Research Article

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Abnormal retention of s-triazine herbicides on porous graphitic carbon

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Abstract: Porous graphitic carbon (PGC) is a widely used stationary phase for reversed-phase high-performance liquid chromatography (HPLC) that allows separation of structurally similar compounds retained in mixed form on a flat graphite surface. Such a stationary phase can be used in analytical chemistry to provide good separation and selectivity in pesticide monitoring. In this article, we studied the chromatographic behavior of five common triazine herbicides (simazine, atrazine, desmetryn, propazine, prometryn) on PGC *vis-à-vis* octadecyl-functionalized silica gel (ODS). It was found that the herbicides studied have an abnormal elution order on PGC compared to ODS. PGC was also characterized by higher selectivity of analyte separation. This behavior of triazine herbicides on PGC cannot be explained either with the help of existing theory or by mathematical modeling of adsorption processes on graphite. Therefore, we have proposed a possible retention mechanism, explaining the effects observed, due to the shielding of the amino group in the triazine ring by alkyl substituents, which decreases the “polar retention effect” of PGC. Satisfactory separation efficacy was obtained with the proposed analytical method, using convenient UV-detection and without resort to laborious techniques such as HPLC coupled with mass spectrometry.

Keywords: high-performance liquid chromatography, triazine herbicides, porous graphitic carbon, retention mechanism

1 Introduction

Porous graphitic carbon (PGC) is a versatile stationary phase that was used in high-performance liquid chromatography (HPLC) for the first time by Knox and Gilbert about 30 years ago [1,2]. Since then, numerous investigations have shown that this sorbent has the unique ability to separate isomers as well as substances with a similar structure. In this regard, the scope of application of columns, packed with PGC, is constantly expanding [3–5]. Currently, sorbents for liquid chromatography based on PGC are produced under the trade name *Hypercarb*. It consists of porous spherical carbon particles, composed of flat layers of hexagonal structures on the molecular level, built of sp^2 -hybridized carbon atoms [6]. Therefore, the stationary phase, consisting of pure carbon, is assumed to be completely nonpolar. However, *Hypercarb* has some properties that significantly set it apart from classical nonpolar stationary phases.

First, a flat PGC surface causes a steric effect because the unbranched substituents and planar molecular parts can approach the sorbent surface more effectively, and, consequently, the branched and non-planar molecules elute earlier than planar and linear ones [7]. Furthermore, Kaliszan et al. [8] were the first to mention the mixed properties of *Hypercarb* with reference to electron distribution in sorbate molecules, which is important for the interpretation of the retention patterns. They discovered a correlation between the location of polar segments of molecules and the values of the retention factor. Tanaka et al. compared the retention behavior of PGC with the behavior of sorbents based on octadecyl-functionalized silica gel (ODS). These authors noticed that any substituent in the benzene ring, whether polar or nonpolar, induces an increase in retention on PGC [9]. Another retention feature is the so-called “polar retention effect” [6,10]: enhanced retention of molecules with a high dipole moment through an interaction between partial charges of a molecule and a polarized π -electron graphite system.

Therefore, the interaction energy of sorbates on PGC surface is determined by a combination of two factors: by

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the structure of alkyl substituents, and by the type and location of the functional groups relative to the sorbent surface [11] and to alkyl substituents [12]. To date, the influence of these factors is well studied for substituted aromatic compounds [10,13,14], but the impact of substituents in the heteroaromatic ring (not in the benzene one) remains uninvestigated. The chemical properties of such compounds are determined by the substituents in the heteroaromatic ring as the ring itself only participates in the charge delocalization. Thus, substituted heterocycles retention behavior differs significantly from similarly substituted benzenes [15].

To illustrate this, five well-known triazine herbicides with different structures (propazine, prometryn, atrazine, desmetryn, simazine), which can demonstrate different types of interaction with carbon surface, were chosen (Figure 1). Triazine herbicides are alkyl-substituted derivatives of 1,3,5-triazine and behave as weak bases, demonstrating electron-donor properties [16–19].

Different HPLC techniques residue analysis in soils and water bodies for these substances, using various bonded columns, are described in the literature [20–24]. Among them, columns packed with ODS are most popular owing to their wide application in the reversed-phase HPLC [20–22]. The chromatographic separation of this class of compounds on PGC has also been studied, but to a much lesser extent [25]. To the best of our knowledge, there are no studies dedicated to the investigation of retention mechanisms of triazines on PGC.

A molecular statistical approach is extensively used for modeling of adsorption processes and possible retention mechanisms characterization on carbon sorbents from gases and liquids [7,26]. However, the calculated data are not always consistent with the experimental ones [12]. Therefore, it is important to apply such methods for understanding retention behavior. In addition, it can allow

predicting the chromatographic behavior of heterocyclic compounds on PGC.

Hence, triazine derivatives retention mechanisms from solutions on PGC surface in HPLC in comparison with their adsorption on ODS surface were studied in this article with the use of molecular modeling. The conducted study allowed the full picture of separation properties of triazines to be obtained on both phases and the possibility of prediction of heterocycles retention on PGC.

2 Materials and methods

2.1 Chemicals and samples

Chemical standards of simazine, atrazine, desmetryn, propazine, and prometryn were purchased from Sigma-Aldrich, USA. The purity of each compound was above 99%. HPLC-grade acetonitrile was obtained from Merck (Darmstadt, Germany). Deionized water was obtained from a Milli-Q purification system (Millipore, USA). Stock standard solutions of each herbicide with a concentration of $1.00 \text{ mg}\cdot\text{mL}^{-1}$ were individually prepared by dissolving the corresponding weighed portions of each compound in acetonitrile and stored in amber glass vials at 4°C and protected from light. The working solutions for experiments with concentrations of $10 \text{ }\mu\text{g}\cdot\text{mL}^{-1}$ were prepared by diluting in acetonitrile by 100 times just before use.

2.2 Instrumentation

An Agilent 1260 chromatographic system (Agilent Technologies, USA) equipped with a binary pump, degasser,

Figure 1: Structural formulas of studied heterocyclic triazine herbicides.

autosampler, column thermostat compartment, and multiple wavelength detector was used for analysis. Chromatographic separations were performed on a *Hypercarb* column packed with porous graphitic carbon (2.1 mm × 100 mm, particle size 3.5 μm) from Thermo Scientific (Waltham, USA) and a C18 analytical column ZORBAX Eclipse XDB (2.1 mm × 100 mm, particle size 3.5 μm) from Agilent Technologies (Santa Clara, USA). OpenLab Chemstation Software (C.01.07) was utilized to operate the system and to process the chromatographic data. The injection volume was 5 μL and the column temperature was 35°C.

2.3 HPLC conditions

The study of selectivity of stationary phases was performed in gradient and isocratic elution modes. The flow rate of the mobile phase was 0.15 mL·min⁻¹. Mobile phases A and B consisted of HPLC-grade water and acetonitrile, respectively. Elution program was the following: 5–93% gradient B at 0–5.0 min; constant 93% B at 5.0–20.0 min; 93–5% gradient B at 20.0–25.0 min; and constant 5% B at 25.0–30.0 min. UV detection was carried out using an absorption wavelength of 248 nm for all compounds. The individual compounds were identified by their retention times.

2.4 Molecular modeling

Molecular modeling was carried out by the technique used in ref. [26]; details are given in Appendix. According to the previous studies [26,27], the interaction between adsorbate and the flat graphitic surface can be characterized using the *in vacuo* adsorption simulation. It allows distinguishing [12] steric effects that are related only with the adsorbate shape and the flatness of the surface from more complex effects. The *in vacuo* molecular simulations were carried out using the Metropolis Monte-Carlo algorithm as described before [12,28–30].

3 Results

First, a test separation was performed using a smooth gradient from 5% to 100% acetonitrile over 60 min. On the obtained chromatogram, the separated peaks of substances were observed at acetonitrile contents differing

from each other by less than 15%. This means that the substances to be separated are characterized by close retention values on PGC, which makes it possible to develop a method for their separation with an isocratic elution mode. An attempt to apply mobile phase with a low concentration of acetonitrile resulted in asymmetric chromatographic peaks and poor separation of two pairs of compounds (prometryn and atrazine; desmetryn and simazine). This is most likely due to the weak solubility of almost all sorbates in water. The optimized composition of the mobile phase was 93% acetonitrile.

As all the investigated compounds are weak bases, we attempted to improve the separation effectiveness by adding formic acid as an anionic mobile phase modifier. An acidic modifier, as supposed, should have protonated the graphite surface, involving the interaction with π -electrons and, therefore, decreasing interactions between sorbates and a charged surface [31]. However, addition of 0.01% formic acid modifier resulted only in a slight increase of retention time and caused peak broadening. Raising the concentration further to 0.05% did not significantly change the retention behavior. It could be a result of a poor competing ability of modifier compared to analyte and demonstrates that the interaction mechanism of PGC with analytes is more complex.

Elution conditions, which provided optimal separation on PGC, were applied to analysis on ODS for comparison of retention characteristics. The separation performance on PGC seemed to be much better than on ODS, where separation of atrazine and desmetryn was not possible under given conditions. UV-chromatograms of triazine herbicides mixture (Figure 2) during its analysis on PGC (Figure 2a) and on ODS (Figure 2b) columns and also overlapped chromatograms of individual herbicides solutions on ODS column (Figure 2c) were obtained. While we observed the complete separation of atrazine and desmetryn on the PGC column (Figure 2a), on the ODS column they elute as one broad chromatographic peak (Figure 2b), and when analyzing solutions of individual substances, it can be concluded that they elute almost at the same time (Figure 2c).

The efficiencies of both column types for atrazine and desmetryn separation were relatively close, while their selectivity and, consequently, resolution differed dramatically. This result was expected particularly because of the close values of partition coefficients (lipophilicity, $\log P$) for this pair of compounds. Insufficient selectivity of ODS for desmetryn and atrazine may become a problem when carrying out a simultaneous analysis of the herbicide's complex mixture, for example, in environmental monitoring when more complex analysis methods, such as HPLC coupled with mass spectrometry, is not

Figure 2: Chromatograms of triazine herbicides mixture solution on PGC (a) and on ODS (b) columns; overlapped chromatogram of individual herbicides solutions on ODS column (c).

available. Thus, research in the applicability of more selective stationary phases to meet this challenge is an important aspect.

4 Discussion

4.1 Adsorption behavior of herbicides on ODS

To gain an insight into the selectivity and retention mechanism, we considered retention processes on ODS and PGC separately. Several physicochemical parameters of the triazine compounds are shown in Figure 3, by analyzing which it is possible to explain some patterns of chromatographic behavior. On the left side of Figure 3, two series of homologous analytes (simazine, atrazine, and propazine; desmetryn and prometryn) are arranged in order of increase in molar weight and $\log P$ for illustrative purposes. On the right side of Figure 3, in column (Figure 3a) sorbates are arranged in order of elution on ODS, in column (Figure 3b) – in order of elution on PGC. As shown in Figure 3, the elution order of homologous analytes on ODS (simazine, atrazine, and propazine; desmetryn and prometryn) is determined by their molar mass and lipophilicity. It was also discovered that atrazine and desmetryn, both having close values of molar mass and lipophilicity, are impossible to separate in

reversed phase HPLC, and their retention time coincided with each other. On the contrary, elution order on PGC was completely different (propazine, atrazine, and simazine; prometryn and desmetryn) and much greater separation performance was observed.

Thus, retention on ODS is described as purely hydrophobic, and selectivity of separation in the case of analysis of compounds, which have a similar structure, molecular size, and hydrophobicity, is shown to be unsatisfactory. Retention behavior on PGC, on the other hand, is characterized by a more complex mechanism, determined by multiple factors and interaction types, which will be discussed in detail in the following section.

4.2 Comparison of adsorption behavior on PGC and ODS: Origin of observed selectivity

Even though *Hypercarb* was considered as a typical hydrophobic sorbent for reversed-phase chromatography, the retention order of substances on it does not always follow values of molecular hydrophobicity of the analytes, which is only one important factor. Abnormal elution order of triazine herbicides during adsorption on PGC has already been mentioned in the literature before [32], but it has not been properly substantiated. It was noted that only steric hindrances and the impossibility of adopting enough flat

Figure 3: On the left side: values of molar weight (M_w) and log P of triazine herbicides. On the right side: retention times (t_R) of herbicides on ODS (a) and PGC (b).

conformation relative to the PGC surface are likely crucial factors [25].

In this study, an attempt to explain the reason for increased selectivity of PGC in the separation of triazine herbicides by molecular modeling has been made. In such modeling, only the interaction between molecule and carbon surface is taken into account. Values of adsorption constant (K_{ads}), obtained by computer simulation *in vacuo*, allowed estimating contribution of steric effects in retention on the flat graphite surface. According to calculated data, propazine and prometryn, which have the highest values of the logarithm of adsorption constant ($\ln K_{ads}$), equal to 24.3 and 26.2, respectively, are expected to interact more with the sorbent surface, than other investigating compounds, and, therefore, to retain longer. Atrazine and desmetryn (values of $\ln K_{ads}$ are 22.8 and 22.9, respectively) were supposed to show a similar pattern of interaction with the flat graphite surface and, thus, would not have been separated. Lastly, simazine

($\ln K_{ads} = 21.3$), the lowest homologous compound in the chlorine-containing series, is expected to have the weakest retention. It is obvious that all calculated data paint a picture that is the exact opposite of the practically obtained one. Assumption of the dominant influence of dispersion interactions, on which such statistical calculations are based, cannot explain the real retention.

To suggest which interactions can affect retention on PGC, we turn to Figure 3 again. It can be seen that the retention of homologous analytes on PGC (Figure 3b) does not increase with the growth of molar mass and lipophilicity, but rather decreases with their growth. The absence of correlation between values of retention factor and logarithm of lipophilicity, when adsorption takes place on PGC, in comparison with the existing one on ODS, was reported earlier [9,10]. This demonstrates higher contribution of electrostatic forces, such as inductive and orientation ones, and electron transfer phenomenon compared to classical hydrophobic interactions, which are essential in

retention on ODS. All this leads to a significant increase in retention of polar compounds, in particular, the addition of any donor or acceptor substitute in the benzene ring. During adsorption of such molecules, probably, graphite surface polarization occurs because of the overlapping of hybridized orbitals [10].

According to the data, it can be expected that more polar compounds will retain longer, and in the investigating system, this factor will prevail over molar mass and the number of alkyl groups in substitutes. This suggestion is also confirmed by comparison of another important physicochemical parameter – topological polar surface area (TPSA) of a molecule, which is defined as the surface sum of all polar atoms, including their attached hydrogen atoms [33]. For chlorine- and sulfur-containing herbicides, TPSA values equal 62.7 and 88.0 Å², respectively. This explains the fact that, provided close values of molar mass and lipophilicity, sulfur-containing herbicides, having a higher value of TPSA, retain longer than chlorine-containing ones.

All studied analytes have similar s-triazine rings substituted by two amino groups in positions 4 and 6. Consequently, separation of a mixture containing such compounds happens only because of alkyl groups, which substitute hydrogen in amino groups. Nevertheless, if only the length of alkyl substitute defined retention, elution would have been of the same order, as theoretically expected [10]. In the given system, the extent of shielding of the amino group by alkyl substitute plays a crucial role, but not its location related to the flat graphite surface. The main interactions, which characterize retention, are likely to be the induction ones that arise in the molecule approaching the graphite surface. Dipole induction occurs during the overlapping of p-orbitals of amino groups and PGC, which can be a special case of the so-called “polar retention effect” [6]. In the case of amino group, shielding by a bulky alkyl substitute such as in propazine and prometryn by isopropyl groups, nitrogen atom, containing a lone-electron pair, becomes unavailable for interaction with the graphite surface. Such molecules do not elute immediately, being retained by hydrophobic interactions, but there is a lack of connecting points with the flat graphite surface. Meanwhile, homologous of propazine and prometryn, atrazine and desmetryn, respectively, which have one more available amino group, will be increasingly retained. Thus, the most unshielded amino groups are present in simazine, and this compound will have the biggest retention time of all.

Additionally, amino groups in the heteroaromatic ring can affect retention not only because of electrostatic

forces or charge transfer but also due to the formation of hydrogen bonds with residual hydroxyl groups on the PGC surface. The effect of amino group, shielding by alkyl substituents will play a similar role.

5 Conclusion

Chromatographic behavior of several triazine herbicides during separation on PGC surface, compared with that one on ODS, was studied. To the best of our knowledge, the retention patterns on PGC described in the literature, deal only with aliphatic and aromatic compounds. Therefore, using the existing theory for heteroaromatic compounds is incorrect and cannot serve as an explanation of their elution order and improved separation on PGC in comparison with ODS. In this respect, we proposed the retention mechanism of triazine herbicides on PGC, based on the electrostatic interactions between polar substituents in the heterocyclic ring and the flat graphite surface. It was found that partial shielding of the amino group takes place as the alkyl substituent becomes bulkier. Consequently, the interaction between the nitrogen atom and the graphite surface decreases, and the “polar retention effect” of PGC declines as well. The proposed mechanism explains the abnormal retention order of analytes as well as increased separation selectivity on PGC compared to ODS. The analytical method developed allows satisfactory separation of triazine herbicides using the convenient HPLC-UV technique. It was shown that in the modeling of the adsorption processes on graphite using molecular calculation technique, not only steric effects but also the contribution of other interaction types, including the formation of hydrogen bonds, should be taken into consideration.

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Appendix

The adsorption constant from the gas phase *in vacuo* is computed the following way:

$$K_1 = \frac{V}{A} \cdot \frac{N_{\text{ads}}}{N_{\text{vol}}} = \frac{V \int e^{\frac{(\Phi_{\text{int}}(\vec{r}) + \Phi_{\text{ads}}(\vec{r}))}{kT}} d\vec{r}}{A \int_{\text{vol}} e^{\frac{\Phi_{\text{int}}(\vec{r})}{kT}} d\vec{r}} \quad (\text{A1})$$

where V – the volume of a system, A – surface of a sorbent, N_{ads} – number of molecules on a surface, N_{vol} – number of molecules in a volume, Φ_{ads} – the potential energy of the surface-adsorbate interaction and Φ_{int} – internal conformational energy of the molecule [12,27,28].

General AMBER force field (GAFF) was used to compute E_{int} . The non-bonded interactions parameters, the functional form, and mixing rules from GAFF were used for the interaction with the surface as well. The following Lennard-Jones parameters were used for graphite atoms: $\epsilon = 0.295 \text{ kJ} \cdot \text{mol}^{-1}$; $r = 1.908 \text{ \AA}$. The potential energy of surface-adsorbate interaction is computed considering the graphene sheets as uniformly filled with carbon atoms. Lennard-Jones potential for each of the adsorbate atoms was integrated over graphene sheets analytically:

$$\begin{aligned} \Phi &= \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \sum_{n=0}^{\infty} \frac{C_{12}}{(x^2 + y^2 + (z + nd)^2)^6} \\ &\quad - \frac{C_6}{(x^2 + y^2 + (z + nd)^2)^3} dx dy \quad (\text{A2}) \\ &= \pi \left(\frac{1}{5d^{10}} C_{12} \zeta \left(10, \frac{z}{d} \right) - \frac{1}{2d^4} C_6 \zeta \left(4, \frac{z}{d} \right) \right) \end{aligned}$$

where C_{12} , C_6 – parameters of Lennard-Jones potential for the atom of a molecule with an atom of graphite, $\vartheta = 0.385 \text{ nm}^{-2}$ – surface density of graphite atoms, $d = 0.365 \text{ nm}$ – the distance between graphite sheets, ζ – Hurwitz zeta function, x, y, z – coordinates of the adsorbate atom. The axis z is perpendicular to the surface.

Integration over the conformations of the molecule was done using the Metropolis Monte-Carlo algorithm [30]. Rotations of a random σ -bond (excluding bonds of hydrogen and chlorine) for a random angle were conducted as random moves, as well as rotations of the molecule around the center of mass. For each configuration, the internal energy was computed, and the configuration was accepted/rejected using the Metropolis algorithm rules. Molecules were considered [31] as harmonically oscillating along z axis near minimum of potential energy along this axis. 5,000,000 Monte-Carlo steps were done for each molecule; the random error of integration is not more than 0.02 in terms of the logarithm of the adsorption constant ($\text{cm}^3 \cdot \text{m}^{-2}$).