Elucidation of retention mechanisms on hypercrosslinked polystyrene used as column packing material for...

Elucidation of retention mechanisms on hypercrosslinked polystyrene used as column packing material for high-performance liquid chromatography

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Abstract

Establishing of basic retention mechanisms was considered the key target during the development of new column packing materials. To extract, from an appropriate retention data matrix on hypercrosslinked polystyrene Chromalite 5HGN, certain factors that can be brought in an obvious correspondence with known retention mechanisms, the principal component analysis (PCA) was applied. The approach was used to elucidate the adsorption properties of the above novel HPLC packing. Besides HPLC, knowledge of retention mechanisms helps to reveal perspective application area for the hypercrosslinked polystyrene-type materials in solid-phase extraction (SPE) and low-pressure preparative LC.
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1. Introduction

In recent time, various new polymeric materials for the solid-phase extraction (SPE) [1,2] and liquid chromatography [3,4] have been developed and suggested by manufacturers. Although many polymeric-type adsorption materials exhibit distinct advantages over widely spread modified silicas, in fact, their proportion in SPE and LC applications (with the exception of ion exchange and affinity chromatography) still remains very small. The rather low level of interest and even distrust of common users in new polymeric packing materials usually results from both the lack of application data and bad understanding of specific retention mechanisms on such adsorption materials. Even an occasional observation of a unique selectivity in retention of standard compounds on new materials does not make the use of the latter sufficiently predictable, unless the reasons for the inversions of elution orders are clarified. Therefore, we believe that the development of novel adsorption materials and examination of their properties should be focused from the very beginning on the elucidation of retention mechanisms. Their knowledge gives a better insight into the chromatographic system and clarifies perspectives, benefits and optimal application fields of obtained materials.

In academic research however, no general approaches to the elucidation of retention mechanisms can be found. In our point, establishing of factors that control the retention of a representative series of solutes by using principal component analysis (PCA) could help considerably in the revealing of the nature of most important solute–sorbent interactions. In the present contribution, the PCA approach was used, in order to evaluate properties of hypercrosslinked polystyrene, novel column packing material for HPLC and SPE.

2. Hypercrosslinked polystyrene as column packing material

Mechanical robustness, inertness, pH stability, compatibility with both polar and non-polar organic solvents, and even water—here are desirable properties of modern HPLC packings. These requirements are best met by the new generation of polymeric adsorbent materials, hypercrosslinked polystyrene [5]. Principally differing from conventional styrene-divinylbenzene copolymers, hy-
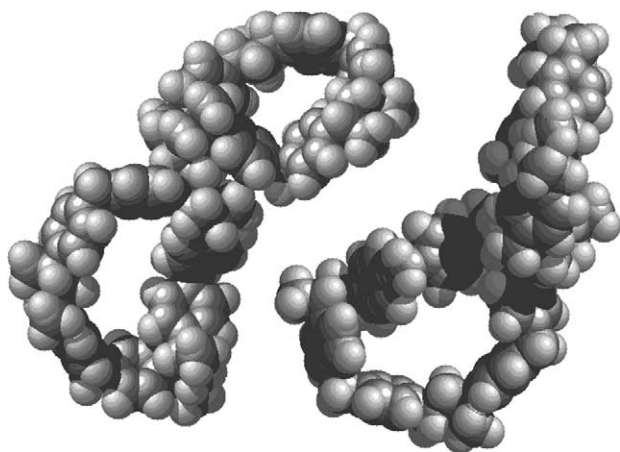
Fig. 1. Typical network elements of hypercrosslinked polystyrene.

percrosslinked polystyrene is obtained by an extensive post-crosslinking of long polystyrene chains in the presence of excess of good solvent (from the thermodynamic point of view, a solvent is good for polystyrene if it dissolves linear polymer chains or causes swelling of a crosslinked material). Preferably, post-crosslinking is achieved by introducing methylene $-CH_2-$ bridges between phenyl groups of polystyrene in ethylene dichloride. The structure of hypercrosslinked polystyrene is an expanded, rigid and dense three-dimensional network. The main structural element of this network is a spatially non-planar cycle formed by crosslinking bridges and very short chain segments confined between the branching points. Fig. 1 illustrates size and shape of smallest possible unstrained network cycles. Larger cycles are also formed under conditions of statistical post-crosslinking of the initial polystyrene chains. The resulting rigid, open-work-type hypercrosslinked network displays extremely high apparent inner surface area (up to 1000–1500 m^2/g) and almost identical solvent uptake in both polar and non-polar media, which explains good compatibility of the material with all mobile phases, from hexane to methanol and water. The whole interior of the hypercrosslinked polystyrene bead is accessible to small analytes, as if the rather homogeneous network were composed of fine "pores" of about 2.0–4.0 nm in diameter [5].

Hypercrosslinked polystyrene materials have already found wide application for large-scale adsorption technologies (Macronet Hypersol series, Purolite, UK) and for SPE (Purosep, Purolite, UK; Isolute-ENV+, IST, UK; LiChrolut EN, Merck). However, there are only a few examples illustrating the applicability of this material in the capacity of stationary phases in HPLC [6–9].

Here, the chromatographic data we present was obtained on a HPLC column packed with experimental Chromalite 5HGN (Purolite, UK). This is a monosized 5 μm beaded "Macronet" material of the hypercrosslinked (H) polystyrene family, of the gel-type (G), non-activated (N).

Due to the compatibility with any type mobile phases, different chromatographic modes can be realized on the Macronet Gel packing. While using highly polar solvents or their mixtures with water as mobile phase, the packing functions like alkyl-modified silica (though possessing very high hydrophobicity and unusual selectivity) or polystyrene–divinylbenzene (PS-DVB) packings as RPR-1 (Hamilton) [10], or PLRP (Polymer Labs), since under conditions of the highly polar environment all hypercrosslinked polystyrene chains mainly enter dispersion-type (hydrophobic) interactions with the analytes.

In non-polar organic solvents, the peculiar feature of hypercrosslinked polystyrene appears to be the exceptionally strong pi-electron donating-accepting ability, which causes a predominant retention of compounds that contain aromatic pi-systems or functional groups with lone electron pairs (for instance, carbonyl group). This mode of chromatography was earlier named by us the "quasi-normal-phase mode" (QNP mode), the word "quasi" pointing out the absence of any polar groups in the structure of the adsorbent.

It will be shown further that retention mechanisms on the hypercrosslinked polystyrene will differ depending on experimental conditions, first of all depending on the mobile phase composition and the nature of analytes. The basic overlapping mechanisms were found to involve pi-interactions, dispersive interactions, and size exclusion, though we understand that the notions of "pi-interactions", "dispersive interactions" and even "retention mechanisms" are rather vague in chromatographic science.

3. The role of pi-interactions in LC on hypercrosslinked polystyrene and some related packings

Let us consider a molecule of a hypothetic analyte (Fig. 2) that exhibits four parts: a permanent dipole, a hydrogen-donating group, an aliphatic chain and a pi-electron system. In the conventional normal-phase mode of chromatography, the retention is caused by the adsorbent-adsorbate interactions that are due to hydrogen bonding, permanent
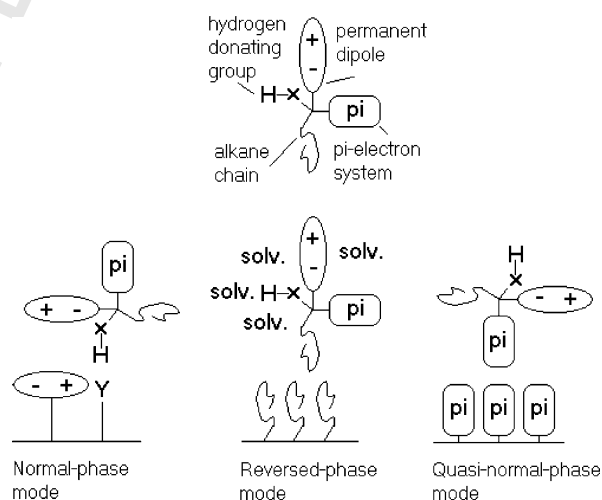

Fig. 2. Scheme of principal solute/sorbent interaction mechanisms under different chromatography conditions.

Table 1
Selectivity values α for the pair anthracene/phenol on a series of packings revealing pi-electron donating-accepting properties under normal-phase conditions. Mobile phase, hexane-2-propanol (93:7, v/v)

Stationary phase	Selectivity α, anthracene/phenol
Silica (Separon SGX, Tessek)	0
Kromasil DMB (Eka Chemicals AB)	0.16
Pirkle ULMO R, R (Regis Technologies)	0.72
Chiralcel OJ-H (Diacel Chemicals)	3.41
Hypercrosslinked polystyrene	Very large

Table 2
Selectivity values α for the pair nitrobenzene/benzene on a series of packings revealing pi-electron donating-accepting properties under reversed-phase conditions

Stationary phase	Selectivity α, nitrobenzene/benzene
Hypercrosslinked polystyrene	1.48
Porous graphitic carbon Hypercarb (Shandon)	1.37[a]
PRP-1 (Hamilton)	1.12[a]
C$_{18}$ packing LiChrosorb RP-18 (Merck)	0.78[a]

In the case of hypercrosslinked polystyrene packing the mobile phase is acetonitrile:THF:water (70:10:20, v/v).

[a] Data taken from [12], the mobile phase is methanol–water.

dipole-dipole and permanent dipole-induced dipole interactions. In the reversed-phase mode, the retention is mainly controlled by the dispersive interactions between hydrophobic analyte and adsorbent fragments and the analyte-mobile phase solvation effects. In the case of the Chromalite 5HGN packing, another situation may take place in which planar stacking of the analyte pi-systems and the adsorbent pi-electron donating-accepting fragments plays the decisive role. This situation often occurs in non-aqueous non-polar environments mentioned above as the "quasi-normal-phase" mode of chromatography [9].

Hypercrosslinked polystyrene is not the only adsorption material that exhibits pi-electron donating-accepting properties. In fact, rather simple tests indicating the presence and strength of pi-interactions in a chromatographic system under quasi-normal-phase and/or normal-phase conditions can be suggested. We used the selectivity factor α for the anthracene–phenol pair, determined under appropriate arbitrary conditions. From data presented in Table 1 for the normal-phase mode one can see that the value of selectivity α for anthracene–phenol is zero for bare silica gel that does not have any pi-system-containing fragments on the surface. The corresponding value for the hypercrosslinked polystyrene exhibiting strong pi-interaction activity is very large, since anthracene is retained nearly irreversibly under these conditions. Other packings that contain aromatic systems, like pyrene- (fluorene)-modified silica packings, chiral Pirkle-type (Regis Technologies) columns and Chiralcel OD (Diacel Chemicals), also display pi-interaction activity (Table 1). Porous graphitic carbon (PGC) [11] can be expected to reveal under quasi-normal-phase conditions a strong pi-interaction activity, comparable to that of hypercrosslinked polystyrene.

The separation selectivity of the pair benzene-nitrobenzene can be used as a criterion of the contribution to retention from pi-interactions in the reversed-phase mode of chromatography (Table 2). Pi-interactions are stronger in the case of nitrobenzene than with benzene, thus the value of selectivity benzene-nitrobenzene is minimal for C$_{18}$ packing (no pi-interactions) and it is a maximum for hypercrosslinked polystyrene. Interestingly, porous graphitic carbon yields to Chromalite 5HGN with respect to pi-electron donating-accepting ability according to the above criterion.

The next important subject to mention is the chemical or physical nature of the pi-pi-interactions. In our point, one can consider pi-interactions as special kind of dispersive interactions between conjugated pi-electron systems of high polarizability, including charge transfer interactions. Hennion et al. [12] established an interesting regularity in the retention on porous graphitic carbon of mono-, bi- and trisubstituted benzenes. The retention of the latter was observed to increase with an increase of pi-electron density gradients in molecules, named the local dipoles. Even the electron resonance structures of the analyte molecules were found to be applicable to the estimation of their retention in quasi-normal-phase chromatography. Remarkably, retention of bi- and trisubstituted benzenes on both porous graphitic carbon and hypercrosslinked polystyrene drops in the order *meta-*, *para-*, *ortho-* for all possible combinations of the pi-donor or pi-acceptor activity of substituents. The reason obviously is that in the case of *meta*-substitution, the magnitude of the resonance effect is always the highest, thus providing maximum local pi-electron density dipoles.

4. Application of PCA to the elucidation of retention mechanisms

Generally the retention of an analyte is the sum of different types of its interaction with the stationary and mobile phase. In an attempt to discriminate between certain interaction mechanisms and estimate their contribution to retention we processed the experimental retention data by applying PCA.

PCA became a useful tool for the characterization of stationary phases in chromatography [13]. The main assumption of PCA is that the matrix of observed quantitative characteristics of a given system can be represented as a combination of a smaller amount of hypothetical unobserved linearly independent characteristics, named factors. Thus, if there are any strong correlations between observed characteristics of the system, PCA will reduce the amount of initial experimental data, without any loss in their self-descriptiveness. In this way, all experimental data will be finally described by a limited number of extracted factors,

which can be considered as "objective" tendencies of a system. However, in order to get some meaningful information from the experimental data matrix, one must interpret the factors calculated at the end.

In our previous PCA experiments [9], we extracted factors from the matrix of $\log k'$ values, where the objects (lines) were adsorbates (mono-substituted benzenes) and the subjects (columns) were the testing conditions. (In our experiments the mobile phase compositions have been varying, but the column temperature or model mixtures of adsorbates may serve as variables for PCA, as well). The PCA procedure results in factors, which are the linear independent characteristics of the chromatographic packing material within the range of conditions examined. In this way, PCA factors can play a role of parameters that reflect the prevalence of certain retention mechanisms in a given chromatographic system. This approach was earlier used to reveal the electrostatic character of adsorption of substituted benzoic acids on silica gel [14,15]. We used PCA to evaluate the contribution of pi-interactions to the retention on hypercrosslinked polystyrene in quasi-normal-phase mode [9].

5. Experimental

5.1. Apparatus

The chromatographic system consisted of HPLC pump (Bischoff) with a manual injection valve (Rheodyne) equipped with 20 μl sample loop and UV detector (Knauer).

A HPLC column 250 mm × 4.6 mm, i.d. was packed with an experimental monosized spherical 5 μm Macronet Gel neutral hypercrosslinked polystyrene beads, Chromalite 5HGN (Purolite, UK). The C_{18} column was 250 mm × 4.6 mm, i.d. Zorbax SB-C_{18}. All chromatograms were obtained at a flow rate of 1 ml/min and ambient temperature with a UV detector at 254 nm.

5.2. Chromatographic and PCA experiments

To elucidate retention mechanisms on hypercrosslinked polystyrene two sets of experiments were carried out. In the first series of experiments the Macronet Gel column was examined under quasi normal-phase conditions. Three mobile phases, pentane –CH_2Cl_2– isopropanol of different compositions were applied (60:20:20), (70:20:10) and (85:5:20), at a flow rate of 1.0 ml/min. The experimental test mixture was composed of 13 adsorbates, four aromatic hydrocarbons (benzene, toluene, naphthalene and anthracene), seven monosubstituted benzenes (acetophenone, benzaldehyde, phenol, anisol, aniline, acetanilide, bromobenzene, nitrobenzene), and acetone.

The second experimental series was carried out on Macronet Gel and silica-bonded Zorbax SB-C_{18} packings under reversed phase conditions. The test mixture was composed of 8 adsorbates: benzene, toluene, naphthalene, acetophenone, phenol, acetanilide, bromobenzene, nitrobenzene. When using Macronet Gel as stationary phase, three mobile phases were tried, acetonitrile:tetrahydrofuram (THF):water (70:10:20), acetoni-trile:CH_2Cl_2:water (80:10:10) and acetonitrile:isopropanol:water (70:20:10). In the experiment with Zorbax SB-C_{18}, two mobile phases were tried, acetonitrile:water (70:30) and (60:40).

The retention data were processed by the method of principal factor analysis [9]. Two factors F11 and F12 with contributions 95.76 and 3.76%, respectively, were extracted from the retention data matrix on Macronet Gel under the quasi normal-phase conditions. Only one factor F2 with a contribution of 99.85% was extracted from the data describing retention on Macronet Gel under the reversed-phase conditions. Similarly, one single factor F3 with contribution 99.96% was derived from the data describing the experiment carried out on Zorbax SB-C_{18} bonded silica [9].

Other application experiments were made with the use of Chromalite 5HGN and Zorbax SB-C_{18} columns under chromatographic conditions specified in legends to corresponding figures.

6. Discussion

6.1. Retention mechanisms on hypercrosslinked polystyrene in different chromatographic modes

Two factors F11 and F12 extracted from data describing the retention on Macronet Gel under quasi normal-phase conditions contribute to the retention of analytes examined in a proportion of 96 and 4%, respectively. The major factor F11 was found to reveal a perfect correlation with the sigma-para Hammet–Taft constants of substituents at the benzene ring of the analytes ($R = 0.994$ and 0.986 for substances with electron-accepting and electron-donating substituents, correspondingly). This constant is generally responsible for the conjugation of a substitute with the reactive center through the pi-system of the benzene ring. Therefore, this factor was interpreted as the one reflecting the activity of the electronic system of the analyte and the intensity of its interaction with the pi-systems of the adsorbent. F11 was named "pi-factor" [9].

The single factors, F2 and F3, were obtained under reversed-phase conditions for the hypercrosslinked polystyrene and C_{18} packings, respectively, with contributions amounting to approximately 99.6 and 100%. This was interpreted as an indication of one single mechanism governing the dependence of the retention of analytes on the mobile phase composition under RP conditions. Moreover, this mechanism should be basically the same for the two packing materials under comparison, since good correlation ($R = 0.948$) was found to exist between F2 and F3, if PAHs are excluded from consideration. Factors F2, F3 were thus named "the reversed-phase mechanism" descriptors. Reversed-phase mechanism is complex and involves both dispersive solute/sorbent interactions and solute sol-

vation effects, which proved impossible to discriminate by the PCA method. The evident failure of PCA in this case does not deal with the method itself, for it differentiates only tendencies that differently influence the retention selectivity. Though the hypercrosslinked polystyrene packing shows much stronger retention and unusual elution order of analytes under reversed-phase conditions compared to the alkyl-modified silica, the above three mobile phase additives do not influence the separation selectivity of the analytes examined on the two packings.

The above minor factor F12 obtained under the quasi-normal-phase conditions for Chromalite 5HGN reveals good correlation with the "reversed-phase" factor F2 ($R = 0.930$) and, therefore, can also be recognized as the "reversed-phase" one. Thus, two particular retention mechanisms on hypercrosslinked polystyrene in quasi-normal-phase mode can be identified: the major mechanism involves pi-interactions, and the minor one is of the reversed-phase origin. It is important that the relative contributions from these two mechanisms can be varied. Increasing concentration of a highly polar additive (2-propanol, methanol or acetonitrile) in the non-polar mobile phase leads to an increase of the reversed-phase mechanism contribution and the shift of the selectivity toward the reversed-phase kind of separation. Using highly polar organic mobile phases, for instance chloroform:methanol of 1:1, makes the contributions from the both mechanisms roughly equal. In our previous work [16], the specificity of such conditions of adsorption on hypercrosslinked polystyrene was reflected by the term "the mixed RP-NP-mode chromatography".

On Fig. 3, three chromatograms of a model mixture under reversed-phase, mixed mode and quasi-normal-phase
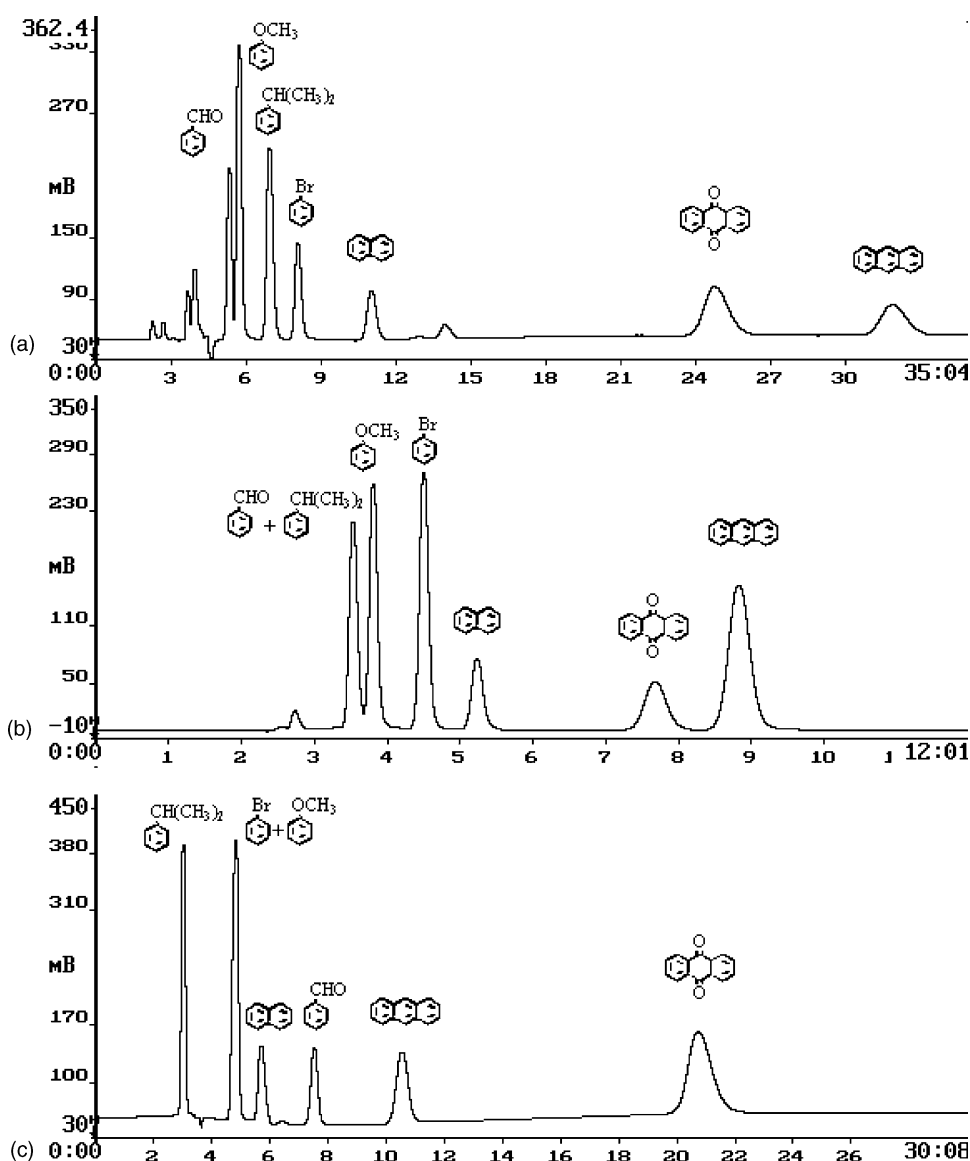

Fig. 3. Test mixture chromatograms in different elution modes on Chromalite 5HGN packing: (a) the reversed-phase mode, mobile phase acetonitrile–2-propanol–water (80:15:5, v/v); (b) the mixed mode, mobile phase chloroform–methanol (1:1, v/v); (c) the quasi-normal-phase mode, mobile phase hexane–chloroform (80:20, v/v).
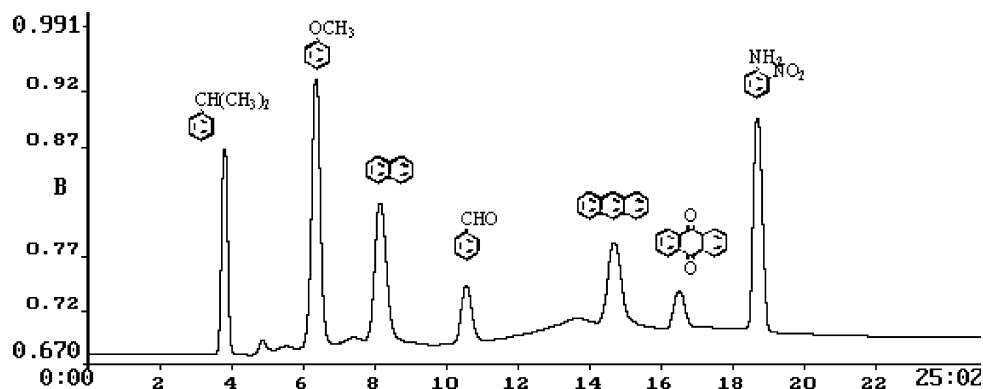
Fig. 4. Example of a gradient run from a quasi-normal-phase to a mixed mode on Chromalite 5HGN. Mobile phase A: hexane–chloroform (80:20, v/v), mobile phase B: chloroform–methanol (2:1, v/v); 0–100% B in 25 min.

conditions are shown, displaying the way in which the corresponding selectivities change while chromatographic conditions switch from the RP to QNP, two extreme types of elution. The explicit decrease in retention over the first step (Fig. 3a and b) should be noted for analytes with aliphatic moieties, such as cumene and all aliphatic compounds, due to the reduction of dispersive interactions with the sorbent. In the second step to QNP mode, retention of carbonyl-containing compounds significantly increases (Fig. 3b and c). This effect is probably due to the desolvation of the carbonyl group, which makes this group available for intensive pi-interactions with the stationary phase. The retention increment from this interaction in the quasi-normal-phase mode is obviously higher for the carbonyl group than for the phenyl group.

Thus, understanding of retention mechanisms and their interplay on a given stationary phase can prove essential for the well targeted tuning of separation conditions.

6.2. Potentials of hypercrosslinked polystyrene in LC and SPE applications

Column equilibration under any conditions with hypercrosslinked polystyrene packings takes little time, and thus various gradient elution modes are possible. On Fig. 4 the chromatogram is shown demonstrating the range of polarities of analytes that can be separated with a gradient that starts with "pure" quasi-normal-phase conditions and finishes with mixed-mode conditions. Changing the basic retention mechanism during the gradient run enhances significantly the flexibility of the method and also opens new opportunities for using hypercrosslinked polystyrene in SPE cartridges for a selective concentration of target compounds from their solutions in organic solvents.

One of the striking flexibility examples justifying the use of hypercrosslinked polystyrene deals with the analysis of aromatics. In fact, several approaches to this problem can be developed, depending on particular tasks. Under
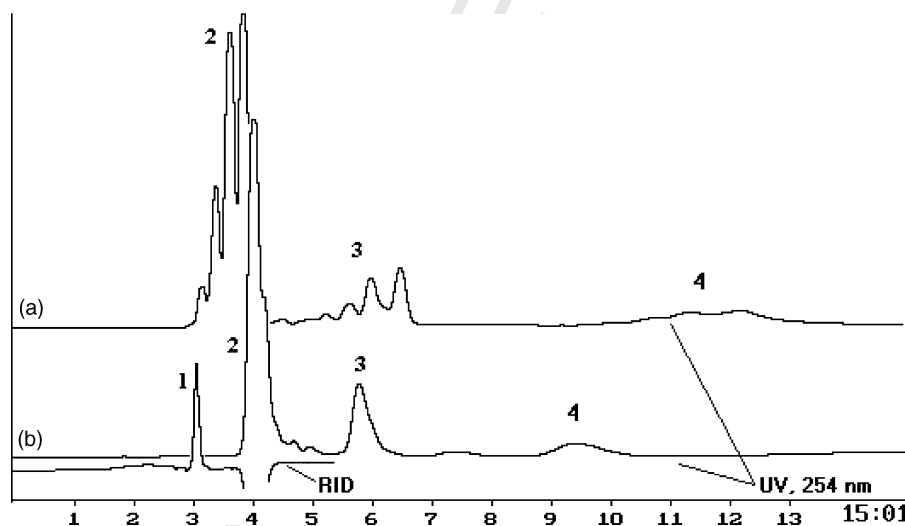

Fig. 5. Group analysis of hydrocarbons in gasoline on Chromalite 5HGN packing in different modes: (a) the quasi-normal-phase mode, mobile phase hexane–chloroform (80:20, v/v); (b) the mixed mode, mobile phase methanol–chloroform (1:1, v/v). (1) Aliphatic compounds, (2) mono-, (3) bi-, (4) triaromatic compounds.
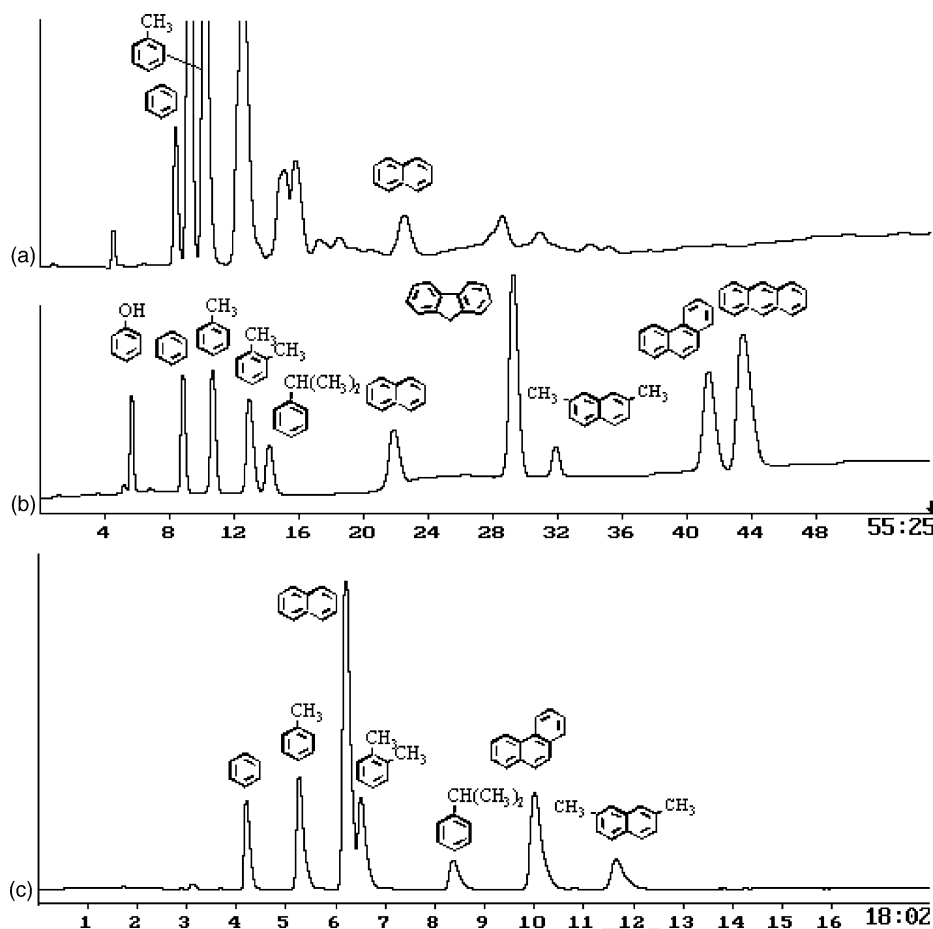
Fig. 6. The analysis of aromatics in the reversed-phase mode on Chromalite 5HGN and Zorbax SB-C$_{18}$ packings. (a) Gasoline Ai-95, stationary phase: Chromalite 5HGN, mobile phase A: acetonitrile–2-propanol–water (55:25:20, v/v), mobile phase B: acetonitrile–2-propanol (70:30, v/v), 0–100% B in 35 min, then 100% B for 20 min; (b) test mixture of 10 aromatic compounds, chromatographic conditions are the same as in (a); (c) test mixture of seven aromatic compounds, stationary phase: Zorbax SB-C$_{18}$, mobile phase: acetonitrile–water (70:30, v/v).

quasi-normal phase conditions (Fig. 5a), besides the good separation of mono-, bi- and triaromatic compounds, separation of alkyl-substituted analogs and isomers takes place within each group. Size exclusion effects in fine pores of the polymer matrix can be expected to contribute to this separation, since unsubstituted benzene and naphthalene elute last in the groups of mono- and biaromatics compounds, respectively.

The mixed-mode elution conditions best suit to the group analysis of aromatics (Fig. 5b), since the peak splitting within each group of mono-, bi- and triaromatic compounds is mainly suppressed. Due to the high group selectivity under these conditions, the separation can be also realized in low-pressure LC an SPE. Thus, concentrating of PAHs from their hexane solutions on hypercrosslinked polystyrene Purosep-200 is an example of a successful quasi-normal-phase SPE application of the material. Preliminary experiments on concentrating aromatics from hexane solutions showed that the more polar, nitrated hypercrosslinked polystyrene retains the PAHs even better than the neutral polymer, for the nitrated material displays stronger pi-electron accepting ability.

In the reversed-phase mode analysis of aromatics, one can take advantage of the unusually strong group-selectivity of the Chromalite 5HGN packing, which permits an acceptable separation of both the groups and several compounds within each group (Fig. 6a and b). On conventional C$_{18}$ packings, groups of mono-, bi- and tri-aromatics strongly overlap (Fig. 6c).

7. Conclusions

Application of PCA technique to the elucidation of retention mechanisms was found to be a convenient approach to reveal the distinct features and potentials of a novel HPLC packing material, hypercrosslinked polystyrene. This adsorption material displays two particular retention mechanisms, one involving pi-interactions between aromatic systems and/or groups with lone electron pairs and another providing the reversed-phase-like elution order due to dispersive interactions and solvation effects.

Hypercrosslinked polystyrene can be used in all non-polar, medium polar and highly polar environments,

428 which correspond to quasi-normal-phase, mixed and
429 reversed-phase chromatographic modes. Each of the modes
430 results in specific retention regularities, thus providing high
431 flexibility of separation methods involving hypercrosslinked
432 polystyrene in HPLC, SPE and LC.

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