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Chromatographic performance of synthetic polycrystalline diamond as a stationary phase in normal phase high performance liquid chromatography

Anton Peristyy, Brett Paull, Pavel N. Nesterenko*

Australian Centre for Research on Separation Science, School of Physical Science, University of Tasmania, Private Bag 75, Hobart, TAS 7001, Australia

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ABSTRACT

The chromatographic properties of high pressure high temperature synthesised diamond (HPHT) are investigated in normal phase mode of high performance liquid chromatography. Purified nonporous irregular shape particles of average particles size 1.2 μm and specific surface area 5.1 $m^2\,g^{-1}$ were used for packing 100 × 4.6 mm ID or 50 × 4.6 mm ID stainless steel columns. The retention behaviour of several classes of compounds including alkyl benzenes, polyaromatic hydrocarbons (PAH), alkylphenylketones, phenols, aromatic acids and bases were studied using *n*-hexane-2-propanol mixtures as mobile phase. The results are compared with those observed for microdispersed sintered detonation nanodiamond (MSDN) and porous graphitic carbon (PGC). HPHT diamond revealed distinctive separation selectivity, which is orthogonal to that observed for porous graphitic carbon; while selectivities of HPHT diamond and microdispersed sintered detonation nanodiamonds are similar. Owing to non-porous particle nature, columns packed with high pressure high temperature diamond exhibited excellent mass transfer and produce separations with maximum column efficiency of 128,200 theoretical plates per meter.

1. Introduction

A renewal of the interest to the application of the carbonaceous adsorbents as stationary phase in high performance liquid chromatography (HPLC) has occurred over the last decade [1,2]. This trend is connected with excellent thermal stability and mechanical properties of carbonaceous materials, which are key properties for the development of future stationary phases in new modes of liquid chromatography, such as high temperature HPLC and ultra-high performance liquid chromatography (UHPLC). For example, the superior thermal stability of porous graphitic carbon (PGC) has been demonstrated in chromatographic analysis of polyolefins at elevated temperatures [3]. The other feature of PGC is unique separation selectivity towards polar analytes including inorganic anions [4], oligosaccharides [5], glycopeptides [6] and other polar organics [1,2]. As a rule, the application of carbonaceous adsorbents in chromatography is generally associated with use of columns packed with various forms of sp^2 carbon.

The other allotropic form of carbon is sp^3 carbon or diamond. The properties of diamond differ significantly from those for PGC. Diamond is a semiconductor with superior mechanical and thermal stability and it has the highest thermal conductivity of all known materials, with negligible thermal expansion during heating [7,8]. The combination of these properties allows the use of diamond at ultra-high pressures and temperatures, with minimal risks of damaging the chromatographic column. Moreover, the use of thermal conductive diamond adsorbents can solve the problem of heat dissipation in fast LC caused by friction between mobile and stationary phases at higher mobile phase linear velocities. Undoubtedly, diamond must be considered as one of the most promising materials for the future construction of stationary phases for HPLC.

The applications in liquid chromatography of various diamond containing materials includes natural diamonds [9], microdispersed sintered detonation nanodiamonds (MSDN) [10–13], nanodiamonds encapsulated in polysaccharide matrices [14,15], nanodiamond composites [16–18] and diamond particles prepared via carbon vapour deposition (CVD) [19]. Diamond based stationary phases have been used in normal-phase [10,13,16] and reversed-phase HPLC [9,12,16–20], hydrophilic interactions liquid chromatography (HILIC) [12,20], ion chromatography [7,11] and electrochemically modulated liquid chromatography [21].

Surprisingly, the chromatographic performance of statically synthesised microparticulated polycrystalline diamond at high pressure and high temperature (HPHT) has not yet been

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* Corresponding author. Tel.: +61 362262165.
E-mail address: Pavel.Nesterenko@utas.edu.au (P.N. Nesterenko).

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systematically studied. The only brief communication on this topic was given as a poster presentation of Ford et al. at a chromatographic symposium in 2000 [22]. Probably, the most significant problem for the application of diamonds in chromatography is inconsistency of their chemical and physical properties, especially for detonation diamonds produced by dynamic synthesis [23]. For example, the value of electrokinetic or zeta potential reported for detonation nanodiamonds in the literature varies from −100 to +100 mV [24]. Such differences in the properties are connected with difficulties in the determination of elemental impurities in diamond and hence with unsatisfactory control of purification during manufacturing [25]. Significant progress in this was achieved recently through introduction of inductively coupled plasma mass spectrometry (ICP-MS) analysis and microwave assisted purification of nanodiamonds [26,27].

There is also significant interest regarding the possibility of using fine irregular nonporous particles in HPLC. It is well known that Michael Tswett used various nonporous irregular particles (e.g. silica oxide, glass and natural sharpening stone, which is microcrystalline type of quartz) for the efficient separation of plant pigments in his original experiments resulting in the discovery of liquid chromatography [28]. The rediscovery of advantages of using fine nonporous particles as column packing occurred in 1984, when Hearn and Unger introduced fine spherical nonporous silica particles of diameter 0.7–2.1 μm for the use in HPLC [29]. Unfortunately, significantly less attention was paid since that time to the investigation of fine nonporous particles of irregular shape [30]. However, microspherical particles of materials like diamond are not available, so researchers have to use angular particles as column packing.

The goal of this current work is connected with the preparation and characterisation of the physicochemical properties of microparticulated non-porous HPHT diamond packed columns and investigation of their chromatographic performance in normal-phase high performance liquid chromatography (NP-HPLC), with a focus on adsorption properties, retention mechanism and separation selectivity. The properties of HPHT diamond are also compared with the properties of PGC and MSDN adsorbents.

2. Experimental

2.1. Materials and reagents

Deionised water (DIW) from Milli-Q (Milli-Q, USA) system was used for the sedimentation and preparation of solutions for purification of diamond. HPLC grade 2-propanol and n-hexane (both from Chem-Supply, Gillman, SA, Australia) were used for the preparation of mobile phases. Aqueous solutions of NaOH and HNO_3 (both from Chem-Supply, Gillman, SA, Australia) were used for fractionation by sedimentation and purification of HPHT diamond before column packing. KOH (Sigma–Aldrich, Castle Hill, NSW, Australia), methanesulphonic acid (Thermo Fisher, Scoresby, VIC, Australia), $NaNO_3$ (VWR International, Murarrie, QLD, Australia), Na_3PO_4 (VWR International, Murarrie, QLD, Australia), Na_2SO_4 (Sigma–Aldrich, Castle Hill, NSW, Australia) and Na_2CO_3 (Ajax Chemicals, Thermo Fisher, Scoresby, VIC, Australia) were used for preparation of pH buffers and for the investigation of the influence of column conditioning upon the retention. Pure analyte standards for the characterisation of HPHT diamond were supplied by Sigma–Aldrich (Castle Hill, NSW, Australia).

2.2. Instrumentation

A nanoseries zetasizer Model Zen3600 (Malvern Instruments, Malvern, Worcestershire, UK) was used for zeta potential measurements. Smoluchowski approximation for large particle size (1–2 μm) and high ionic strength (0.1 M) was used according to work [31]. Specific surface areas were calculated using Brunauer–Emmett–Teller (BET) method from data on low-temperature nitrogen adsorption/desorption collected with a TriStar II 3020 (Micrometrics Gemini, Georgia, USA) instrument. Before measurements were taken the samples were heated at 80 °C in vacuum overnight. Imaging of HPHT diamond particles was carried out using Hitachi SU-70 (Hitachi Ltd., Chiyoda, Tokyo, TKY, Japan) field emission scanning electron microscope (SEM) and 1.5keV electron beam. All samples were sputtered with platinum prior to analysis. An Oxford Aztec 2.3 EDS/EBSD system was used for the investigation of diamond surface composition and the presence of impurities by Energy-dispersive X-ray spectroscopy (EDS). FT-IR spectra of HPHT diamond were obtained using Bruker MPA infrared spectrometer (Billerica, MA, USA). Prior to measuring IR spectra, HPHT diamond powder was dried overnight at 90 °C in vacuum of 0.4 atm. Potassium bromide tablets containing 5% w/w dried diamond powder was used for taking spectra.

Accela 1250 UHPLC (Thermo Fisher Scientific, Waltham, MA, USA) was used for evaluation of HPHT diamond, MSDN and PGC columns. Photometric detection at 254 nm was used unless otherwise stated. ChromQuest (TM) software was used for operating the UHPLC system and processing of chromatographic data. Column efficiency and peak asymmetry were calculated according to recommendations of IUPAC [32].

Empty stainless steel columns were purchased from Phenomenex (Lane Cove West, NSW, Australia). A Hypercarb^{TM} column (100 × 4.6 mm ID) packed with 5 μm porous graphitic carbon (PGC) particles (Shandon HPLC, Runcorn, Cheshire, UK) and a 150 × 4.0 mm ID column packed with 3-6 μm particles of microdispersed sintered detonation nanodiamond (MSDN, see description in [13]) were used for comparative studies.

Column conditioning included flushing with 2-propanol for 20 min at a flow rate of 0.1 ml min^{-1}, then with DIW for 20 min at 0.2 ml min^{-1}, followed by buffer for 1.5 h at 0.2 ml min^{-1}, before finally repeating flushing with DIW and 2-propanol. After that, the column was equilibrated by pumping mobile phase until stable retention times were achieved within ±0.5%.

2.3. Purification and fractionation of HPHT diamond particles

Industrial non-porous HPHT diamond (Grade 2, fraction of 1-2 μm particle size) was purchased from Hunan Real Tech Superabrasive & Tool Co. Ltd. (Changsha, Hunan, China). As it was previously reported, ICP-MS analysis of this batch of HPHT diamond powder showed the presence of 2.96 wt.% of elemental impurities (H %, N% and O% are not counted) [25,26]. The major impurities include 25.3 mg g^{-1} of Si, 1.3 mg g^{-1} of W, 0.6 mg g^{-1} of Ta, 0.5 mg g^{-1} of P, 0.4 mg g^{-1} of Al and 0.3 mg g^{-1} of each of Mn and S. The origin of silicon at such a high concentration level was due to the presence of 5.4 wt % of silica used as anti-caking agent for the processing and storage of the diamond powder. The elevated concentrations of tungsten and tantalum are due to reaction of diamond with construction materials containing these metals with formation of respective carbides at high temperatures during synthesis.

These major impurities must be located at the surface of non-porous diamond particles and may significantly modify the adsorption properties of diamond. For this reason, before packing the HPHT diamond, the material was purified by boiling in 40 wt% NaOH and by treatment with 5 M HNO_3, following by intensive washing with DIW between and after each treatment. Purity of subsequent material was checked by an absence of the white precipitate of silica hydrogel after acidification of 40% NaOH solution used for washing, with concentrated HNO_3. Energy-dispersive X-ray spectroscopy (EDS) was additionally used to confirm the