

SEARCH OF LIQUID CHROMATOGRAPHIC CLEAN-UP MATERIALS FOR RAPID PCB ANALYSIS AND EVALUATION OF THEIR SEPARATION CHARACTERISTICS

Tetsuya Sawatsubashi¹, Chisato Tsukahara¹, Keigo Baba², Akiko Shinoda³, Etsumasa Ohi⁴, Norio Miura⁵

¹ Mitsubishi Heavy Industries, Ltd. Nagasaki Research & Development Center, 5-717-1, Fukahori, Nagasaki, Nagasaki 851-0392, Japan

² Choryo Engineering Co., Ltd., 5-717-1, Fukahori, Nagasaki, Nagasaki 851-0392, Japan

³ Showa Denko K.K., 5-1, Ogi, Kawasaki, Kanagawa 210-0867, Japan

⁴ Shimadzu techno-research, Inc., 1, Nishinokyo-Shimoai, Nagakyo, Kyoto, Kyoto 604-8436, Japan

⁵ Kyushu University, Art, Science and Technology Center for Cooperative Research, 6-1, Kasuga-kouen, Kasuga, Fukuoka 816-8580, Japan

Abstract

In order to find out excellent liquid chromatographic clean-up material for rapid PCB analysis, we examined here the separation characteristics of PCB and insulating oil for polymer gels, normal-phase silica gels, reversed-phase silica gels, carbon material and ion-exchange material. Among the various materials examined, the polymer gels were found to give rather good high separation performance without various pretreatments. Especially, the poly (hydroxymethacrylate) gel could separate PCB completely from insulating oil. However, under the present condition, poly (hydroxymethacrylate) gel required rather long time for PCB separation. Thus, polyvinyl alcohol gel was confirmed to be most suitable for rapid PCB analysis because of the least required quantity of fraction liquid as well as the highest resolution. It is expected that the separation performances of poly (hydroxymethacrylate) gel can be improved further by applying a gradient method.

1. Introduction

Polychlorinated biphenyl (PCB) was synthesized for the first time in Germany in 1881 as a “dream chemical” having excellent chemical stability and electrical insulation property. Since then, it has been manufactured in large quantities and are used for many industrial products. However, triggered by environmental problems caused by PCB, its toxicity has drawn attention as one of persistent organic pollutants (POPs). Recently, its treatment has become the global issue calling for urgent solution [1,2]. When treating PCB, we are required to rapidly detect PCB discharged from decomposition and treatment equipment. However, because the standard PCB analysis method [3] requires long analysis time (more than 3 days) in addition to complicated operation, it is too difficult to provide speedy feedback in accordance with the treatment conditions. As a result, various rapid PCB analysis techniques [4] have been devised as an alternative analysis method so far. Unfortunately, these methods can be analyzed only under the specific conditions, and besides, an actual application to PCB treatment plants requires complex handling process.

In PCB analysis, the interference of insulation oil is particularly remarkable. Since the insulation oil has the similar behavior as PCB and requires various pretreatments to remove it, it is a big issue to be solved to remove insulating oil from a sample rapidly and effectively. Therefore, in this study, we searched for the most suitable liquid chromatographic clean-up material for rapid PCB analysis by evaluating the separation characteristics of PCB as well as insulating oil for the materials reported so far [5-11] and also for the new materials under the identical conditions.

2. Materials and Methods

2.1 Clean-up Materials

Among the various liquid chromatographic clean-up materials for rapid PCB separation, we selected here five categorical materials, such as polymer gels, normal-phase silica gels, reversed-phase silica gels, carbon material and ion-exchange material, as shown in Table 1. Then, their separation characteristics of PCB and insulating oil were evaluated.

Table 1 Clean-up Materials Examined

Gel	Functional Group	Column	Size
Polymer gel	Polyvinyl alcohol	Shodex CLNpak PAE-800	ϕ 8×300 mm, 5 μ m
	Styrene-Divinylbenzene copolymer	Shodex CLNpak EV-2000 8F	ϕ 8×300 mm, 16 μ m
	Poly (hydroxymethacrylate)	Shodex ODP2-HP 8F	ϕ 8×300 mm, 5 μ m
Normal-phase silica gel	Silanol	GLS Inertsil SIL-150	ϕ 4.6×250 mm, 5 μ m
	Diol	GLS Inertsil Diol	
	Diol (pore size 300 Å)	GLS Inertsil WP300 Diol	
	Cyanopropyl	GLS Inertsil CN-3	
	Nitro	GLS Nucleosil 100-NO2	
	Aminopropyl	GLS Inertsil NH2	
Reversed-phase silica gel	Amino-Cyano	GLS Partsil5 PAC	ϕ 4.6×250 mm, 5 μ m
	Octyl	GLS Inertsil C8-3	
	Octadecyl	GLS Inertsil ODS-80A	
	Octadecyl (polymeric)	GLS Inertsil ODS-P	
	Triacetyl	Nomura Develosil C30-UG-5	
	Phenyl	GLS Inertsil PH	
Carbon	Porous graphite carbon	Thermo Hypersil Hypercarb	ϕ 4.6×100 mm, 7 μ m
Ion-exchange	Benzenesulfonic acid	Waters Spherisorb SCX	ϕ 4.6×250 mm, 5 μ m

2.2 Experimental Conditions

We examined the separation characteristics of PCB and insulating oil under the experimental conditions given in Table 2. As a mobile phase, three kinds of solvents were selected among various available solvents listed in the table. The elution time of PCB as well as insulating oil was confirmed according to λ_{\max} of the photodiode array (PDA) detector. As for the column diameter in this examination, 8 mm was used for the polymer gels, and 4.6 mm for others. By considering that the column cross-section area of polymer gels was about three times larger than those of other columns, the sample injection volume and the flow-rate were determined.

Table 2 Experimental Conditions

Standard	PCB : GL science KC-Mix (400 mg/l) Insulating oil : Idemitsu transformer oil H (5000 mg/l)
Instrument	Shimadzu LC-10A series (SCL-10A _{VP} , SIL-10AD _{VP} , LC-10AT _{VP} , CTO-10AC, DGU-14A, SPD-M10A _{VP})
Mobile phase	Kishida chemical (HPLC grade) methanol, acetone, toluene, cyclohexane, THF, acetonitrile, ethyl acetate
Flow-rate	0.5 ml/min (ϕ 4.6 mm column), 1.5 ml/min (ϕ 8 mm column)
Oven temp.	40°C
Injection volume	10 μ l (ϕ 4.6 mm column), 30 μ l (ϕ 8 mm column)

2.3 Evaluation Method for Separation

Separation resolution of PCB from insulating oil was evaluated based on the chromatograms. The formula used for calculating resolution is as follows:

$$R_s = \frac{2(t_{Rb} - t_{Ra})}{(t_{Ea} - t_{Sa}) + (t_{Eb} - t_{Sb})} \quad (1)$$

Here, R_s , t_R , t_S , t_E , and subscripts of a, b mean resolution, peak retention time, peak start time, peak end time, and former and latter eluted materials, respectively.

3. Results and Discussion

3.1 Evaluation of Separation Characteristics

Figure 1 shows resolution in the most suitable mobile phase for each clean-up material. The resolution values for polymer gels are in the range of 0.4–0.65 which are higher than those (0.03–0.3) for normal/reversed-phase silica gels, carbon material and ion-exchange material. It is obvious that the polymer gels show the most excellent separation performance among the materials examined here. In the polymer gels, the resolution becomes higher in order of styrene-divinylbenzene copolymer gel, polyvinyl alcohol (PVA) gel, and poly (hydroxymethacrylate) gel. Especially, poly (hydroxymethacrylate) gel shows peculiar separation characteristics, which enables complete separation of PCB from insulating oil. On the other hand, in the normal-phase silica gels, the resolution of the diol is the highest, and it becomes lower in order of aminopropyl, cyanopropyl, silanol, amino-cyano, and nitro. In the reversed-phase silica gels, the resolution of the triacontyl is the highest, and it becomes lower in order of monomeric octadecyl, octyl, polymeric octadecyl, dichlorophenyl, and phenyl. The resolution of the porous graphite carbon (PGC) material and the benzenesulfonic acid are not higher than those of polymer gels.

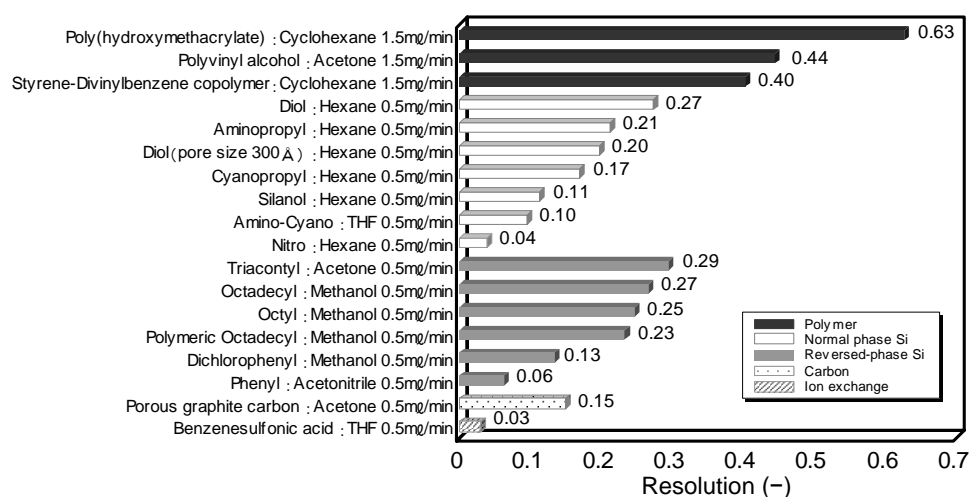


Fig.1 Comparison of the resolution for each of various materials

3.2 Evaluation of Fraction Characteristics

The PCB fraction liquid volume for each clean-up material was estimated by using the following formula:

$$V_f = (t_{Epcb} - t_{Spcb}) \times L \quad (2)$$

Here, V_f , t_{Spcb} , t_{Epcb} and L mean fraction liquid volume, PCB peak start time, peak end time and flow-rate, respectively.

Figure 2 compares the PCB fraction liquid volume for each clean-up material. In the normal/reversed-phase silica gels, the fraction liquid volume is as little as 1–10 ml. On the other hand, in the polymer gels, the fraction liquid volume is as much as 1.5–75 ml. Especially in the poly (hydroxymethacrylate) gel, since the separation requires long time, about 75 ml is required to be fractionated. Thus the PCB fraction liquid volume becomes more than 1000 times of the sample injection volume. In this case, the PCB concentration in the solvent becomes so low that the high-enrichment procedure is required after the clean-up. In contrast, the fraction liquid volume of PVA gel is extremely low in the polymer gels, and only about 1.5 ml is needed to be fractionated, which enables rapid separation similarly in the case of the normal/reversed-phase silica gels. Therefore the PVA gel giving not only the least fraction liquid volume but also the highest resolution can be considered to be the most suitable material for rapid PCB analysis.

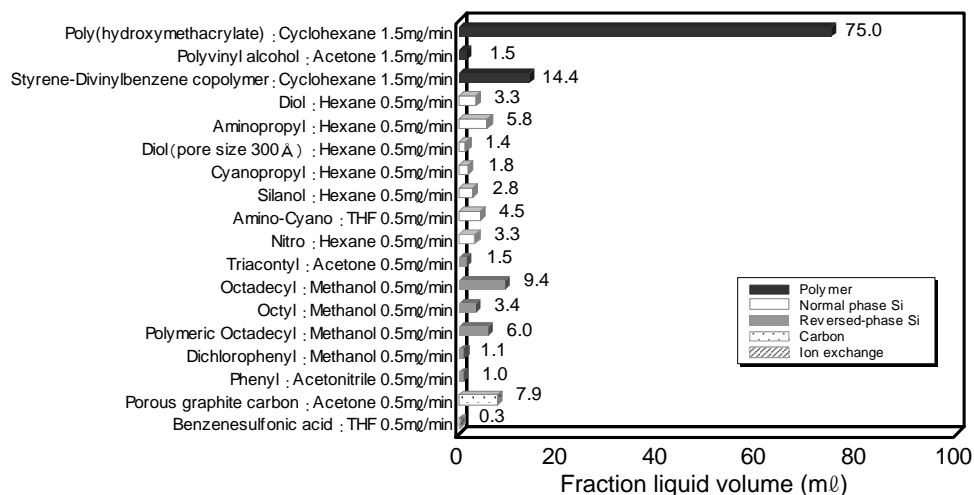


Fig.2 Comparison of the fraction liquid volume for each of various materials

4. Conclusions

For rapid PCB analysis, we need to select clean-up material which can remove insulation oil efficiently with the least PCB fraction liquid volume. As a result of this study, polymer gels with high resolution are efficient, and among them, polyvinyl alcohol gel was confirmed to be most suitable for rapid PCB analysis because of the least required quantity of fraction liquid as well as the highest resolution. Polyvinyl alcohol gel has structurally the wide range of solvent selectivity from aqueous polarizable solvent to non-polarizable solvent, and possesses a feature of being able to clean up samples without pretreatment processes. Moreover, polyvinyl alcohol gel has the function of size exclusion mode which can separate not only compounds of higher-molecular weight or lower-molecular weight than PCB but even phthalate ester. Thus, the polyvinyl alcohol gel can be evaluated to be most suitable for PCB clean-up material due to its wide range of selectivity, which enables precise quantitative analysis of PCB in less time than that of the standard analysis method by combining with GC-ECD or GC/LRMS.

On the other hand, the poly (hydroxymethacrylate) gel can be expected to be an efficient clean-up material in future which enables least quantity of fraction liquid as well as complete separation of PCB from insulation oil within a relatively short time by changing the mobile phase from cyclohexane to acetone after separating the insulating oil by applying the gradient method.

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