to the chromatographic community for nearly two decades [1–9]. Carbon phases do not suffer from many of the disadvantages of silica-based sorbents; they do not have the severe pH limitations nor do they show secondary interactions with silanol groups ascribed to most silica-based phases. Furthermore, carbon phases have radically *different* selectivities

compared to traditional bonded phase RPLC media. In fact, they have properties associated with both reversed-phase and normal-phase sorbents [1,3,4,7,10,11]. Currently, the most common commercial carbon stationary phase is a porous graphitic carbon (PGC).

Given the commercial availability of PGC, it is not surprising that the majority of retention studies have focused on this carbon-based stationary phase. These studies clearly reveal that graphitic surfaces show a greater increase in retention upon addition of methylene groups than do any bonded phase materials [4,10,12]. Further, these studies show that the flat rigid surface structure provides good stereoselective discrimination, especially in the case of geometric

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isomers and some diastereomers. Others have explored the intermolecular forces involved in the retention process and concluded that electronic and dipolar interactions contribute significantly to retention on PGC [2,8,9,13–16]. Knox's review of the retention characteristics of PGC is excellent [7].

Recently, an alternative carbon type stationary was introduced. This carbon media is made by passing organic vapors over very hot porous zirconia [17–21]. Prior work on carbon-coated zirconia phases (C/ZrO<sub>2</sub>) indicates many chromatographic similarities to PGC even though the manufacturing processes for the two phases are radically different. Most significantly carbon-coated zirconia phases exhibit high isomer selectivity [17,21,22], enhanced retention of polar analytes compared to bonded phase silicas, and increased retention due to electronic and dipolar interactions [13,23]. Additionally, these phases are very thermally stable and offer interesting selectivity differences relative to conventional reversed phases that make them excellent choices for use in combination with conventional phases in the thermally tuned tandem column concept [24–27].

These interesting characteristics of the carbon stationary phase have led us to investigate its "isomeric" selectivity in more detail. By geometrical arguments alone, a solid surface is expected to show improved ability to separate positional isomers compared to a motile bonded ligand; this is illustrated in Fig. 1. Upon examining the structure of the solutes,

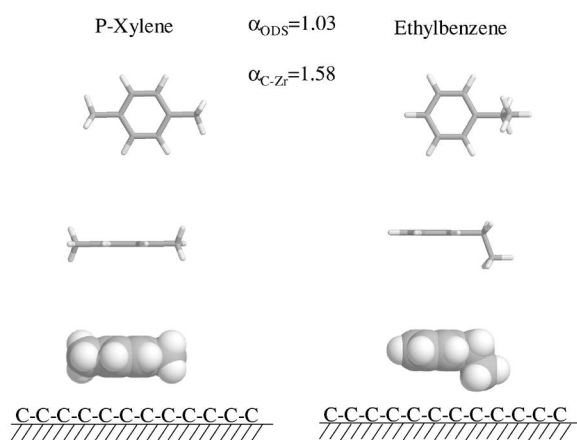


Fig. 1. Solute shape comparison between *p*-xylene and ethylbenzene related to expected chromatographic retention and selectivity on C/ZrO<sub>2</sub>.

*p*-xylene and ethylbenzene, one expects and observes substantial chromatographic selectivity differences on C/ZrO<sub>2</sub> compared to the same separation on alkyl bonded phases. Furthermore, the extensive data on PGC's ability to separate positional isomers [7,11,12,28], phenols [29–31], anilines [32–34], and ionizable benzene derivatives [35,36], suggests the need to compare such retention behavior for additional types of carbon stationary phases. The objective of this work is to better understand retention behavior of polar analytes on C/ZrO<sub>2</sub> compared to that on PGC and traditional bonded phases. This study examines the retention behavior of isomeric benzenes possessing nonionizable substituents in reversed-phase liquid chromatography (RPLC). The elution orders of different sets of isomers and the relative contributions of various functional groups to retention have been examined in order to compare retentive characteristics of different carbon phases and to examine contributions to retention on C/ZrO<sub>2</sub>.

## 2. Experimental

### 2.1. Reagents

The chemicals, reagent-grade or better quality, used in this study were obtained from the following suppliers: hexane, toluene, acetonitrile (ACN) and tetrahydrofuran (THF) were HPLC grade and obtained from Fisher Scientific (Fairlawn, NJ); 2-propanol and acetone were obtained from Mallinckrodt (Paris, KY); all solutes were obtained from Aldrich (Milwaukee, WI). Water for the HPLC mobile phase was purified by passing it through a Barnstead/Thermolyne (Dubuque, IA) Nanopure water purification system with an "Organic-Free" final cartridge followed by a 0.2- $\mu\text{m}$  particle filter.

### 2.2. Carbon support preparation

A single lot of porous zirconia particles was used in this work. The particle characteristics are given in Table 1. Chemical vapor deposition of heptane created a carbon stationary phase on porous zirconia particles (PICA-7) produced by the polymerization-induced colloid aggregation method [37]. The chemi-

Table 1  
Physical characteristics of stationary phases

Phase	$d_p^a$ ( $\mu\text{m}$ )	SA <sup>b</sup> ( $\text{m}^2/\text{g}$ )	$d_{\text{pore}}^c$ ( $\text{\AA}$ )	% C <sup>d</sup> (w/w)
C/ZrO <sub>2</sub>	2.5	32.5	194	1.7
SB-C <sub>18</sub> <sup>e</sup>	5	180	80	10

<sup>a</sup> Average particle diameter ( $\mu\text{m}$ ).

<sup>b</sup> Surface area ( $\text{m}^2/\text{g}$ ).

<sup>c</sup> Average pore diameter ( $\text{\AA}$ ).

<sup>d</sup> Weight percent carbon by elemental analysis.

<sup>e</sup> Reported by manufacturer.

cal vapor deposition (CVD) process used a tube furnace in which heptane vapors were passed over the porous ZrO<sub>2</sub> particles at an elevated temperature ( $\sim 700^\circ\text{C}$ ) and at reduced pressure ( $\sim 5$  to 10 Torr) for approximately 1.5 h [17,21]. The reduced pressure is maintained using a vacuum pump while the carbon source is slowly introduced. After completion of CVD the carbon-coated particles were rinsed with tetrahydrofuran, and Soxhlet extracted overnight with toluene to remove soluble pyrolysis products. The resulting material, denoted Hp-C/ZrO<sub>2</sub>, was packed into a column and used as a reversed-phase support. For purposes of comparison a commercially available conventional octadecyl silica chromatographic phase, Zorbax SB-C<sub>18</sub> (Rockland Technologies, Newport, DE, USA), was also examined.

### 2.3. Column packing

Column blanks were Precision Bore 316 stainless steel tubing (Alltech) 5 cm in length having a 0.25 inch O.D., 0.46 cm I.D. 316 stainless steel column end fittings were used with 2- $\mu\text{m}$  stainless steel frits (Alltech). The columns were packed using an upward stirred slurry technique. For a 50 $\times$ 4.6 mm column blank, approximately 2 g of particles were dispersed in 25 ml of 90:10 hexane/2-propanol via ultrasonication and this mixture was forced, by a Haskel pneumatic pump, into the column using pure 2-propanol at 5500–6000 p.s.i.

### 2.4. Chromatographic studies

All studies were conducted on a Hewlett-Packard (Palo Alto, CA) 1090 high-performance liquid chromatograph with a DR5 solvent delivery system and a filter photometric detector. Reported chromatographic

parameters were averages of at least triplicate determinations of each solute and detection was at 254 nm. Column dead time was measured with acetone. Uracil and sodium nitrate cannot be used as dead volume markers because they are either slightly retained on the carbon support or interact with residual ZrO<sub>2</sub> resulting in broadened peaks.

## 3. Results and discussion

The analysis of isomeric and highly polar solutes can be particularly troublesome using conventional bonded phase HPLC media. Some analytes exhibit low retention and poor selectivity; the high solubility of such polar components in aqueous–organic mobile phases may be a serious challenge to the analyst. New types of RPLC materials have been designed for the analysis of very low hydrophobicity solutes. They generally incorporate a polar moiety into the bonded alkyl chain to enhance retention of particular solutes or allow the use of highly aqueous mobile phases [38–41]. However, such materials often fails to discriminate between isomers. The use of normal-phase HPLC to separate polar isomers has many drawbacks. Metal oxide adsorbents, especially silica and alumina, are very sensitive to trace quantities of water in the system. Consequently, the adsorbent's surface activity fluctuates greatly and retention becomes irreproducible unless great care is taken to control the amount of water in the system. A solid surface, having shape discrimination abilities while operating in the now preferred reversed-phase mode should be more ideal for such analyses.

### 3.1. Substituted benzenes

A chemically simple set of solutes is needed to compare and contrast the retention properties of carbon-based stationary phases and conventional bonded phase media. Within a relatively small set of mono- and disubstituted benzenes we explored a wide range of solute polarity, conjugation, structure, and electron density. The retention factors for all isomers were measured over a range of ACN/water compositions. The isomer elution order did not change on either phase over the composition range tested; consequently, the chromatographic conditions

were optimized for maximum selectivity. The retention and selectivity data are shown in Table 2.

From a practical perspective, chromatographic

selectivity pays large dividends in terms of resolution. The lowest selectivity value defines the overall quality of the separation. For the disubsti-

Table 2  
Optimized selectivity of disubstituted benzenes<sup>a</sup>

Benzene derivative	$k'_{\text{ODS}}$	$k'_{\text{CARB}}$	$\alpha_{\text{ODS}}^b$	$\alpha_{\text{CARB}}^b$	ODS	CARB
1,2-Dimethyl	7.62 <sup>c</sup>	5.93 <sup>d</sup>	1.11	1.08	o < m < p	m < p < o
1,3-Dimethyl	8.46 <sup>c</sup>	4.37 <sup>d</sup>	1.01	1.26		
1,4-Dimethyl	8.51 <sup>c</sup>	4.71 <sup>d</sup>				
1,2-Dichloro	7.58 <sup>d</sup>	2.24 <sup>e</sup>	1.13	1.02	o < p < m	m < p < o
1,3-Dichloro	9.19 <sup>d</sup>	1.99 <sup>e</sup>	1.07	1.10		
1,4-Dichloro	8.57 <sup>d</sup>	2.03 <sup>e</sup>				
1,2-Dibromo	4.80 <sup>c</sup>	4.49 <sup>e</sup>	1.20	1.07	o < p < m	m < p < o
1,3-Dibromo	6.25 <sup>c</sup>	3.52 <sup>e</sup>	1.08	1.20		
1,4-Dibromo	5.77 <sup>c</sup>	3.76 <sup>e</sup>				
1,2-Dicyano	7.09 <sup>f</sup>	2.76 <sup>g</sup>	1.05	1.06	m < o < p	m < p < o
1,3-Dicyano	6.74 <sup>f</sup>	2.43 <sup>g</sup>	1.08	1.08		
1,4-Dicyano	7.69 <sup>f</sup>	2.57 <sup>g</sup>				
1,2-Dihydroxy	0.50 <sup>f</sup>	– <sup>h</sup>	1.55	–	o < m < p	m < p
1,3-Dihydroxy	0.77 <sup>f</sup>	0.96 <sup>h</sup>	1.70	1.68		
1,4-Dihydroxy	1.32 <sup>f</sup>	1.61 <sup>h</sup>				
1,2-Dimethoxy	3.28 <sup>i</sup>	3.12 <sup>d</sup>	1.66	1.79	o < p < m	o < p < m
1,3-Dimethoxy	6.59 <sup>i</sup>	6.23 <sup>d</sup>	1.21	1.11		
1,4-Dimethoxy	5.45 <sup>i</sup>	5.60 <sup>d</sup>				
1,2-Dialdehyde	1.38 <sup>f</sup>	3.34 <sup>j</sup>	2.90	1.64	o < m < p	o < m < p
1,3-Dialdehyde	4.00 <sup>f</sup>	5.48 <sup>j</sup>	1.16	1.05		
1,4-Dialdehyde	4.66 <sup>f</sup>	5.74 <sup>j</sup>				
Dimethylphthalate	2.93 <sup>k</sup>	1.30 <sup>l</sup>	1.77	9.60	o < m < p	o ≪ m < p
Dimethylisophthalate	5.20 <sup>k</sup>	12.49 <sup>l</sup>	1.06	1.08		
Dimethylterephthalate	5.53 <sup>k</sup>	13.54 <sup>l</sup>				
1,2-Dinitro	2.56 <sup>h</sup>	1.62 <sup>l</sup>	1.04	4.50	o < m < p	o ≪ m < p
1,3-Dinitro	2.67 <sup>h</sup>	7.30 <sup>l</sup>	1.02	1.09		
1,4-Dinitro	2.73 <sup>h</sup>	7.98 <sup>l</sup>				

<sup>a</sup> 50 × 4.6 mm columns, 1 ml/min, 30 °C, 2-μl injections, 254-nm detection.

<sup>b</sup> Selectivity factors.

<sup>c</sup> 60:40 ACN/water.

<sup>d</sup> 50:50 ACN/water.

<sup>e</sup> 80:20 ACN/water.

<sup>f</sup> 20:80 ACN/water.

<sup>g</sup> 70:30 ACN/water.

<sup>h</sup> 45:55 ACN/water, the 1,2-dihydroxy derivative chelates to the hard Lewis acid sites on zirconia that are not blocked by carbon. No elution is observed.

<sup>i</sup> 35:65 ACN/water.

<sup>j</sup> 65:35 ACN/water.

<sup>k</sup> 40:60 ACN/water.

<sup>l</sup> 75:25 ACN/water.

tuted benzenes both the C/ZrO<sub>2</sub> and ODS phases show eight selectivity values below 1.10 (Table 2); thus, these separations are fairly challenging. Furthermore, each phase excels at only a few separations. Neither phase is clearly superior for the analysis of isomeric solute sets despite numerous reports in the literature indicating that carbon phases are very sensitive to changes in substituent position [11,17,35,36].

Upon comparison of the optimized selectivity factors and isomer elution order, the differences in the retention characteristics of each phase become clear. The ortho-isomers comprised of small electron-rich substituents are more retained than the meta- or para-isomers (the first four entries in Table 2). This makes sense from a dipolar standpoint. The electrons in the isomeric derivatives are probably more able to induce a more significant dipole in the carbon surface when the substituents are in the ortho position. In the meta- and para- case, local dipoles still exist, but the electronic distribution around the molecule becomes more symmetric leading to a different set of induced dipoles in the carbon surface. Furthermore, the elution order is essentially the opposite of the ODS phase. This result suggests that the contribution of dipole-induced dipole interactions is small on conventional bonded phases, but extremely large on carbon phases. This interpretation agrees well with retention analyses on both carbon and bonded-phase RPLC media [7,13,14]. Larger substituents exhibit the same elution sequence regardless of the nature of the stationary phase. The order on ODS makes complete intuitive sense. The net dipole of the molecule decreases as the substituents become more symmetrical about the molecule; consequently, the para isomer, being highly symmetric, is most retained and elutes last. By a similar argument the ortho isomer should elute first. The elution order on the carbon phase is much more complex than it is consistent with a simple dipolar effect. We observe enormous selectivity changes as a function of the substituent position. For the last four substituents listed in Table 2, the steric hindrance of the 1,2-disubstituted benzene is large; the electron clouds overlap and distort the shape of the molecule. Consequently, the nature of the interaction with the carbon surface changes dramatically as one moves to a less “congested” substitution pattern. Not only

does carbon show a dipole-induced dipole effect, but it exhibits shape specificity.

The above two characteristics, electronic/dipolar effects and shape specificity, working in concert with one another in the retention of solutes makes carbon distinctly different from conventional bonded phase media. That difference can and sometimes does lead to profound enhancement in the selectivity and resolution of chemical separations. However, on the whole, even for analysis of disubstituted benzenes, there is no clear cut, universal advantage to using a carbon phase or a bonded phase.

### 3.2. Functional group contributions

Another way to evaluate the unique character of carbon-based stationary phases is to examine functional group contributions to retention. We chose benzene as a reference compound (RH) and then calculated the ratio of retention factors between the functionalized molecule (RX) and benzene. This is expressed, in Eq. (1), as the difference between the logarithm of retention factors of the two analytes that vary only by the presence and absence of the functional group ( $\tau_x$ ) [28]. R represents the aromatic ring and X represents the substituent. If the resulting quantity is multiplied by  $-RT$  the product is the change in free energy of retention resulting from addition of the functional group.

$$\tau_x = \ln k'_{RX} - \ln k'_{RH} \quad (1)$$

The above approach was applied to both mono-substituted and para-disubstituted benzene compounds. We chose only the para-disubstituted compounds to avoid various types of intra-molecular (ortho) effects. However, this does not eliminate the well known resonance interaction of para-substituents. In the case of disubstituted solutes, the difference between the substituted and non-substituted molecule consists of contributions from two functional groups; consequently, the logarithmic difference is divided by two to allow comparison to a single functional group. Since this approach is based on the ratio of retention factors, the resultant conclusions are free from phase ratio arguments.

#### 3.2.1. Monofunctional derivatives

Figs. 2 and 3 illustrate the dramatic difference

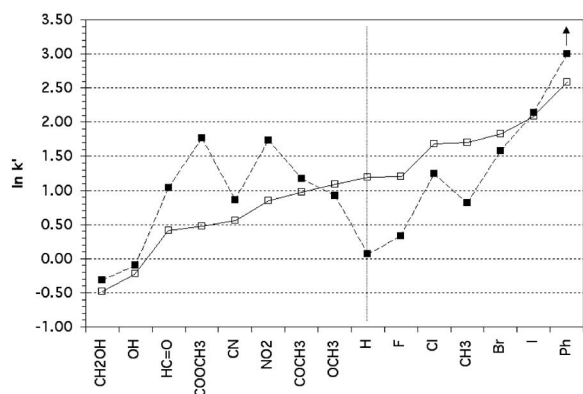


Fig. 2. Retention comparison of monosubstituted benzene derivatives in the same eluent. Vertical line indicates retention of benzene. Conditions: 50:50 ACN/water, all else as in experimental. Symbols: ■, C/ZrO<sub>2</sub>, 2.5  $\mu$ m; □, SB-C<sub>18</sub>, 5  $\mu$ m.

between the functional group contribution to retention for mono-substituted benzenes on the two phases. When a polar functional group is added to the benzene ring, regardless of its electron donating or withdrawing nature, retention, relative to benzene, generally decreases for the ODS phase. Retention does not begin to increase until a halogen or hydrocarbon is added to benzene.

On C/ZrO<sub>2</sub> it is very clear that substitution of the benzene ring with any functional group results in an increase in retention. The only exceptions to this

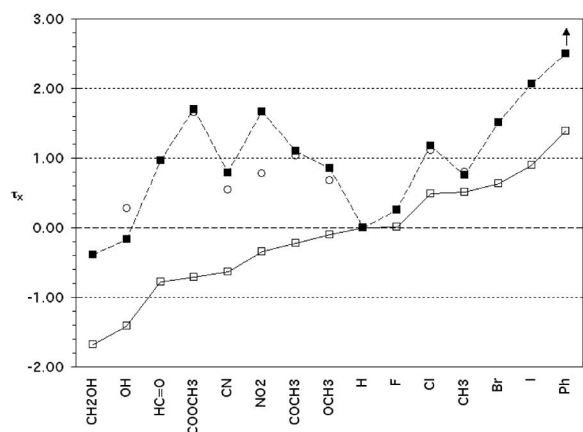


Fig. 3. Plot of  $\tau_x$  for monosubstituted benzenes against functional group type. Conditions: 50:50 ACN/water, all else as in Experimental. Symbols: ■, C/ZrO<sub>2</sub>, 2.5  $\mu$ m; □, SB-C<sub>18</sub>, 5  $\mu$ m; ○, PGC from Ref. [28].

trend are two compounds containing hydrogen bond donor groups (–OH, –CH<sub>2</sub>OH). Given a hydro-organic mobile phase and the ability of water to participate in hydrogen bonding processes as donor or acceptor, this observation is not surprising. The  $\tau_x$  values for PGC are very similar (see ○, Fig. 3) to those on C/ZrO<sub>2</sub> (■, Fig. 3). The good agreement between the  $\tau_x$  values is quite interesting given the different conditions under which these parameters were calculated. Only phenol and nitrobenzene show any substantial difference between the two types of carbon phases. This is somewhat surprising given the fact that the PGC phases are highly graphitized whereas the average thickness of the carbon on the C/ZrO<sub>2</sub> phase is only about one monolayer.

Because functional group substitution of the benzene ring generally increases retention on carbon phases, this suggests the existence of a strong contribution from dipolarity and/or dipole-induced dipoles to retention on carbon in addition to large dispersive forces. As with PGC, the retention increases regardless of the electronic nature of the substituent. Consequently, the exact nature of the chemical interaction with carbon is rather complex. As pointed out above, the increase in retention upon addition of a polar functionality can be quite useful for the separation of analytes which are so water soluble as to be unretained or nearly unretained on conventional hydrocarbon-like phases.

### 3.2.2. Para-disubstituted derivatives

Fig. 4 shows the same analysis for *para*-disubstituted compounds. Again, the behavior of the disubstituted compounds on the ODS phase mirrors the mono-substituted patterns. On the other hand, the carbon phase shows a dramatic increase in the relative retention of the disubstituted benzenes, so much so that *the percent organic content of the mobile phase had to be increased to obtain reasonable analysis times*. In agreement with observations on PGC, an increase in retention was always seen upon addition of a second functional group [28]. It is interesting to note that the largest increases in relative retention are observed with 1,4-dinitrobenzene and dimethylterephthalate.

Knox and Ross [7] have coined the term *Polar Retention Effect on Graphite*, or PREG, for solute retention behavior on PGC that is thought to arise

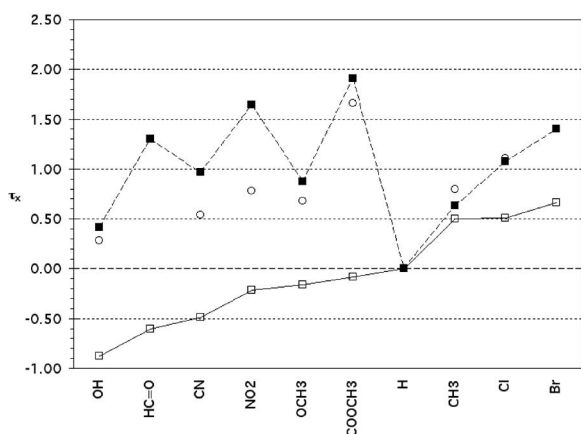


Fig. 4. Plot of  $\tau_x$  for para-disubstituted benzenes against functional group type. Conditions: 50:50 ACN/water, all else as in Experimental. Symbols: ■, C/ZrO<sub>2</sub>, 2.5  $\mu$ m, 75:25 ACN/water; □, SB-C<sub>18</sub>, 5  $\mu$ m, 50:50 ACN/water; ○, PGC from Ref. [28].

from some type of molecule-graphite electronic effects and increases upon addition of polar groups to a molecule. The C/ZrO<sub>2</sub> shows very similar retention behavior compared to PGC but is very likely not a graphitic carbon. Perhaps some sort of common structure between these two different carbon materials, such as a smaller microcrystalline

surface, gives rise to the PREG phenomenon. The above observations suggest that PREG is more generally related to a variety of carbon-based materials rather than graphitic phases in particular.

### 3.3. Dinitrotoluenes and nitroxylenes

Small nitroaromatics form an important class of polar isomeric compounds. They are frequently found in the environment as by-products of munitions manufacturers and users. In particular, the closing of various military installations in this country has brought the problem to the forefront of environmental concerns. Not only are they found in soil, but they leach into aquifers. Fig. 5 shows the separation of nitroxylylene and dinitrotoluene isomers on C/ZrO<sub>2</sub>. In each case, the carbon phase exhibits reasonable retention and resolution with a significant fraction of organic modifier in the mobile phase. The same analysis on a bonded phase material is quite challenging as shown by Weber and Hilmi [17,42]. It is important to note that the separations on C/ZrO<sub>2</sub> are not merely a function of an efficiency advantage. Reduced plate heights for the nitroxylenes and dinitrotoluenes fall between 4 and 7 on C/ZrO<sub>2</sub> whereas on SB-C<sub>18</sub> they are well under 3.

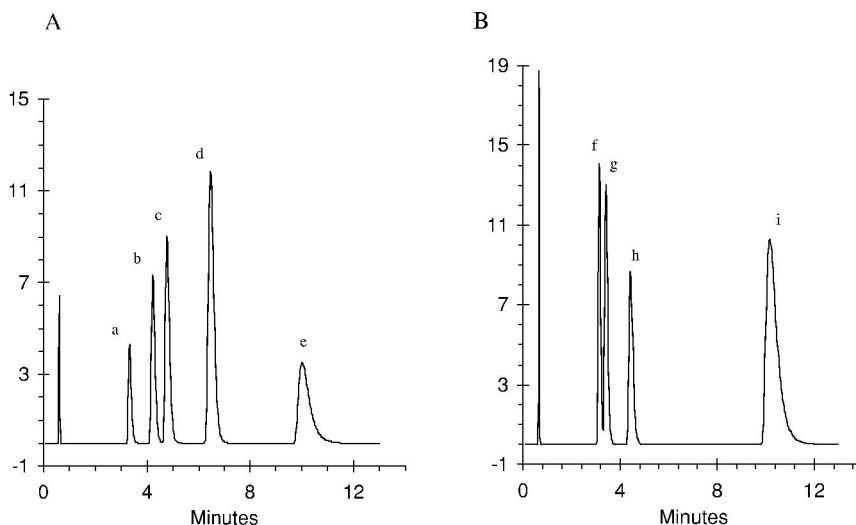


Fig. 5. Separation of polar nitrosubstituted isomers on C/ZrO<sub>2</sub>. Conditions: 50×4.6 mm, 1 ml/min, 30 °C, 2- $\mu$ l injections, 254-nm detection. (A) Nitroxylenes, 65:35 ACN/water. Peak identity: a, 2-nitro-*m*-xylene; b, 3-nitro-*o*-xylene; c, 2-nitro-*p*-xylene; d, 5-nitro-*m*-xylene; and e, 4-nitro-*o*-xylene. (B) Dinitrotoluenes, 70:30 ACN/water. Peak identity: f, 3,4-dinitrotoluene; g, 2,6-dinitrotoluene; h, 2,3-dinitrotoluene; and i, 2,4-dinitrotoluene.

The elution order of the dinitrotoluenes follows the dipolar nature of the molecule. This agrees with our postulate that there is a dipolar or electronic contribution to retention on carbon; the larger solute dipole induces a dipole in the stationary phase and what results is a substantial increase in retention. A similar trend is observed with the nitroxyls; however, the steric bulk of the groups also contributes to the retention and elution order. The first two eluting nitroxylene isomers all have the methyl and nitro substituents adjacent. As congestion around the nitro group decreases, retention increases; we infer that the nitro substituent appreciably interacts with the carbon phase and strongly influences retention and selectivity. A similar phenomenon is observed for the dinitrotoluenes. Steric crowding around the nitro group, whether it is a methyl or another nitro group decreases retention. However, when the orientation of the nitro substituents permit their electronic character to fully interact with the carbon surface, a substantial increase in retention and selectivity is observed as illustrated by the elution of 2,4-dinitrotoluene compared to 2,3-dinitrotoluene. Therefore, carbon HPLC media is not only sensitive to the electronic nature of the solute, but also to its shape [4,10].

#### 4. Conclusion

The analysis of isomeric and polar solutes on C/ZrO<sub>2</sub> in comparison to ODS and PGC revealed many differences and similarities. The separation of substituted benzenes shows that there is no clear cut advantage to using a carbon stationary phase over a bonded phase silica for the analysis of these solutes. This was surprising given the well documented ability of carbon stationary phases to discriminate between isomeric species. Additionally, comparison of the functional group contributions to retention illustrated the dramatic differences between C/ZrO<sub>2</sub> and ODS; virtually all additions of substituents led to an increase in retention on C/ZrO<sub>2</sub> and PGC. This stands in stark contrast to bonded phase media. We also found that both types of carbon media show shape specificity, that is the solute structure presented to the surface appears to have a dramatic impact on retention and selectivity. It appears that

factors leading to solute retention on carbon phases, in particular the phenomenon of PREG, is not tightly linked to a large crystalline surface such as a graphitic ribbon, but perhaps a smaller microcrystalline surface structure. If this were not the case, we should have observed substantial differences in retention between PGC and C/ZrO<sub>2</sub>. Furthermore, the data suggest that any approach describing the fundamental retention characteristics of carbon HPLC phases must include an element somehow related to or correlated with solute shape.

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