Analysis of PCBs in Transformer Oil with a Sulfoxide Bonded SPE Phase and GC-MS

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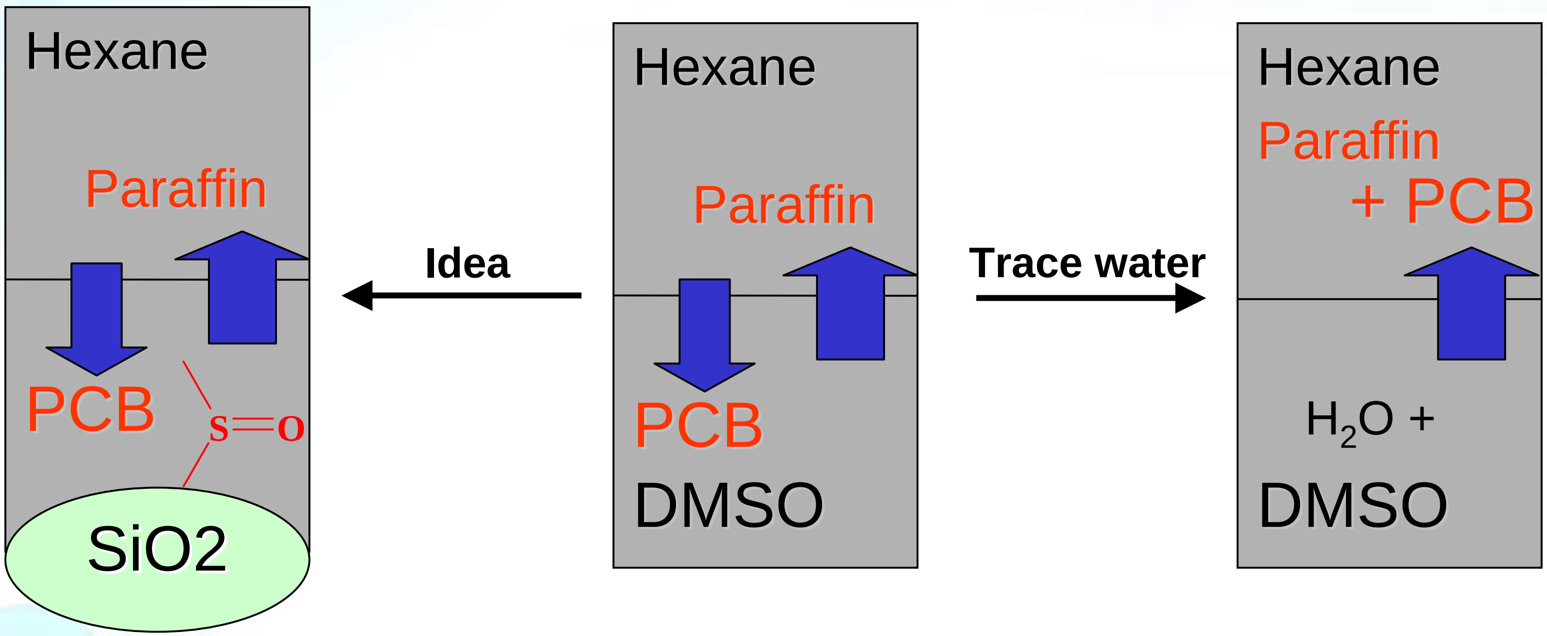
Abstract

Polychlorinated biphenyls (PCBs) were once widely used as dielectric fluids and other applications. Although accurate determination of PCBs is essential to evaluate their risk and to manage PCB-waste treatment properly, the sample matrices themselves are often the root of problems in analyses. 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.

Abstract (contd.)

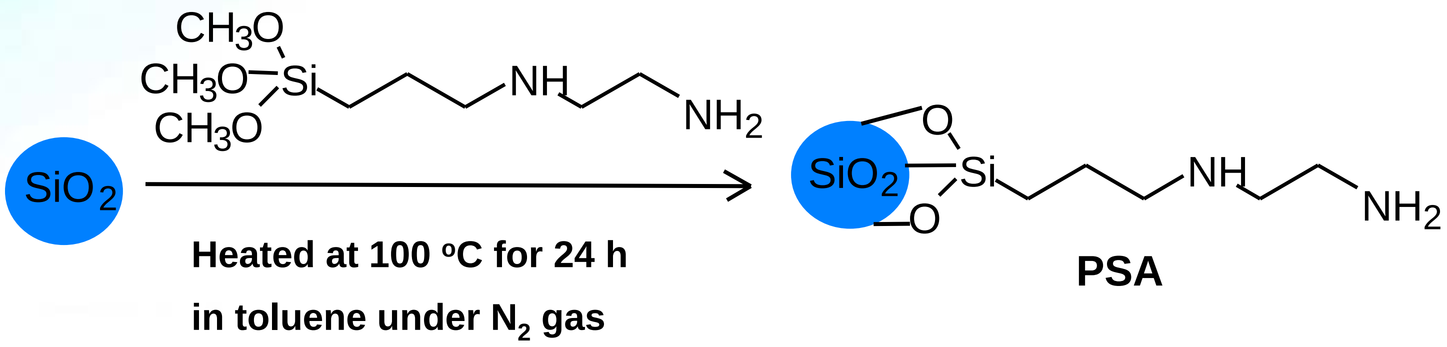
Liquid chromatography (LC) techniques, such as normal-phase LC using polar residue-bonded silica,(2,3) are relatively simple and reliable for cleanup of PCBs. However, relatively large amounts of stationary phases and large amounts of mobile phases are necessary to separate PCBs from mineral oil matrices, because of their chemical and physical similarity. Because DMSO extraction is effective to selectively extract aromatics from aliphatic hydrocarbons, we expected that stationary phases modified with sulfoxide residue would be effective for this purpose.(4) In this study, some sulfoxide-bonded silica stationary phases were synthesized, and their abilities to separate PCBs from mineral oil were investigated.

Concept of Sulfoxide Stationary Phase



Stationary Phase Synthesis

Preparation of PSA phase:



Spherical Silica gel (40-75 mm)

Specific Surface area: 500 m^2/g

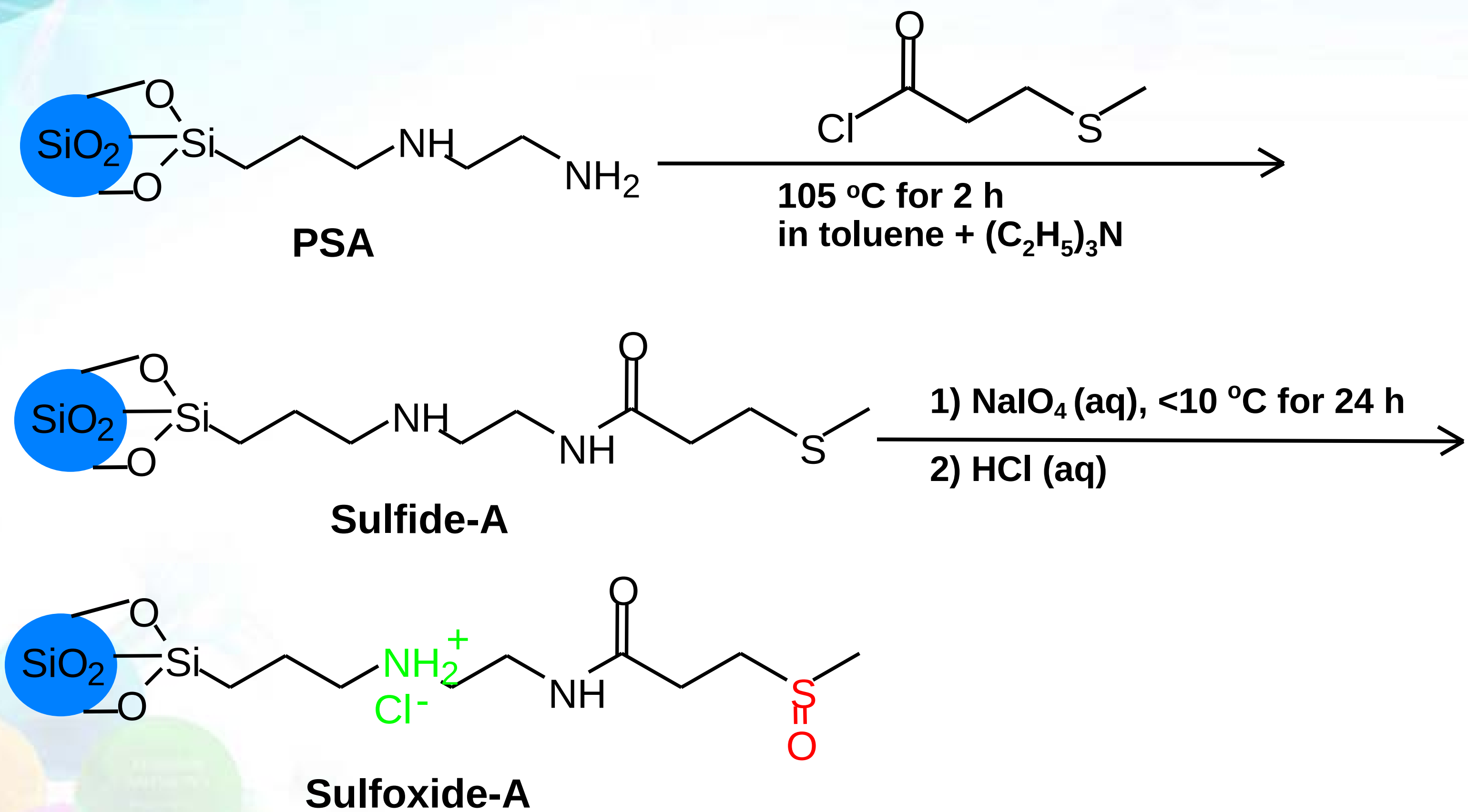
Pore size: 70 Å

N-(3-(aminoethyl)propylamino)silica (PSA)

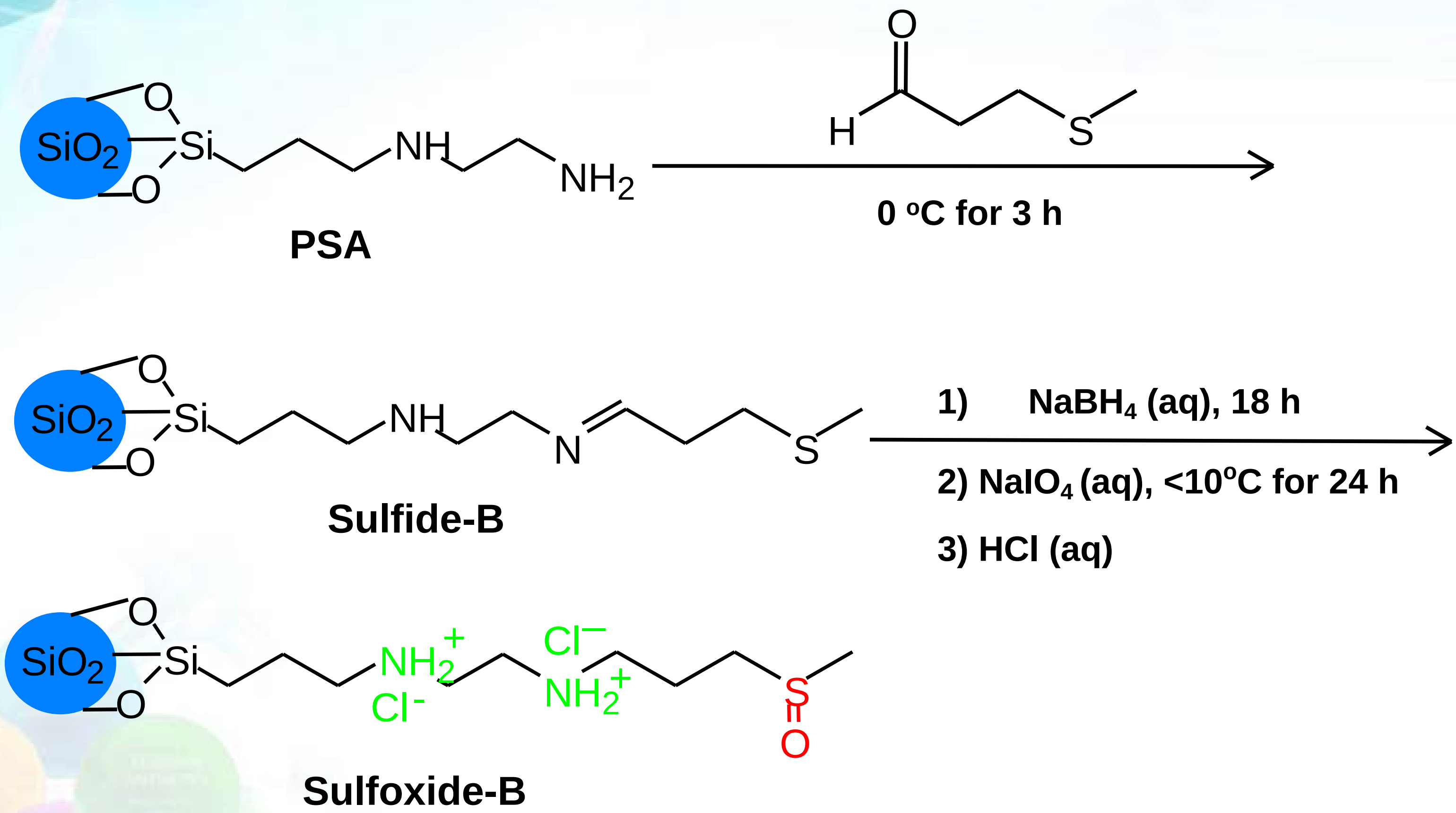
Coverage: 3.09 mmol/m^2

Ion Exchange capacity: 0.98-1.05 meq/g

Preparation of Sulfoxide Bonded Phase 1



Preparation of Sulfoxide Bonded Phase 2



Elemental Contents and Oxidation States of Sulfur

	Element content (%)			Oxidation state of sulfur		
	C	N	S	Sulfide	Sulfoxide	Sulfone
PSA	8.1	3.6	<0.1	N/A	N/A	N/A
Sulfide-A	12.9 (13.6)	2.9 (3.2)	4.0 (3.6)	major	---	---
Sulfoxide-A	12.9 (12.9)	2.9 (3.0)	4.0 (3.4)	---	major	minor
Sulfoxide-B	10.0 (13.1)	2.3 (3.1)	2.6 (3.5)	minor	major	minor

Notes: The values in the parentheses represent the theoretical ones (reaction yields = 100%).
Elemental analysis: Combustion/GC-TCD method with an automatic element analyzer (EA1110, CE Instruments, Milan, Italy).
Identification of oxidation state of sulfur: Sulfur Ka fluorescence spectra by HRXRF (Konishi et al.(5)) with a Technos XFRA 190 (Technos, Osaka, Japan).

PCB Separation from Mineral Oil

Elution profiles of oil and PCB homologues

Eluent solvent: Hexane (0-25 mL) and then Acetone (25-35 mL)

Samples loading: 0.2 mL Insulation oil and PCB: Technical PCBs +PCB3, PCB15 and PCB209

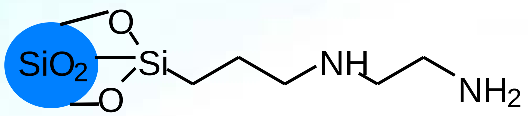
Glass Column: Open glass column (10 mm I.D.)
Stationary phase 2.5 g (ca. 50 mm height)

Elution profile: Mineral oil and then PCB.
(Oil: evaporate under N_2 and then gravimetric measurement;
PCBs: Measured with a GC/HRMS system(6))

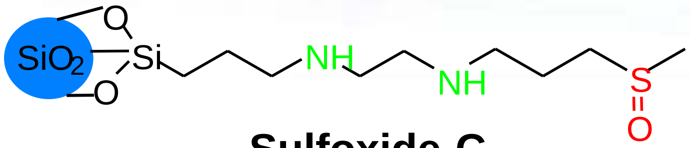
Oil Samples

- Commercial insulation oil: Japan Industrial Standard JIS C2320-1999, insulating oil, Class 1-2/4 (paraffin oil).
- PCB: Kanechlor mixture solution (Kanechlor 300, 400, 500, and 600 , GL Sciences, Tokyo, Japan).
- Neat PCB3, PCB15 and PCB209: Cambridge Isotope Laboratories (Andover, MA, USA).

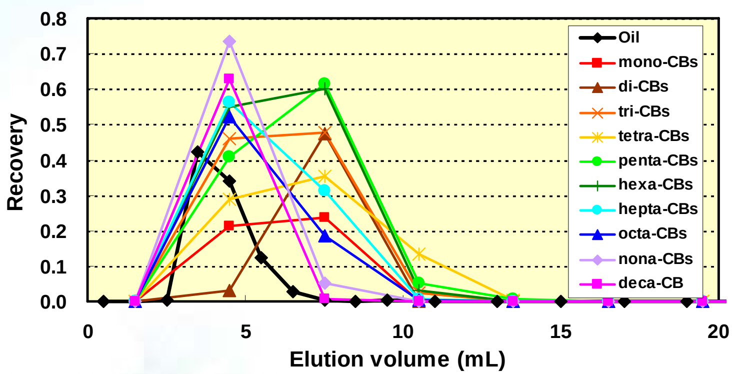
Elution Profiles of Oil and PCB Homologue

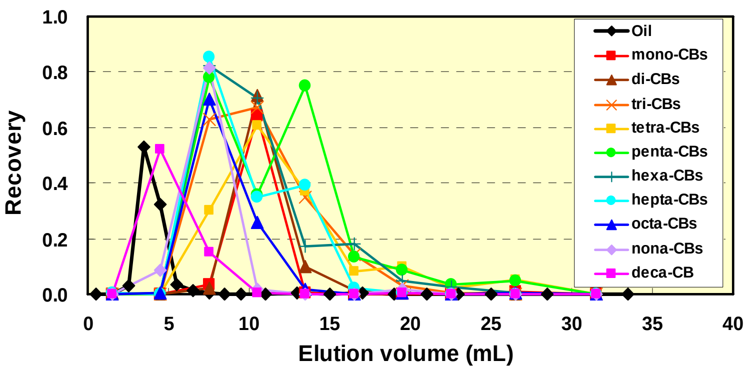


PSA

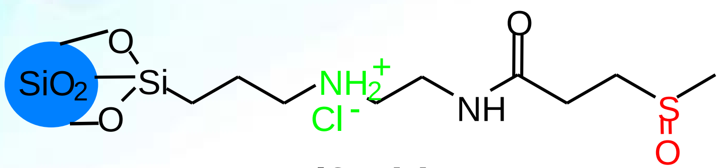


Sulfoxide-C

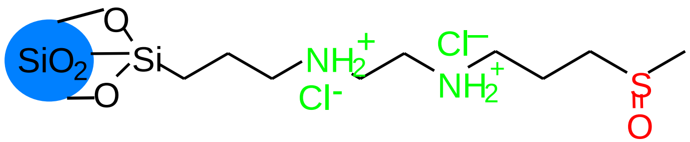




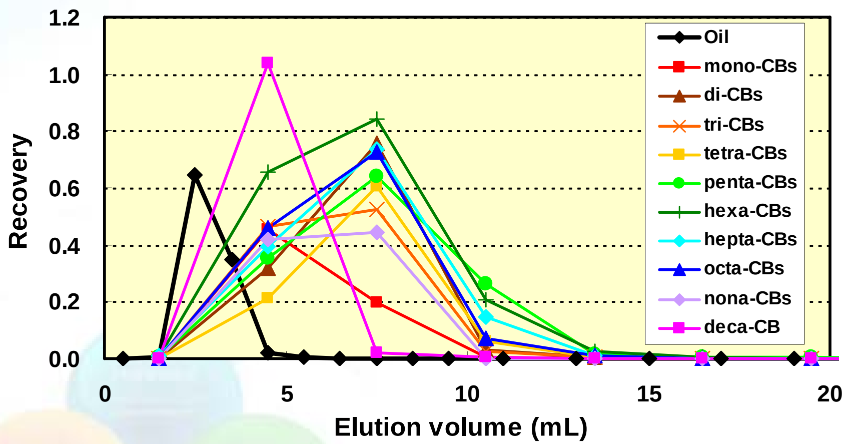
Elution Profiles of Oil and PCB Homologue (contd.)

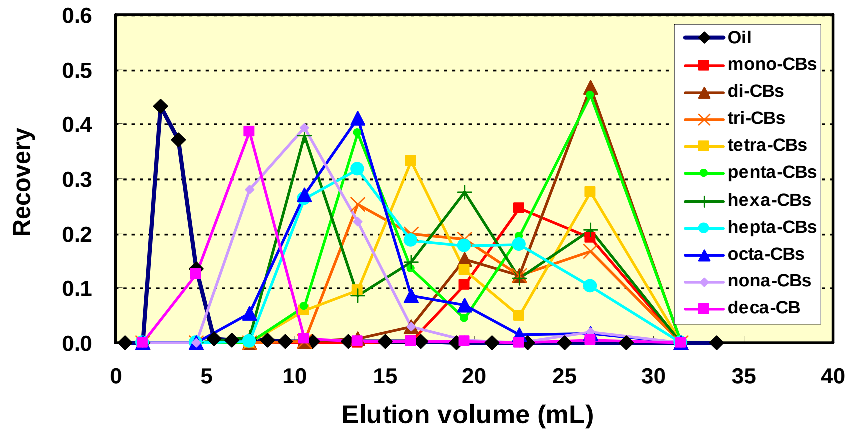


Sulfoxide-A



Sulfoxide-B





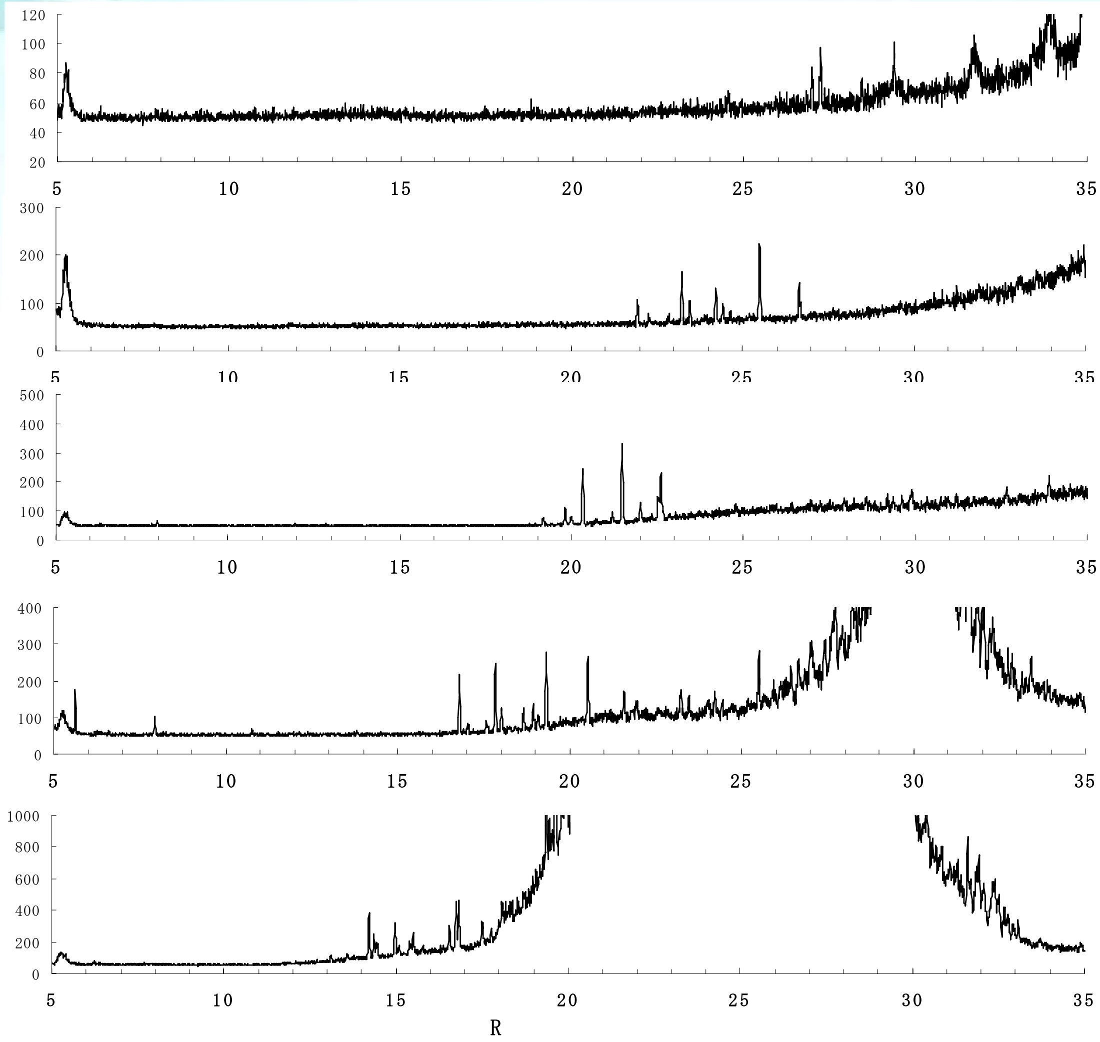
PCB Cleanup with a Sulfoxide-A Packed Column

Supelclean™ Sulfoxide Sulfoxide-A (6 g) packed Glass column (15.6 mm I.D.)

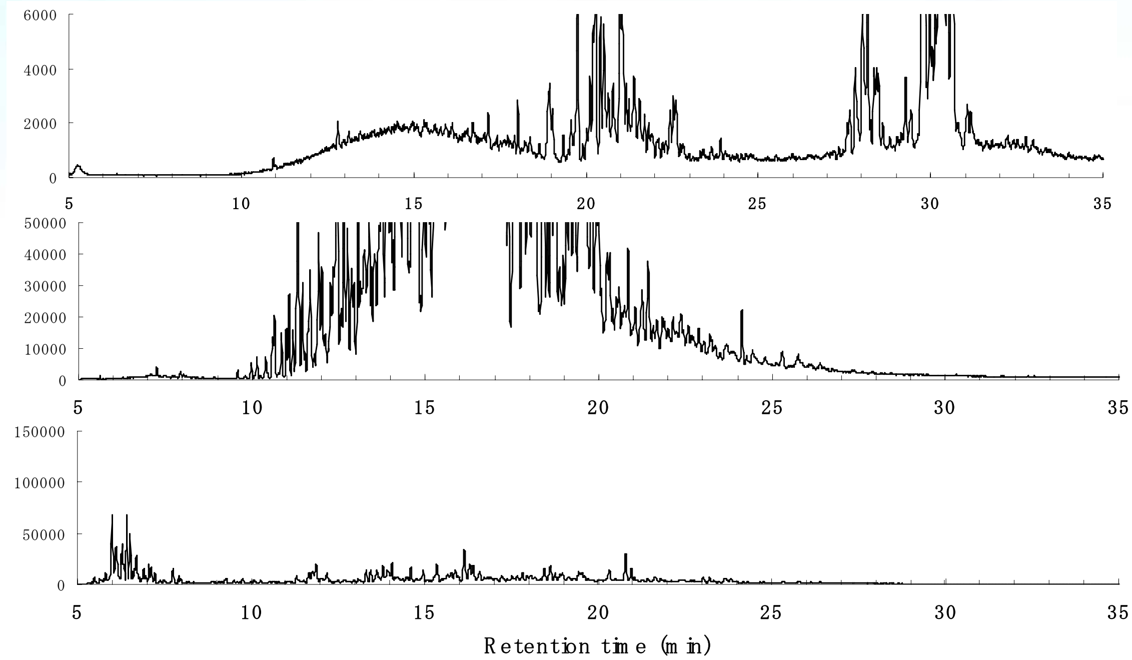
Established method for PCB separation

- Wash with Acetone (20 mL)
- Condition with Hexane (40 mL)
- Load sample oil (Oil 0.2 mL+ Hexane 0.2 mL)
- Elute with Hexane (12 mL)
- Oil
- Elute with Hexane (25 mL)
- PCBs
- Concentrate under N_2 gas
- GC/QMS or GC/HRMS

Chromatograms of PCB Homologues

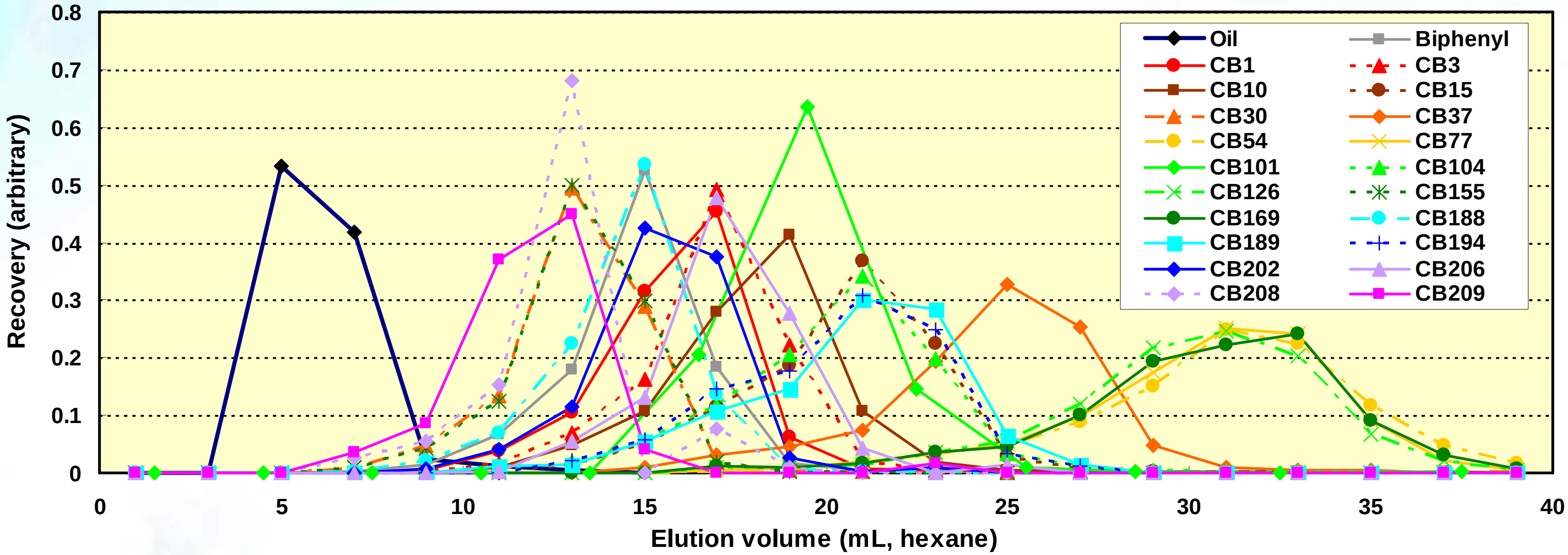


Chromatograms of PCB Homologues (contd.)



PCB, KC mixture 0.5 mg/kg - insulation oil; Cleanup with the Supelclean Sulfoxide; GC/QMS, Agilent 5973N MSD; Column, DB-5

Elution of Insulation Oil and PCB Congeners from Supelclean Sulfoxide



Data obtained from two experiments were overlapped: Run 1, Oil (Insulation oil) and CB101; Run 2, Other CB congeners (BP-WD, Wellington Laboratory) and biphenyl

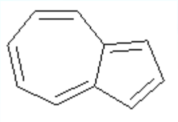
Observed Concentrations of PCB Homologues in a PCB-Fortified Insulation Oil (n=3)

		mono-CBs	di-CBs	tri-CBs	tetra-CBs	penta-CBs	hexa-CBs	hepta-CBs	octa-CBs	nona-CBs	deca-CB	total-PCB
Conc. (mg/kg)	**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	--

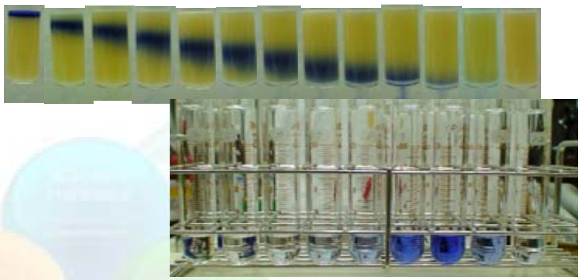
Preparation conc., 3.7 mg total-PCBs/kg-oil; PCB, measured with a GC/QMS system(6); Recovery, Recovery yields of spiked internal standards (^{13}C-labeled PCBs)

Influence of Moisture on Separation

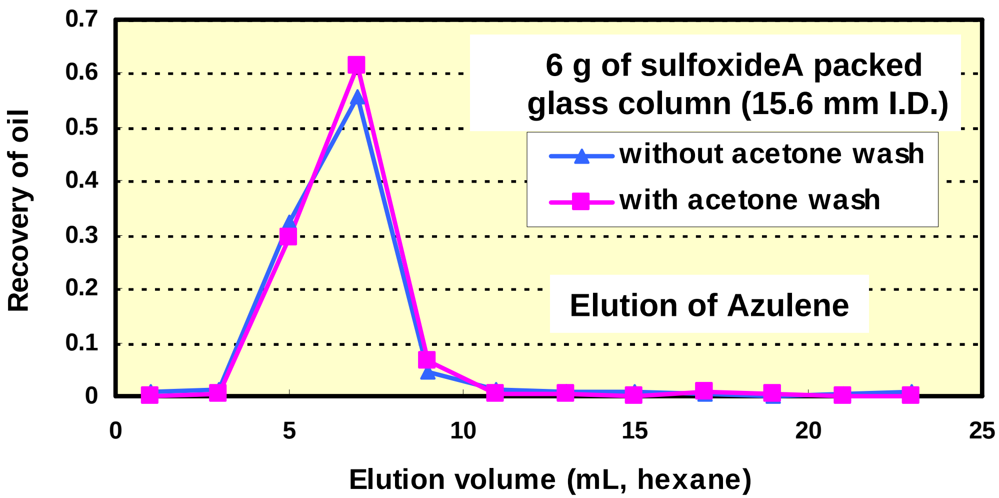
Elution profile of Azulene:



1. **Similar to PCBs**
2. **Visible**



1. Moisture in column weakened retention of azulene (and PCBs).
2. To remove adsorbed moisture, 20 mL of acetone was necessary.
3. To remove residual acetone, 40 mL of hexane was necessary.



Conclusions

1. PCBs were strongly retained by the sulfoxide-bonded stationary phases compared with other polar stationary phases, such as amino residue bonded silica, that have been used for cleanup of PCBs in normal-phase mode.
2. Introduction of amino-salts was also effective to enhance retention of PCBs.
3. Removal of moisture adsorbed on the stationary phase prior to use was effective to enhance retention of PCBs.
4. The main PCB homologues, tri- to heptachlorinated biphenyls, in the insulation oil sample containing Japanese legal regulation level of PCB (0.5 mg/kg) could be determined with the GC/QMS system after cleanup of the SulfoxideA packed column.

Conclusions (contd.)

5. 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.

Acknowledgement

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