Journal of Chromatography A, 1210 (2008) 68–75

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Preparation of a sulfoxide group and ammonium-salt bonded silica stationary phase for separation of polychlorinated biphenyls from mineral oils

Masahiko Numata[a,*], Toshiro Kaneko[b], Qiding Mi[b,c], Michael Ye[b,c], Satoshi Kawamata[a], Mayumi Matsuo[a], Takashi Yarita[a]

[a] National Metrology Institute of Japan, AIST, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8563, Japan
[b] Sigma-Aldrich Japan K.K., 2-2-24, Higashi-shinagawa, Shinagawa-ku, Tokyo 140-0002, Japan
[c] Supelco, Supelco Park, Bellefonte, PA 16823-0048, USA

ARTICLE INFO

Article history:
Received 2 July 2008
Received in revised form 6 September 2008
Accepted 10 September 2008
Available online 16 September 2008

Keywords:
Polychlorinated biphenyl (PCB)
Sulfoxide
Ammonium-salt
Stationary phase
Mineral oil
Cleanup
GC–MS

ABSTRACT

In this study, a silica stationary phase modified with sulfoxide group and ammonium-salt was prepared for the separation of polychlorinated biphenyls (PCBs) from mineral oils, and its properties were investigated. Organic sulfide was attached to a diamino (primary and secondary amino) bonded silica surface by an amide bond, and the bonded sulfide groups were oxidized with periodate to afford sulfoxide groups bonded to the stationary phase. The secondary amino groups in the spacer chain were converted to ammonium-salt by the addition of hydrochloric acid. The sulfoxide group and ammonium-salt bonded stationary phase was tested for their suitability as adsorbent for SPE-type preparative short columns and for an analytical HPLC-type separation. The new stationary phase (1.2 mmol of sulfur bonded per gram) separated PCBs from mineral oils (paraffin-based transformer oils) more efficiently than previously reported stationary phases including sulfoxide group or ammonium-salt bonded ones. The quantitative chromatographic parameters for an aliphatic hydrocarbon (eicosane) and some PCB congeners also indicated strong retention of highly chlorinated biphenyls by the sulfoxide and ammonium-salt bonded silica compared with simple aminopropyl, sulfoxide group or ammonium-salt bonded ones. A cleanup procedure was established for simple determination of PCBs in mineral oil samples using sulfoxide group and ammonium-salt bonded silica packed column fractionation. The analytical method, combination of the cleanup procedure, and measurement with a GC–high resolution (magnetic sector) MS or a GC–quadrupole MS were validated using mineral oil certified reference materials.

1. Introduction

Polychlorinated biphenyls (PCBs) were once widely used for various applications such as dielectric fluids, heat-transfer fluids, and in paints [1]. However, some PCB congeners have dioxin-like toxicity, and more toxic products such as polychlorinated dibenzofurans are easily generated from PCB by heating. Although accurate determination of PCBs is essential to estimate their risk and to manage PCB waste treatment properly, the sample matrices themselves are often the root of problems in analyses. Because hydrocarbons and PCBs behave similarly during pretreatment processes for PCB analysis, residual matrix components sometimes interfere with PCB measurements and damage analytical instruments.

Even when highly selective instruments are used, direct determination of PCB in complex matrices is difficult. Sulfuric acid treatment [2] and saponification [3] have been applied to remove unsaturated hydrocarbons, lipids, and other contaminants. To separate PCBs from aliphatic hydrocarbons or lipids, partitioning between nonpolar solvents and non-proton polar solvents, such as dimethyl sulfoxide (DMSO) [4–7], acetonitrile [8], and dimethyl formamide [9], is effective. However, these liquid–liquid partitioning procedures are not only tedious and time-consuming, but can also be hazardous for operators because relatively large amount of chemicals are handled manually.

Liquid chromatography (LC) techniques, such as gel permeation chromatography [10,11] and normal-phase LC, are relatively simple and reliable for cleanup of PCBs. A variety of adsorbents, including silica gel [12], Florisil® [12], alumina [12], and polar residue-bonded silica [13–19] have been used for normal-phase LC. However, relatively large amounts of stationary phases (i.e., long columns) and large amounts of mobile phases are necessary to separate PCBs from mineral oil matrices by using these chromatographic techniques.

Andersson et al. found that the conversion of sulfide to sulfoxide or sulfone on a silica-based adsorbent could be applicable to

---

* Corresponding author. Tel.: +81 298 61 2254.
E-mail address: mas-numata@aist.go.jp (M. Numata).

0021-9673/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2008.09.038

tune polarity of the stationary phases for reverse phase LC [20]. In addition, unique retention behaviors of aromatic compounds, such as PCBs and polyaromatic hydrocarbons on sulfoxide or sulfone bonded stationary phases have been reported [20,21]. We have also found that stationary phases modified with sulfoxide or sulfone groups were effective for separation of PCBs from mineral oils in normal phase mode [22]. Since ammonium-salt bonded stationary phases were also effective for this purpose [23], the effect of combining both groups on the separation of PCBs from mineral oils was investigated in this study.

2. Experimental

2.1. Chemicals

A commercial paraffin-based transformer oil (PCB-free, Supelco, Bellefonte, PA, USA) was used in this study. Certified reference materials (CRMs) for the analysis of PCBs in insulation oil and fuel oil, NMIJ CRM 7902-a, CRM 7903-a, CRM 7904-a and CRM 7905-a [24] (the National Metrology Institute of Japan, Tsukuba, Japan) were used for the method validation.

A technical PCB product, a Kanechlor mixture solution (containing Kanechlor 300, 400, 500, and 600: 100 ± 10 μg mL^{-1} each in hexane solution) was supplied by GL Sciences (Tokyo, Japan). Neat CB3, CB15, CB101, and CB209; and a mixture solution of 20 native (chlorinated) biphenyls for GC window definition were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Ten $^{13}C_{12}$-labeled congener solutions: $^{13}C_{12}$-CBs: #3, #8, #28, #52, #101, #153, #180, #194, #206 and #209; and a native PCB mixture solution, BP-MS (mixture of 64 native PCB congeners) were obtained from Wellington Laboratories (Guelph, Canada). The PCB congener numbers are IUPAC numbers [25].

The pre-modified amino (Flash-NH_2) and diamino (primary and secondary amine, PSA) bonded silica supports, were manufactured by Supelco (Bellefonte, PA, USA) and possessed the following characteristics: particle diameter, 40–75 μm; pore size, 7 nm; specific surface area, 500 m^2 g^{-1}; spherical particle. Silica SPE cartridges (Isolute-SILICA, 500 mg in a 3-mL cartridge, International Sorbent Technology, Hengoed, U.K.) were used for preliminary cleanup of the mineral oil samples. The sulfoxide and ammonium-salt modified silica, PSA–SO (Fig. 1) is a commercially available SPE material, Supelclean Sulfoxide, supplied by Supelco. Commercialized columns, also supplied by Supelco, packed with 3.0 g of PSA–SO stationary phase (polypropylene column, 12.75 mm i.d.; length of the stationary phase layer, 27 mm; dry-packing), and 6.0 g of PSA–SO stationary phase (glass column, 15.6 mm i.d.; length of the stationary phase layer, 43 mm; dry-packing) were used for some experiments.

Other reagents used for the modification of the silica surface, elution solvents, reagents for XRXRF and Karl Fischer titration experiments were as follows. Toluene, triethylamine, sodium metaperiodate, hydrochloric acid, acetone, anolyte for Karl Fischer titration (HYDRANAL-Coulomat AK), catholyte for Karl Fischer titration (HYDARANAL-Coulomat CG-K), were obtained from Sigma–Aldrich (St. Louis, MO, USA), 3-methylthiopropionic chloride was obtained from TCI America (Portland, OR, USA). Diphenylsulfoxide and DL-methionine sulfoxide, were obtained from Tokyo Kasei Kogyo (Tokyo, Japan). Acetone hexane and nonane were obtained from Kanto Chemical (Tokyo, Japan). Hydrogen peroxide was obtained from Wako Pure Chemical Industries (Osaka, Japan).

2.2. Preparation of sulfoxide modified silica

A sulfoxide modified silica stationary phase (NH_2–SO in Fig. 1) was prepared by the method described in the previous report [22]. Spherical aminopropyl silica, Flash-NH_2 (NH_2 in Fig. 1) was used as the base material to prepare the sulfoxide-bonded silica stationary phase instead of the irregular shape silica [24].

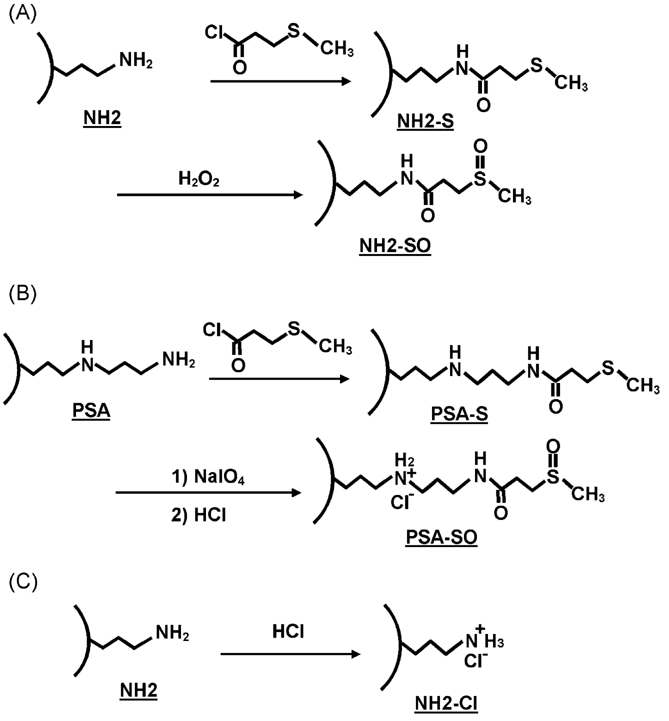

Fig. 1. Synthesis and structures of the modified stationary phases, (A) NH_2 to NH_2–SO; (B) PSA to PSA–SO; (C) NH_2 to NH_2–Cl.

2.3. Preparation of sulfoxide and ammonium-salt modified silica

Sulfoxide groups were bonded on the amino groups on the surface of the PSA–silica by a modified method described in the previous paper [22]. The PSA bonded silica (75 g), toluene (500 mL) and 3-methylthiopropionic chloride (25 mL), were placed in a flask equipped with a mechanical stirrer and condenser, and then triethylamine (25 mL) was added slowly. The mixture was heated at 105 °C. After 2 h of reaction, the mixture was cooled to room temperature. The sulfide-bonded silica (PSA–S in Fig. 1) was washed consecutively with toluene, methanol and water. Sulfide groups on the modified silica were oxidized with an aqueous solution of sodium metaperiodate (1.2 g mol of metaperiodate/mol of sulfur in the sulfide-bonded silica) at below 10 °C for 24 h, and then reacted with 500 mL of 0.1 M hydrochloric acid. The sulfoxide and ammonium-salt bonded silica (PSA–SO in Fig. 1) was washed with 500 mL of water three times, 500 mL of methanol three times, and 500 mL of acetone once and was then dried under vacuum. We used the same batch of PSA–SO for preliminary open-column, HPLC and GC/MS quantification experiments, and other batches for elemental analysis and open column separation.

2.4. Preparation of ammonium-salt bonded silica

Propylammonium chloride-bonded silica (NH_2–Cl in Fig. 1) was prepared as follows. Hydrochloric acid (0.1 M) was added to 3.0 g of NH_2 until the pH of the supernatant became less than 2. Then the mixture was washed with water and acetone, and most of the acetone was evaporated under a nitrogen gas stream. Next, the modified silica was dried under vacuum [23].