Properties of microdispersed sintered nanodiamonds as a stationary phase for normal-phase high performance liquid chromatography

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ABSTRACT

The chromatographic properties of microdispersed sintered nanodiamonds (MSND) are studied under conditions of normal-phase HPLC. The retention characteristics of 30 substances representing four classes of aromatic compounds including monoalkylbenzenes, polymethylbenzenes, di-n-alkyl phthalates and polyaromatic hydrocarbons in n-alkane mobile phases have been measured. The selectivity of MSND was compared with literature data for other common adsorbents including silica gel, alumina and porous graphitic carbon (PGC). MSND shows the distinctive adsorption properties especially in a stronger retention of aromatic hydrocarbons and in the better selectivity of the separation of geometric isomers. The significant improvement in separation efficiency up to 45,300 theoretical plates per meter, was achieved for the first time for the columns packed with diamond related materials (DRM).

1. Introduction

The development of new stationary phases remains one of the most challenging tasks in the development of high performance liquid chromatography (HPLC). Many different stationary phases have been investigated as an alternative to the traditional adsorbents since the introduction of HPLC and no perfect material has been suggested yet. In the last five years, there has been increasing demand towards the mechanical, hydrolytic and thermal stability of the column packing with the development of ultra-performance liquid chromatography (UPLC). The unique physicochemical properties of diamond such as excellent mechanical stability at high pressures, chemical resistance to strong acids or bases, absence of swelling or shrinking in different organic solvents as well as the possibility of chemical modification of the surface make diamond related materials (DRM) potentially an "ideal" stationary phase for the use in HPLC/UPLC.

The earliest attempt of using diamond as a stationary phase in HPLC dates back to 1973, when Telepchak reported the partial separation of benzene and anthracene on a 250 × 3.0 mm I.D. column packed with natural diamond microparticles of 10 μm diameter using a methanol–water (30:70) eluent [1]. After almost 30 years

of the first publication, Patel et al. [2] investigated the possibility of using synthetic porous disperse diamonds (PDD) for the separation of organic substances in both reversed-phase and normal-phase HPLC. This work presented poorly resolved chromatographic peaks of para- and ortho-xylenes separated in heptane on a 100 × 4.6 mm I.D. column packed with 4 μm PDD particles. Both publications noted very poor values for column efficiency, 1500 and 2500 theoretical plates per meter, respectively.

Recently, a significant improvement in separation efficiency was reported for a column packed with microdispersed sintered nanodiamonds (MSND) [3]. The additional purification and careful fractionation of MSND particles on size resulted in a better quality column packing and a higher column efficiency, up to 15,400 theoretical plates per meter, that allowed the baseline separation of a 6–7 component mixture on 150 × 4.0 mm I.D. column in normal-phase HPLC mode. The ion-exchange and complexing properties of MSND were exploited in ion chromatography for the separation of alkaline-earth and transition metal cations [4].

Liu and Lee presented at PittCon 2008 conference an example of the separation of parabens under conditions of ultrahigh pressure liquid chromatography using a 215 mm × 75 μm I.D. fused-silica capillary column packed with 1 μm nonporous synthetic diamond particles [5]. The authors also used polybutadiene-coated diamond particles for the improvement of the separation selectivity. However, the observed column efficiency was significantly less in case of PBD-coated diamond packing as compared with bare diamond particles.

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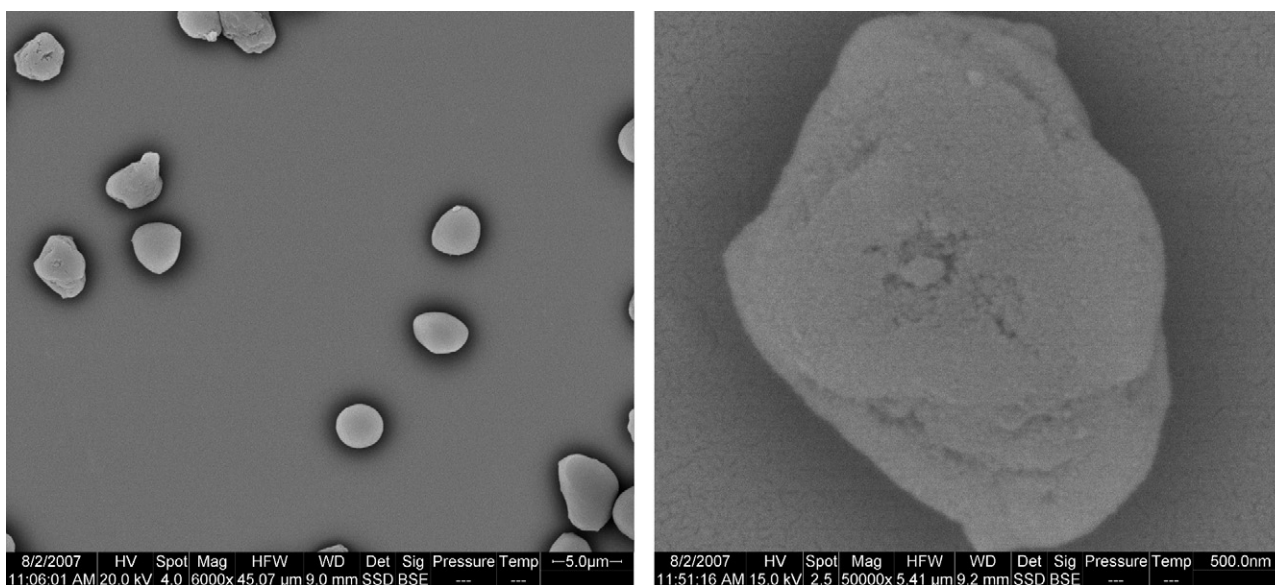E-mail address: Pavel.Nesterenko@utas.edu.au (P.N. Nesterenko).

Fig. 1. SEM micrographs of MSND.

Muna et al. used a chromatographic column packed with 8–12 μm nonporous diamond particles coated with a layer of boron-doped diamond in electrochemically modulated liquid chromatography (EMLC) [6]. EMLC manipulates the retention of solutes by modulation of the potential applied to the electroconducting stationary phase. The pure diamond has a high electrical resistivity of approximately 10^{16} Ωcm. Before its use in EMLC, it was coated with a conducting layer of boron-doped diamond by means of microwave plasma-assisted chemical vapour deposition (CVD). The mixture of three benzenesulfonic acids was separated on a 78 × 3 mm I.D. column at an applied potential +0.3 V with 0.1 M LiClO₄ as the eluent.

Korolkov et al. [7] used normal-phase HPLC for the characterization of the adsorption properties of PDD hydrogenated at 800 °C. However, no separations are presented.

The chemical inertness, absence of cytotoxicity and excellent biocompatibility of diamond related materials (DRM) can be utilized for the isolation and purification of biomolecules. Purtov et al. described the preparation and usage of nanodiamond coated Sepharose 2B for the highly selective isolation of luciferase by low-pressure liquid chromatography [8].

The number of publications on the use of DRM as a stationary phase in column liquid chromatography is still small. The majority of studies in this area are related to the introduction of new types of DRM in chromatographic practice and at present MSND is one of the most interesting adsorbents. However, due to the complex surface chemistry the adsorption properties of MSND need to be investigated more systematically. From the first glance MSND has many polar groups at the surface and can be used in normal-phase HPLC. So, the aim of this current investigation is to study the adsorption and chromatographic properties of MSND and to compare them with the properties of other common adsorbents.

2. Experimental

2.1. Instrumentation

A Shimadzu 10A series HPLC system including two LC-10Ai pumps, Rheodyne 7125 injection valve equipped with a 20 μL sample loop, CTO-10ASvp column oven, SPD-10Avp spectrophotometric detector and SCL-10Avp controller was used. A stainless-steel chromatographic column 150 × 4.0 mm I.D. was slurry packed under constant pressure (40 MPa) with MSND particles in an acetone-ammonium acetate buffer mixture.

Scanning electron microscopy (SEM) images were obtained using an FEI Quanta 600 MLA ESEM microscope combined with Electron Probe Microanalysis (Eindhoven, The Netherlands). FTIR spectra were recorded with Bruker IFS 66 spectrometer (Sydney, Australia). BET surface area measurements of MSND were made using a Micromeritics TriStar II analyser (Norcross, GA, USA).

2.2. Adsorbent preparation and characterization

The final batch of MSND batch was prepared using commercially available PDD 3-6 powder (ALIT Co, Kiev, Ukraine), which was suspended in a water solution. Additional fractionation of the particles based on size was carried out following ultrasonication of the suspension and time controlled sedimentation. The vigorous shaking for prolonged and multiple frictions between particles caused self abrasive polishing and transformation of their original irregular shape. The isolated MSND particles of 3.5–5.0 μm size had approximately oval or spherical shape (Fig. 1). The specific surface area of the final product is 191 m²/g and average pore diameter is about 4.0 nm according to BET measurements of nitrogen adsorption. Before packing the isolated fraction of MSND was washed consecutively with 0.1 M nitric acid, 0.02 M dipicolinic acid, deionized water and 2-propanol.

2.3. Reagents

HPLC-grade *n*-pentane (Panreac, Barcelona, Spain), *n*-hexane and 2-propanol (Khimmed, Moscow, Russia) were used for the preparation of mobile phase. Analytical grade nitric acid and dipicolinic acid were purchased from Khimmed (Moscow, Russia). A series of pure alkylbenzenes, di-*n*-alkyl phthalates, polyaromatic hydrocarbons and other substances were of the highest available grade and used as 3 mM solutions in *n*-hexane.

3. Results and discussion

The synthesis of detonation nanodiamond (ND) was developed in 1963 in USSR [9]. The simplified scheme of the synthesis can be described as the explosion of a mixture of two powerful carbon containing explosives (e.g. trinitrotoluene and hexogen) in a closed

vessel with strong walls under oxygen deficiency. The reaction product is the soot consisting of nanodiamond of average diameter 5–6 nm, graphite and metal impurities. The isolation of ND includes oxidation of the graphite phase with strong oxidants and the removal of metals impurities by strong acid wash. At present ND and their agglomerates are widely used in various polishing compositions.

ND particles are too fine to be used as a column packing, so they can be utilized as aggregates or in the form of in-pore-entrapped organosoles [8,10] or as the coatings of bigger particles of suitable materials [2–4]. One of the most convenient ways of preparing nanodiamond aggregates is a sintering at pressures higher than 3 GPa and temperatures above 1000 °C. The maximum size of the prepared particles is about 30–35 μ, so after sintering the agglomerates are crushed and fractionated on size before use [11,12]. There are different names in use for the nanodiamonds agglomerates including ultradisperse diamond (UDD) and polydisperse diamond (PDD), but the more convenient is microdispersed sintered nanodiamonds (MSND) reflecting the whole preparation process.

MSND particles have a sandstone type of structure comprising of few nanometer range detonation nanodiamonds. Similarly to nanodiamonds, MSND have a very complex surface chemistry because of the harsh conditions used for the synthesis and purification. It should be noted that the chemical properties of nanodiamond vary strongly from one producer to another and no standard procedure for the preparation of ND with chemically homogeneous surface has been established. Anyway, about 20 different functional groups bonded to sp^2 and sp^3 forms of carbon have been found at the surface of ND [13]. The major functional groups are carboxylic, hydroxyls and ethers providing ion-exchange and hydrophilic properties to the surface of MSND. It means that MSND can be used as a stationary phase in normal-phase HPLC, IC, hydrophilic interaction liquid chromatography (HILIC). The potential use of diamonds as a separation medium is recently reviewed [14].

3.1. Physical and chemical properties of nanodiamond and related materials

Because very small size nanoparticles can't be directly used as a column packing in chromatography, so few approaches have been used to explore the potential of using ND. The packing prepared by mixing nine parts of CaF$_2$ particles of diameter 0.21–0.60 mm with one part of nanodiamonds was used for GC of corrosive gases [15]. Recently, Purtov et al. [8] used polysaccharide based Sepharose 2B support with hydrosols of ND particles retained in the pores for low-pressure liquid chromatography of biomolecules. However, only MSND possesses all properties to be used in HPLC.

According to producer's data PDD 3-6 contains 12% particles of diameter less than 3 μm, 75% – less than 3–5 μm and the rest are particles of diameter 5–7 μm. The specific surface area 153 m^2/g of PDD 3-6 is due to the presence of mesopores with a diameter between 1.2 and 7.5 nm, and total pore volume 0.38 mL/g [10]. Yushin et al. [12] reported about trimodal distribution of pores on size in PDD 3-6 with maxima at 0.7, 1.4 and 3.2 nm. The MSND batch used in our investigation had a slightly higher specific surface area 191 m^2/g. In general terms, both pore size and surface area of MSND meet the requirements to be used as column packing in HPLC.

MSND particles comprise ND particles, so the adsorption properties for the both of materials should be similar. The surface chemistry of ND is complex and depends substantially on their oxidative isolation from the post blast soot and purification [13,16,17]. Before oxidative purification, the ND fraction contains different carbon forms (83–89%), nitrogen (>3%), hydrogen (0.8–3.3%), oxygen (up to 4%), and an incombustible residue (0.5–8.0%) [16,18]. At the same time carbon in ND is represented
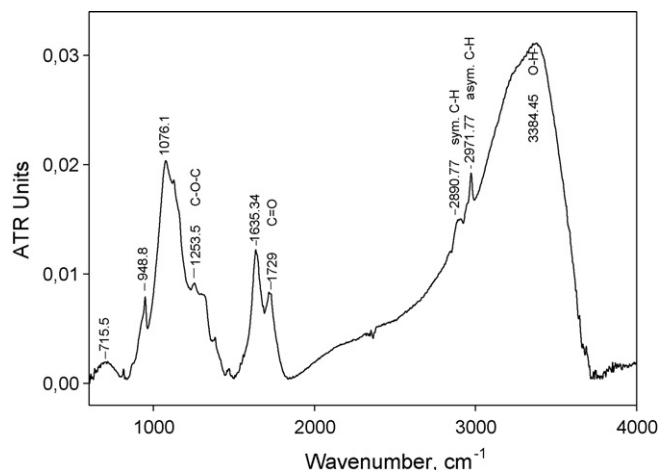

Fig. 2. FTIR spectrum of MSND.

by a mixture of sp^3 diamond (90–97%) and sp^2 graphite (3–10%). Incombustible residue usually consists of metals and metal oxides. The oxidative treatment removes the graphite phase and significantly increases the oxygen content up to 9.0–10.5% [19]. After the treatment ND contains 0.34–2.52 μeq/m^2 of protogenic groups, whereas the total concentration of groups containing active hydrogen varies between 0.49 and 7.52 μeq/m^2 [17,20]. The significantly higher concentration of carboxylic groups, 9.6 μeq/m^2, at the surface of oxidized diamond has been also reported [19]. For comparison, the concentration of silanols on a fully hydroxylated silica surface is about 8 μmol/m^2 [21]. Obviously, the high concentration of negatively charged groups at the surface of ND is responsible for the high values of zeta-potential up to −100 mV [22].

According to FTIR spectra ND surface contains mainly oxygen-containing carboxyl, carbonyl, hydroxyl, lactone and ether functional groups [17,23,24]. The presence of a minor amount of other polar groups –NH$_2$, =NH, –NO$_2$, and non-polar – >C=C<, –CH$_3$, =CH$_2$ and C–H has been also noted. The total concentration of functional groups can reach 15 μmol/m^2 or 9 groups/nm^2 which is almost twice as much as the concentration of silanol groups on fully hydroxylated silica surface [19,21]. Fig. 2 shows the FTIR spectrum of MSND sample with distinctive absorption bands at 2971.77 and 2890.77 cm^{-1} due to asymmetric and symmetric stretching C–H vibration, at 1729 cm^{-1} for the stretching vibration of carbonyl groups and at 1253.5 cm^{-1} for ether groups. The stretching and deformation O–H vibrations are responsible for absorption peaks at 3384.45 and 1076.1 cm^{-1}, respectively.

Thus, MSND is a hydrophilic polar adsorbent having a developed mesoporous structure and surface area sufficient to provide a reasonable loading capacity for a chromatographic column. The combination of these properties makes possible the use of bare MSND in normal-phase HPLC as it was recently demonstrated [2,3]. Normal-phase HPLC can provide substantial information on adsorption properties of detonation ND.

3.2. Adsorption properties of MSND

3.2.1. Retention of alkylbenzenes

A simple and informative approach characterising the adsorption properties of adsorbents was proposed by Kiselev and co-workers [25]. He suggested the construction of retention-structure diagrams for alkylbenzenes with varying number of substituents and length of alkyl group. The diagrams are inclined to have a Y-type shape formed by two dependences. The left branch of the diagram represents the plot of the logarithms of the retention factors of polymethylbenzenes (as log k) against the number

Table 1
Retention factors (k) of alkylbenzenes on various stationary phases with n-pentane as eluent.

| No.	Compound	MSND	Silica gel [26]	Alumina [30]	PGC[a] [32]	PGC[b] [34]
1	Benzene	7.12	0.57	0.26	0.18	0.09
2	Toluene	9.97	0.58	0.33	0.45	0.16
3	p-Xylene	11.15	0.59	0.42	1.22	0.22
4	m-Xylene	12.48	0.57	0.48	1.04	0.22
5	o-Xylene	18.74	0.67	0.57	1.26	0.37
6	1,2,4-Trimethylbenzene	19.67	0.68	0.62	3.27	
7	1,3,5-Trimethylbenzene	12.69	0.58	0.53	2.31	
8	1,2,4,5-Tetramethylbenzene	24.40	0.71	1.14	9.78	
9	Hexamethylbenzene	65.35	0.97	3.40		
10	Ethylbenzene	8.43	0.53	0.32	0.47	
11	n-Propylbenzene	10.12	0.50	0.29	0.67	
12	Isopropylbenzene	4.69	0.54	0.27	0.35	
13	n-Butylbenzene	11.16	0.47	0.32	1.03	
14	sec-Butylbenzene	3.97		0.24	0.47	
15	$tert$-Butylbenzene	3.74	0.53	0.27	0.39	
16	n-Amylbenzene	12.88	0.45	0.34	1.89	
17	n-Nonylbenzene	19.10		0.37	18.96	
18	n-Decylbenzene	29.06	0.36	0.41	33.96	
19	m-Diisopropylbenzene	2.29	0.45	0.20	0.41	
20	1,3,5-Triisopropylbenzene	0.77				

[a] In methanol.
[b] In n-heptane.
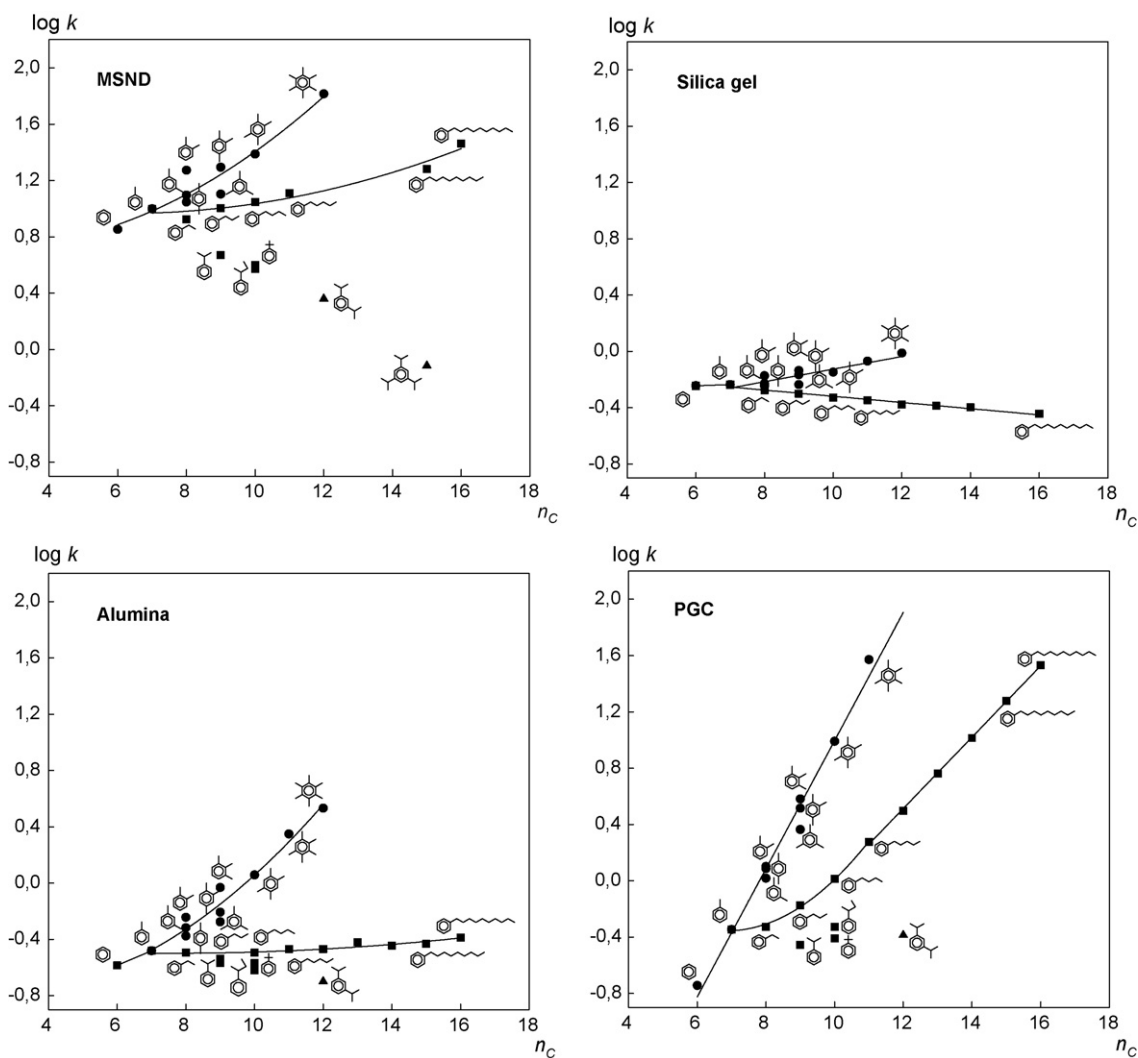
Fig. 3. Dependence of retention (as log k) of alkylbenzenes on carbon number (n_C) in n-pentane (MSND, silica gel and alumina) and in methanol (PGC). The plots for silica gel, alumina and PGC are rebuilt according to published data [26,30,32] to fit the same scale for all plots.

Table 2
The increments for methyl substitution $\alpha(CH_3)$ in benzene ring and for introduction of methylene group $\alpha(CH_2)$ alkyl chain of n-monoalkylbenzenes.

Adsorbent	Eluent	$\alpha(CH_3)$	$\alpha(CH_2)$
MSND	Pentane	0.158 ± 0.020; ($n = 9$)	0.059 ± 0.008; ($n = 7$)
Silica gel [26,32]	Pentane	0.046 ± 0.008; ($n = 10$)	-0.020 ± 0.001; ($n = 9$)
Alumina [30,32]	Pentane	0.195 ± 0.017; ($n = 11$)	0.018 ± 0.003; ($n = 10$)
PGC 70B-CL [32]	Methanol	0.460 ± 0.020; ($n = 9$)	0.247 ± 0.004; ($n = 8$)
PGC [34]	Heptane	0.309 ± 0.059; ($n = 4$)	No data

of carbons in the molecule (n_C) and the right branch–by similar plot built for n-monoalkylbenzens with different alkyl chain length. The retention of the other alkyl substituted benzenes is generally located between these branches. The corresponding diagrams have been built for particulate [25,26] and monolithic silica columns [27], chemically modified silicas [28,29], alumina [28,30], porous methacrylate copolymer [31] and porous graphitic carbon (PGC) [32]. In this current work, the retention of a set of 20 alkylbenzenes on MSND column in n-pentane was studied and compared with literature values for the retention of these compounds on silica, alumina and PGC (Table 1). Because of the lack of data on the retention of alkylbenzenes on PGC in n-alkanes, the data on retention in methanol were also used. The corresponding diagrams $\log k$–n_C for the selected adsorbents are shown in Fig. 3 . There are four factors possibly affecting the retention of alkylbenzenes including (i) the number of alkyl groups, (ii) the length of alkyl group, (iii) the relative position of alkyl substitutes in benzene ring and (iv) the bulkiness of the alkyl groups.

3.2.1.1. Number of alkyl groups. The electron density in the benzene ring defines the interaction energy between the alkylbenzene molecule and the surface of the adsorbents in normal-phase LC. The electron density in the aromatic ring depends on the number of alkyl substitutes due to the donation of electrons through σ bonds also known as positive inductive effect (+*I*-effect). Inductive effect depends on alkyl branching and to a lesser degree on their length. The effect of lengthening the n-alkyl chain in benzene homologues on the electron density in the benzene ring quickly becomes negligible starting with ethyl. Also the further increase of the alkyl chain length leads to a stronger interaction between alkylbenzene molecules and a non-polar mobile phase such as n-hexane or n-pentane. Thus, the number of substitutes in polyalkylbenzenes and the length of n-alkyl chain in monoalkylbenzenes produce the different effects on retention resulting in the inclined Y-shape of the diagram.

The addition of methyl groups to the benzene ring causes a stepwise increase in retention of alkylbenzenes for all selected adsorbents. This is due to the proportional growth of electron density in the benzene ring due to +*I*-effect of methyl groups (Fig. 3). The small variations in retention were noted for dimethyl-, trimethyl- and tetramethyl-positional isomers due to the redistribution of electron density in benzene ring. The corresponding effect, so called *ortho*-effect, will be further considered in Section 3.2.1.3. The slope of the plot $\log k$–n_C for polymethylbenzenes indicates the affinity

of the adsorbent to the increase in electron density in the aromatic ring of adsorbates. Polymethylbenzene molecules, with up to five methyl substituents have a planar structure, so the increase in the number of methyl groups produces a dramatic effect on the retention of polymethylbenzenes on PGC, because of the coplanar orientation between the adsorbate and the flat surface of PGC during adsorption. The value of the slope in case of MSND is closer to that for alumina rather than for silica. Interestingly, the retention of benzene, toluene and xylenes on MSND is significantly stronger than on any other studied adsorbents including PGC (Table 1).

3.2.1.2. Length of alkyl chain in monoalkylbenzenes. The lengthening of the alkyl chain in the monoalkylbenzene molecule results in a more complex retention-structure dependences. There are few reasons for this. On one side, the above mentioned increase of electron density in the benzene ring due to +*I*-effect takes place only for toluene and ethylbenzene and remains constant for other homologues. It resulted in a stronger retention of monoalkylbenzenes compared to benzene for all adsorbents (Table 1). On the other side, starting from n-propylbenzene the longer alkyl chains got "conformational freedom" to interact independently from the benzene ring with both the stationary and mobile phase. So, depending on the adsorbent properties the increment of alkyl chain can result in a linear increase (PGC, MSND, and alumina) or decrease (silica) of $\log k$–n_C (Fig. 3).

The positive increment of the methylene group in the retention of n-alkylbenzenes starting from ethylbenzene means the preferable interaction of long alkyl chain in the molecules of adsorbates with MSND surface rather than interaction with n-pentane used as a mobile phase. The corresponding increments of the methylene group are significantly smaller for alumina and are negative for silica (Table 2). In case of silica, the data was obtained for a fully hydroxylated surface having weaker interactions with alkyl groups as compared with an anhydrous surface. It is difficult to get reliable data on the retention of organic substances on the anhydrous silica because of its strong hydroscopic properties. Thus MSND demonstrates very good separation selectivity towards n-alkylbenzenes. Only PGC has a higher selectivity but it could be due to using more polar methanol as the eluent when alkylbenzenes are forced to interact with non-polar adsorbent.

3.2.1.3. Positioning of alkyl substituents in a benzene ring. The relative position of alkyl substitutes in benzene strongly influences on the retention of alkylbenzenes due to the so called *ortho*-

Table 3
Separation selectivity of isomeric xylenes on different stationary phases.

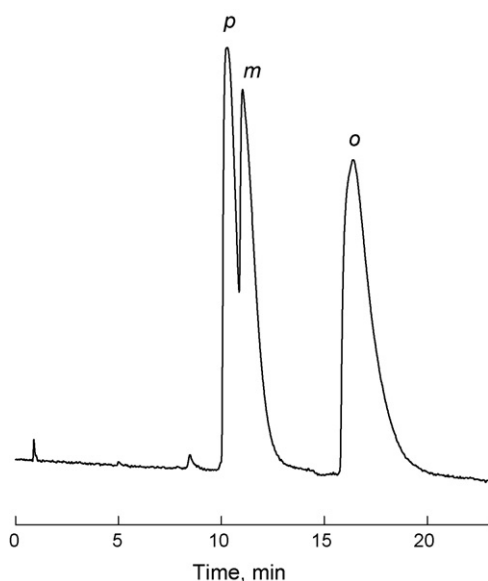| Stationary phase	Eluent	Retention order	Selectivity coefficient, α		
			m/p	o/m	o/p
MSND	Pentane	$p < m < o$	1.12	1.51	1.68
Silica gel [26]	Pentane	$m < p < o$	0.97	1.18	1.14
Alumina [30]	Pentane	$p < m < o$	1.14	1.19	1.36
PGC	Methanol [32,33]	$m < p < o$	0.85	1.21	1.03
	Heptane [34]	$m = p < o$	1.00	1.68	1.68
	Carbon dioxide–methanol (99:1) [35]	$m < p < o$	0.88	1.38	1.19

Fig. 4. Separation of xylenes on 150 mm × 4.0 mm i.d. MSND column. Eluent *n*-pentane. Flow rate 1.5 mL/min. Detection UV 254 nm. Sample volume 5 μL.

Fig. 5. Dependence of retention ($\log k$) on carbon number (n_C) in alkyl radicals in dialkylphtalate molecules on MSND (1, 3) and on silica gel (2), [36]. Eluent: *n*-hexane with addition of 5 vol.% (1), 1 vol.% IPA (3) and 0.1 vol.% IPA (2).

effect [32], when increased retention of the *ortho-* isomer relative to the *meta-* or *para-* forms occurs. The effect can be observed for those of di-, tri- and tetra-methylbenzenes where the *ortho*-positioning of methyl-groups is possible. Isomers with symmetrical arrangement of methyl-groups (*p*-xylene, mesitylene and 1,2,4,5-tetra-methylbenzene) are weaker retained as their polarity is less than that of asymmetrically substituted isomers. As a rule this effect is more profound in adsorption LC. The data on comparison of separation selectivity of isomeric xylenes on different adsorbents are presented in Table 3. The retention order of isomeric xylene *para* < *meta* < *ortho* obtained for MSND is the same as found for alumina, but *meta*-xylene is eluted before *para*-xylene from the silica column. Surprisingly no selectivity was observed for the separation of *meta*- and *para*-xylenes on the column packed with another carbonaceous adsorbent PGC in heptane [34], but the reasonable selectivity has been noted in more polar mobile phases (Table 3). MSND demonstrates the better separation selectivity than the rest of adsorbents, which allows reasonable resolution of the chromatographic peaks (Fig. 4).

3.2.1.4. Bulkiness of alkyl substituent. The bulkiness of the alkyl group can have an affect on the retention of alkylbenzene molecules *via* size exclusion effects, which could be noticeable in the case of MSND having a significant amount of micropores [12]. For example, the retention of isopropylbenzene on the MSND column is two times less than that of *n*-propylbenzene (Table 1). The more profound effect of bulkiness of the substituent on retention is observed for butylbenzenes. The *tert*-butylbenzene ($k = 3.74$) is less retained than *sec*-butylbenzene (3.97) and is three times less than *n*-butylbenzene (11.16). The presence of few bulky substituents in one benzene ring produces a further drop in retention of alkylbenzenes on the MSND column. Thus the retention factor of isopropylbenzene ($k = 4.69$) is twice as high as than for *m*-diisopropylbenzene ($k = 2.29$) and is six times higher than of 1,3,5-triisopropylbenzene ($k = 0.77$). Surprisingly, the substantial increase in electron density of the benzene ring due to presence of several isopropyl substituents (see discussion in Section 3.2.1.1) does not cause any increase of retention times. Obviously, this is connected with the poor alignment of the aromatic molecule having bulky substituents for getting optimum coplanar orientation
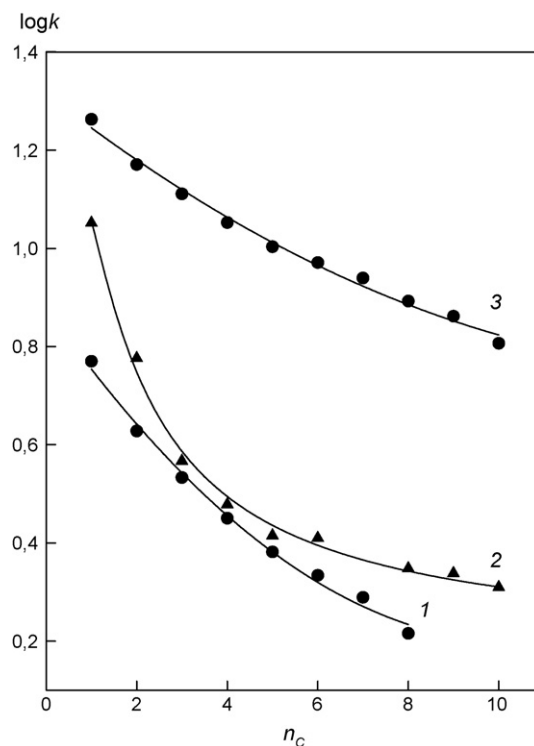
towards the MSND surface during adsorption. The similar regularity has been observed for PGC but not for silica and alumina.

3.2.2. Retention of di-n-alkyl phthalates

One more class of compounds of interest for the characterization of MSND properties is di-*n*-alkyl-*ortho*-phthalates. The retention of alkylphthalates on an MSND column in hexane containing 1–5 vol.% of isopropanol decreases with increase of carbon number in alkyl chains (Fig. 5). The lengthening of alkyl chains in di-*n*-alkylphtalates diminishes the retention, which is opposite to the regularity observed for *n*-alkylbenzenes (see Section 3.1.2.2). The different character of dependences could be due to *ortho*-effect discussed earlier in Section 3.2.1.3 and also because of a stronger interaction of di-*n*-alkylphtalates with mobile phase. Unlike silica (Fig. 5) $\log k$–n_C dependence for MSND is practically linear which is convenient for the chromatographic separation of alkylphtalates homologues. The example of efficient separation of di-*n*-alkyl phthalates on MSND column was presented in our previous communication [3]. This class of substances retains stronger on MSND as compared to silica gel.

3.2.3. Retention of polyaromatic hydrocarbons

The relative retention of polyaromatic hydrocarbons (PAH) on MSND is of particular interest because it can indicate how a flat diamond surface interacts with planar molecules. In his early investigation Telepchak has noted a high separation selectivity of benzene and anthracene on a column packed with natural diamonds [1]. An analogy was also noted in several investigations on chromatographic retention of polyaromatic hydrocarbons (PAH) on another carbonaceous stationary phase PGC. It is well known that PGC has a flat and regular surface which results in enhanced selectivity in the separation of geometric and diastereomeric isomers and in a strong retention of planar molecules like PAH [37,38]. In
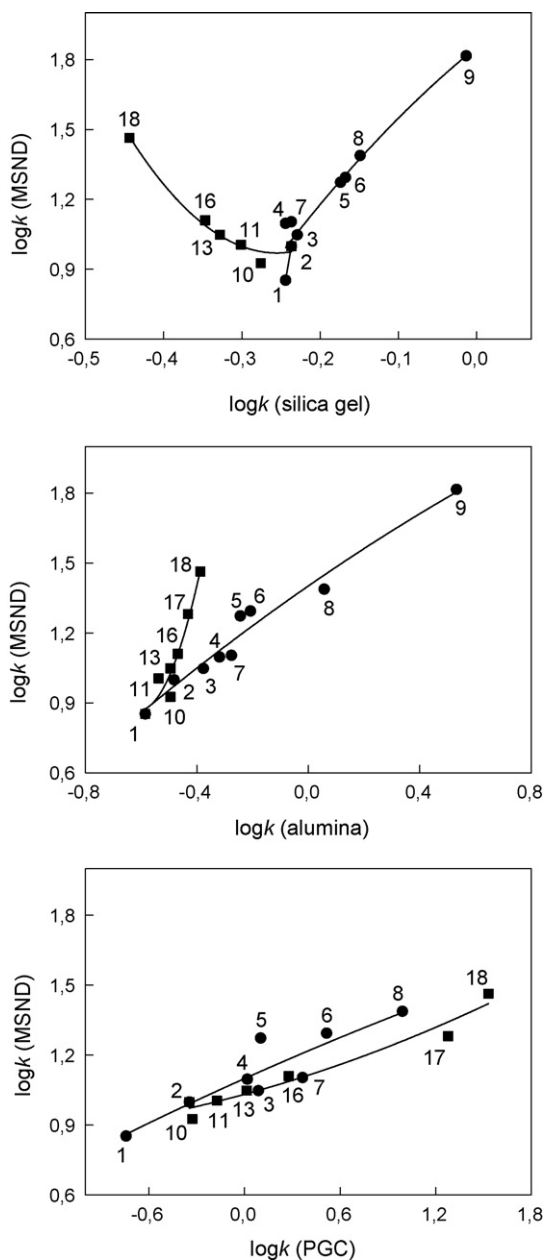
Fig. 6. Correlation between retention (as log *k*) of alkylbenzenes on MSND and silica gel (a, [26]), alumina (b, [30]) and PGC (c, [32]). Solutes numbering is given in Table 1. Analytes: (■) *n*-alkylbenzenes, (●) polymethylbenzenes. Other conditions as in Fig. 3.

Fig. 7. Separation of alkylbenzenes on MSND column. Solutes: (1) 1,3,5-triisopropylbenzene, (2) 1,3-diisopropylbenzene, (3) *tert*-butylbenzene, (4) iso-propylbenzene, (5) benzene, (6) toluene, (7) *n*-amylbenzene, (8) *n*-nonylbenzene. Eluent *n*-pentane. Flow rate 1.0 mL/min. Detection UV 254 nm.

general, the retention of hydrocarbons on PGC is proportional to the number of carbon atoms interacting with the flat surface. So, the high adsorption energy of PAH molecules is connected with coplanar configuration of PAH molecules relatively flat surface of PGC.

According to the contemporary hypothesis ND particles consist of a diamond core with a thin graphite overlay, so the distinctive selectivity in the separation of PAH observed for PGC might take place for MSND too. The obtained results show the strong retention of PAH on the MSND column. The elution of naphthalene ($k = 13.48$) and anthracene ($k > 200$) from the column was achieved only with hexane–isopropanol (60:40) eluent, while benzene is eluted close to the dead volume. The chromatographic peaks of PAH molecules eluted from the MSND column were broad and tailed. The values of the retention factors of benzene and naphthalene retained on PGC
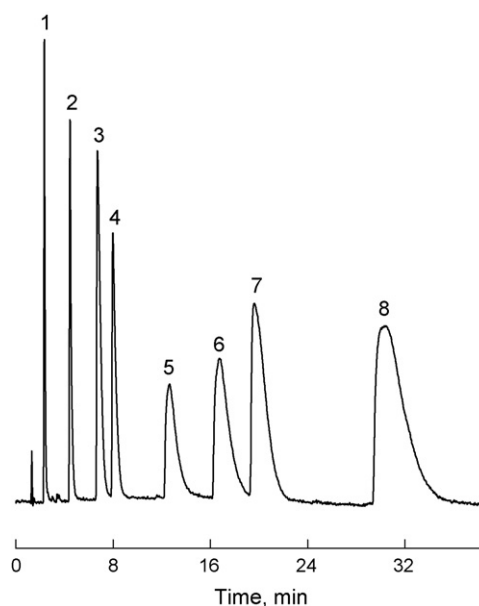
column in methanol are 0.18 and 6.80, respectively [32]. The strong interaction of PAH molecules with both PGC and MSND confirms some similarity between adsorption properties of these adsorbents.

3.2.4. Orthogonality of adsorption properties

To evaluate the difference in adsorption properties of the adsorbents, the orthogonality of the retention as $\log k$–$\log k$ plots was checked for non polar alkylbenzenes. There is a definite correlation between the adsorption properties of adsorbents observed for structurally related groups of non polar substances (Fig. 6). In case of polymethylbenzenes (substances 1–9 from Table 1) the linear increase retention times on MSND is corresponded to the increase of the retention observed for silica and alumina. However, the total plots summarizing all the data points for alkylbenzenes have very distinctive forms for pairs: MSND–silica gel and MSND–alumina because of different type of correlations found for mono-*n*-alkylbenzenes (solutes 1, 10–18). The dependence was linear in the former case and reciprocal in the latter. Almost linear straight correlation between the retention factors of both groups of alkylbenzenes was obtained for the MSND–PGC pair. Nevertheless, it should be taken into account that the literature data for the retention of alkylbenzenes on PGC were obtained by using methanol as mobile phase, so the retention mechanism could be different, more likely reversed-phase type interactions.

3.2.5. Chromatographic performance of MSND

The poor separation efficiency with less than 2500 theoretical plates per meter was a serious obstacle for the application of DRM as a stationary phase in HPLC [1,2]. The significant improvement in efficiency, up to 15,400 theoretical plates per meter, was recently achieved by using MSND as the column packing [4]. In this present investigation, both high separation selectivity and efficiency was demonstrated for MSND column operated under conditions of normal-phase HPLC. The separation of a mixture of eight alkylbenzenes in 30 min was achieved in *n*-pentane (Fig. 7). The peak tailing was noted for all chromatographic peaks, which is a very common case in normal-phase HPLC. The maximum column efficiency of 45,300 theoretical plates per meter was calculated from the chromatographic peak of 1,3-diisopropylbenzene, which

is almost three times higher than reported in our previous work [4]. However, the optimization of the column packing procedure is required concerning the selection of slurry solvent mixture to obtain more stable suspensions of diamond particles. Taking into account the high density of diamond 3.5 g/cm^3 and strong abrasive ability it is not a trivial task.

4. Conclusion

MSND represents a new type of selective and efficient stationary phase for normal-phase HPLC. The idea of this investigation was to characterize the adsorption properties of MSND and to understand its place among other basic stationary phases in HPLC. This primary characterization of MSND provides an important basis for the comparison of various types of synthetic diamond related materials prepared by different technologies or of MSNDs chemically modified with different functional groups.

This detailed study of the adsorption properties of MSND clearly demonstrated the different selectivity of this material as compared with other common adsorbents. For example, MSND reveals the better selectivity in separation of the positional isomers of xylenes. Additional, a more detailed comparison of PGC and MSND adsorbent under the same separation conditions is required to answer on question about similarity of adsorption properties of two different carbon allotropes.

Future work in this area will also be focused on the preparation of more efficient chromatographic columns, careful characterization of the surface properties and investigation of the possibility of using chemically modified MSND. The investigation of the regularities of the retention of polar analytes on MSND could be another important area or further investigation. The preliminary results show interesting possibilities for the application of MSND as the stationary phase in HILIC [39].

Acknowledgements

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