

SULFOXIDE RESIDUE-BONDED SILICA STATIONARY PHASES FOR SEPARATION OF POLYCHLORINATED BIPHENYLS FROM MINERAL OIL

Numata M¹, Kaneko T², Mi QD², Ye M², Kawamata T¹, Otake T¹, Yarita T¹

¹AIST, National Metrology Institute of Japan, Tsukuba, 305-8563 Japan; ²Sigma-Aldrich Japan K.K., Tokyo, 140-0002 Japan

Abstract

Sulfoxide residue-bonded silica stationary phases were prepared for separation of polychlorinated biphenyls (PCBs) from mineral oil. Organic sulfides were attached to the silica surfaces by an amide or imide bond, and the bonded sulfide residues were oxidized to sulfoxide. The modified stationary phases separated PCBs from mineral oil (paraffin-based insulation oil) more efficiently than amino residue-bonded silica or other polar stationary phases that have been used for the cleanup of PCBs. Less than 5 mg of PCB in kg of insulation oil was detectable by GC/QMS measurement with cleanup using only sulfoxide residue-bonded silica.

Introduction

Polychlorinated biphenyls (PCBs) were once widely used as dielectric fluids, heat-transfer fluids, hydraulic fluids, and other applications. 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. Even when highly selective instruments are used, directly determining PCB concentrations in complex matrixes is difficult. To separate PCBs from aliphatic hydrocarbons or lipids, partitioning between nonpolar solvents and non-proton polar solvents, such as dimethyl sulfoxide (DMSO) is effective.¹ However, liquid-liquid partitioning procedures are tedious and time-consuming.

Liquid chromatography (LC) techniques, such as normal-phase LC using polar residue-bonded silica,^{2,3} are relatively simple and reliable for cleanup of PCBs. For accurate determination of PCBs in mineral oil samples, PCBs should be separated from matrices that are composed mainly of aliphatic hydrocarbons prior to GC measurements. However, relatively large amounts of stationary phases and large amounts of mobile phases are necessary to separate PCBs from mineral oil matrices, because of their chemical and physical similarity. In the case of DMSO extraction, the electrophilic sulfur atom interacts with the π -electron cloud of the aromatic rings of the PCBs.¹ Therefore, we expected that stationary phases modified with sulfoxide residue would be effective for the separation of aromatics from aliphatic compounds.⁴ In this study, some sulfoxide-bonded silica stationary phases were synthesized, and their abilities to separate PCBs from mineral oil were investigated.

Materials and Methods

Chemicals

A commercial insulation oil product was used in this study. Its main component was paraffin oil produced from petroleum (specified by Japan Industrial Standard JIS C2320-1999, Insulating Oil, Class 1-4, the class widely used for transformers in substations or other power transmission systems).

A technical PCB, Kanechlor mixture solution (containing Kanechlor 300, 400, 500, and 600: $100 \pm 10 \mu\text{g mL}^{-1}$) was supplied by GL Sciences (Tokyo, Japan). Neat PCB3, PCB15, and PCB209 were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). An internal standard solution was prepared from solutions of each of ten ¹³C₁₂-labeled congeners (mono- to decachlorobiphenyl, Wellington Laboratories, Guelph, Canada).

Stationary phase preparation

1) Preparation of N-(3-(aminoethyl)propylamino)silica (PSA)

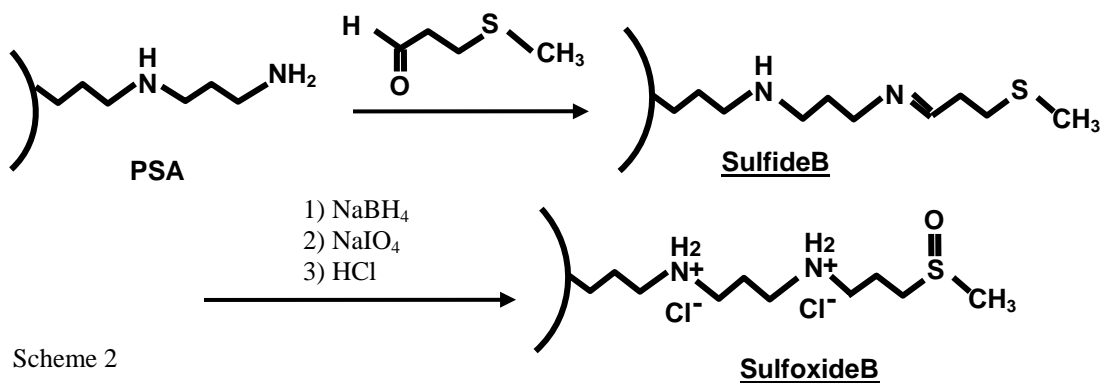
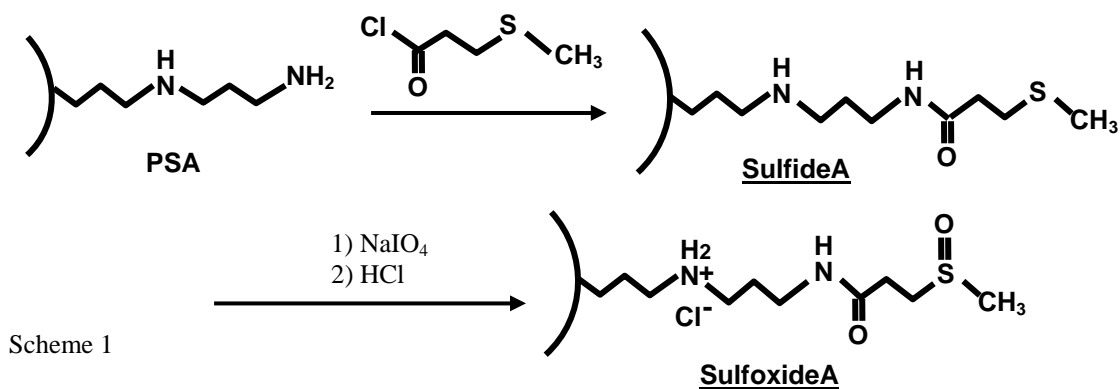
Dried silica gel (average diameter 50 μm , spherical) and N-(3-(trimethoxysilyl)propyl)ethylenediamine were added to toluene. After heating (100 °C, 24 h) under nitrogen gas atmosphere, modified silica was washed and dried (Scheme 1 and 2, PSA).

2) Binding sulfoxide on the surface of silica via an amide bond

PSA, toluene, 3-methylthiopropionic chloride, and triethylamine were placed in a flask equipped with a mechanical stirrer and condenser, and the mixture was heated at 105 °C. After 2 h of reaction, the mixture was cooled to room temperature. The sulfide-bonded silica (Scheme 1, SulfideA) was washed and was then dried. Sulfide on the modified silica was oxidized with aqueous solution of sodium metaperiodate (1.2 g-atoms per 1 g-atom of sulfur in the sulfide-bonded silica) at below 10 °C for 24 h, then reacted with hydrochloric acid (Scheme 1, SulfoxideA).

3) Binding sulfoxide on the surface of silica via an imide bond

The PSA was added to 3-methylthiopropionaldehyde at 0 °C, and the mixture was shaken intermittently for 3 h. Then the solid phase was washed with methanol, and the sulfide-bonded silica was dried under vacuum (Scheme 2, SulfideB). The imide bond was converted to secondary amine by sodium borotetrahydride treatment to improve resistance against hydrolysis. After 18 h of reaction with aqueous solution of sodium borotetrahydride at room temperature, the modified silica was washed. The sulfide residue was oxidized as described above, then reacted with hydrochloric acid (Scheme 2, SulfoxideB).



Column chromatography

The modified silica slurry in acetone was packed into an open glass column (10 mm i.d.). For preliminary investigations of oil and PCB separation, the insulation oil or PCB solution in nonane (Kanechlor mixture, 5 $\mu\text{g g}^{-1}$; PCB3, 0.6 $\mu\text{g g}^{-1}$; PCB15, 0.6 $\mu\text{g g}^{-1}$; PCB209, 0.017 $\mu\text{g g}^{-1}$) was used as a sample. In this study, the oil samples were treated with a silica SPE cartridge (Isolute-SILICA, 500 mg in a 3-mL cartridge, International Sorbent Technology, Hangoed, UK). The oil sample (0.25 mL) was loaded onto the cartridge (conditioned with 10 mL of hexane) and was then eluted with 8 mL of hexane. The eluted fractions were concentrated to 0.25 mL under a nitrogen gas stream. The cleaned oil sample or the PCB-nonane solution (0.25 mL) was loaded onto the column packed with 2.5 g of the modified stationary phases (length of the stationary phase layer, ca. 50 mm), and the samples were eluted with hexane and then with acetone. To determine elution profiles of the oil, the collected fractions were evaporated with a nitrogen gas stream to dryness, and the oil recoveries were calculated

from the mass of the evaporation residue and the mass of the loaded oil. For the determination of PCB elution profiles, the volume of each eluted fraction was reduced to 1.0 mL under a nitrogen gas stream, and PCB concentrations in the fractions were measured with GC/MS.

For the determination of PCB concentration in the oil samples, 0.02 mL of the internal standard solution (the mixture of ten $^{13}\text{C}_{12}$ -PCB congeners in nonane) was added to 0.18 mL of the PCB-fortified insulation oil (PCB $3.7 \mu\text{g g}^{-1}$). The sample was loaded onto a column (8 mm i.d.) packed with 6.0 g of the sulfoxide-bonded stationary phase (length of the stationary phase layer, 108 mm: washed with 20 mL of acetone, conditioned with 40 mL of hexane) and eluted with hexane. The fraction containing PCBs (12–32 mL) was concentrated with a rotary evaporator and nitrogen gas stream to 0.2 mL of volume, and the fraction was analyzed by GC/MS.

Chemical analysis

PCBs were analyzed with a GC/HRMS system (AutoSpec, Micromass, Manchester, UK). A GC/quadrupole mass spectrometer (GC/QMS; 5979 GC/MSD, Agilent) was also used for the quantification of PCBs. The analytes were separated using a GC (Agilent 6890, Agilent Technologies, Palo Alto, CA, USA) equipped with an HT-8 capillary column (50 m x 0.22 mm i.d.; film thickness, 0.25 μm ; SGE, Ringwood, Australia).⁵ Stationary-phase elemental analyses (C, N, S) were performed with an automatic element analyzer (EA1110, CE Instruments, Milan, Italy) by the combustion/GC-TCD method. HRXRF experiments were performed by the modified method of Konishi.⁶ Sulfur K_{α} fluorescence spectra of the sample pellets (mixed with boric acid powder, and pressed) were measured with a Technos XFRA 190, double-crystal spectrometer (Technos, Osaka, Japan) to identify oxidation state of sulfur on the synthesized stationary phases.

Results and Discussion

Characterization of sulfoxide-bonded stationary phases

The element contents and approximate speciation of sulfur in the stationary phases are shown in Table 1.

Table 1 Element contents and sulfur speciation of the tested stationary phases

Bonded residue	Element content (%)			Oxidation state of S		
	C	N	S	Sulfide	Sulfoxide	Sulfone
PSA	8.1	3.6	<0.1	--	--	--
SulfideA	12.9 (13.6)	2.9 (3.2)	4.0 (3.6)	major	--	--
SulfoxideA	12.9 (12.9)	2.9 (3.0)	4.0 (3.4)	--	major	minor
SulfoxideB	10.0 (13.1)	2.3 (3.1)	2.6 (3.5)	minor	major	minor

The values in the parentheses represent the theoretical ones (reaction yields = 100%).

PCB separation from insulation oil sample

Although amino residue-bonded silica has been used in cleanup of samples for PCB analysis, the elution profiles of the mineral oil and highly chlorinated biphenyls overlapped with those of the amino residue bonded silica (2.5 g) packed column (Fig. 1A). Other polar stationary phases (silica, aminopropyl silica, cyanopropyl silica), which have also been used for cleanup of PCBs in normal-phase mode, have nearly the same separation efficiencies under the same conditions. The elution profiles of the mineral oil and PCBs from the sulfide-bonded stationary phases were almost same as in the case of amino residue bonded silica. However, PCBs were strongly retained by the oxidized forms of these stationary phases (Fig. 1B, sulfoxide A; Fig. 1C, sulfoxide B). In the case of sulfoxide A or B, adsorbed water made PCB retention weak. To remove water, acetone washing prior to hexane conditioning was effective.

Determination of PCBs in insulation oils

Small amounts of mineral oil gradually eluted from the Sulfoxide B packed columns with hexane after the main oil peak, and the tailing overlapped with the PCB fractions. Therefore, the Sulfoxide A was used for the following quantification experiment. To validate the pretreatment method for actual samples, Kanechlor-fortified insulation oil (total PCBs concentration, $3.7 \mu\text{g/g}$) was analyzed after the Sulfoxide A packed column cleanup without silica SPE treatment. The results obtained with the GC/QMS system were in good agreement with the

preparation concentration (Table 2).

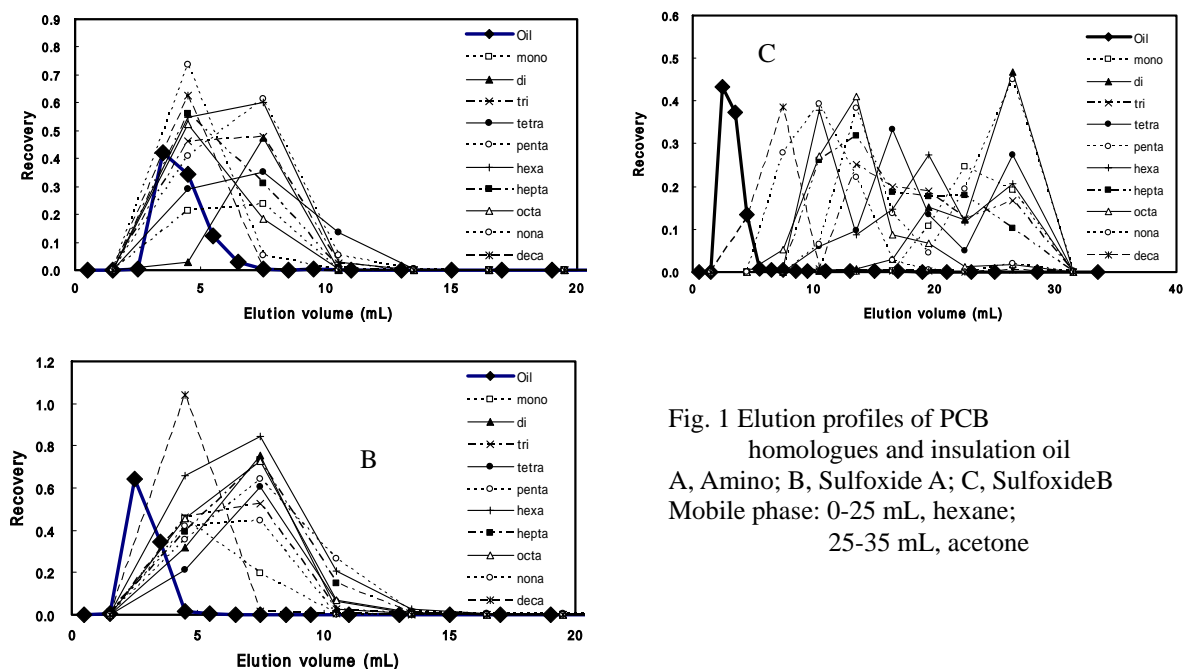


Fig. 1 Elution profiles of PCB homologues and insulation oil
A, Amino; B, Sulfoxide A; C, Sulfoxide B
Mobile phase: 0-25 mL, hexane;
25-35 mL, acetone

Table 2 Observed concentrations of PCB homologues in a PCB-fortified insulation oil (n=3)

		PCB homologue										Total PCB
		mono	di	tri	tetra	penta	hexa	hepta	octa	nona	deca	
Conc.	mean	0.045	0.29	0.80	0.87	0.90	0.35	0.55	0.13	nd	nd	3.9
	SD	0.003	0.05	0.08	0.06	0.08	0.002	0.01	0.004	--	--	0.13
Recovery	mean	102	91	92	108	106	95	97	97	95	9	--
	SD	5.2	2.6	5.1	5.4	6.8	2.8	2.7	3.3	1.2	3.4	--

Recovery: Recovery yields of spiked internal standards (^{13}C -labelled PCBs)

In conclusion, PCBs were more strongly retained by the sulfoxide-bonded stationary phases compared with other polar stationary phases, such as aminopropyl silica, that have been used for cleanup of PCBs in normal-phase mode. Therefore the potential of the stationary phases for effective removal of matrices such as aliphatic hydrocarbons from PCBs, and relatively simple pretreatment for determination of PCBs in waste oil or other samples was demonstrated. The main PCB homologues, tri- to heptachlorinated biphenyls, in the sample containing legal regulation level of PCB (0.5 $\mu\text{g/g}$) could be determined with the GC/QMS system.

Acknowledgements

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