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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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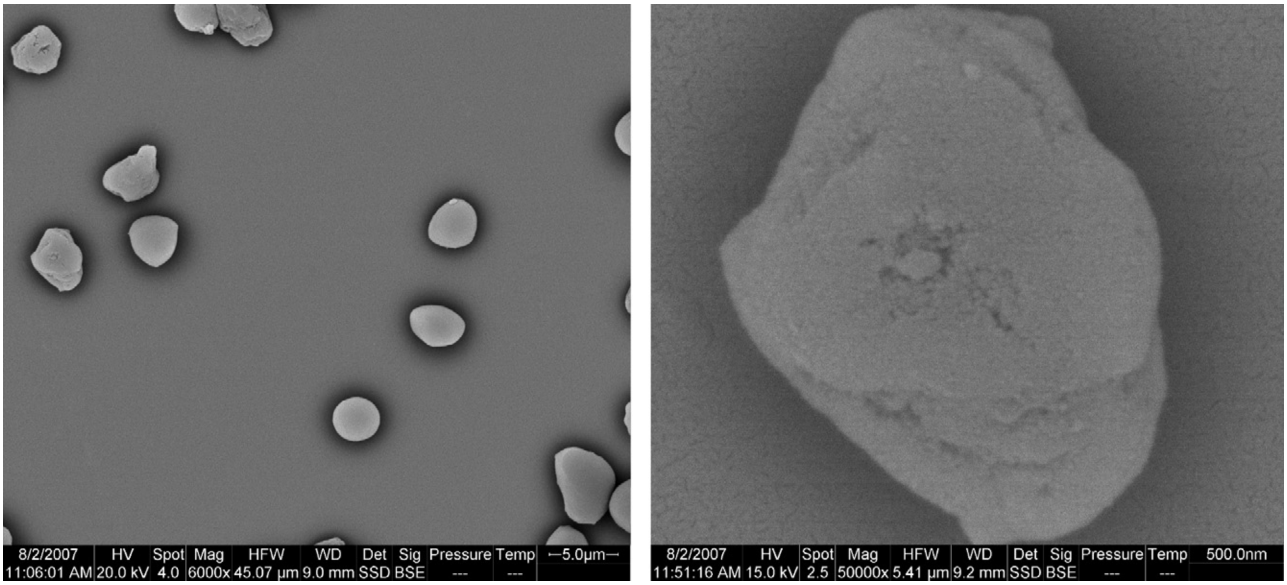

Fig. 1. SEM micrographs of MSND.

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 $LiClO_4$ 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-10A*i* 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 m^2/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