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Preparation and Evaluation of Molding-type Solid-phase Extraction Media Binding with Commercially Available Adhesives

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Abstract

A fabrication method of molding-type solid-phase extraction media (M-SPEM) bound with commercially available adhesive is presented. Six pieces of M-SPEM were prepared by heating each kneaded product of a particulate sorbent and an adhesive inserted into a six-hole cylindrical mold for hardening under an open system and normal pressure. The particulate sorbent contained in M-SPEM was divinylbenzene-based reversed-phase mode solid-phase extractants that we have reported. Examination of several adhesives showed that the moldability of M-SPEM depended on the composition and properties of the adhesive. The optimized procedure can prepare an M-SPEM containing 85 wt% particulate sorbent (particulate sorbent/adhesive=100 mg/17 mg, particle diameter: 90–150 μm), and the M-SPEM has a specific surface area of about 500 $\text{m}^2 \text{g}^{-1}$. The established procedure in this study can bind particulate sorbents together, which showed almost no reductions in the adsorption property and liquid permeability compared with those of the particulate sorbent.

Keywords: molding, commercially available adhesive, solid-phase extraction, particulate sorbent, reversed-phase.

1 **Introduction**

2 Sample pretreatment is an important process for quantitative analysis with high
3 sensitivity and high precision. The solid-phase extraction (SPE) technique is widely used
4 for the extraction or purification of analytes in liquid samples.¹⁻⁵ Various materials have
5 been used as the solid-phase extractants to pretreat a wide range of components. In general,
6 solid-phase extractants are made in particulate form as a fine powder, and these materials
7 can be broadly divided into two types: modified silicas and macroporous polymers.
8 Several solid-phase extractants with various separation modes, such as reversed-phase,^{5,6}
9 ion exchange,^{7,8} chelate,⁹⁻¹¹ hydrophilic interaction chromatography (HILIC),^{12,13} and
10 mixed mode of reversed-phase/ion exchange,^{14,15} have been studied, and nowadays, they
11 are commercially available. We have also developed the reversed-phase¹⁶⁻¹⁸ and the
12 HILIC¹⁹⁻²¹ types of solid-phase extractants.²² These solid-phase extractants (sorbents) are
13 typically used by packing into a column or cartridge, which limits the use and application
14 of the particulate sorbent. In addition, the processes involving packing or pulling out the
15 particulate sorbents are complicated²³ because the scattering and adsorption of particulate
16 sorbents occur due to static electricity. Moreover, after packing the particulate sorbents
17 into the column or cartridge, channeling between particulate sorbents may reduce the
18 extraction efficiency in the SPE process.²⁴

19 These problems can be solved by binding the particulate sorbent using some binding
20 materials. Hereafter, the molded particulate sorbent is called an “adsorption medium”.
21 Disk-like adsorption media²⁵⁻²⁷ and porous sintered material^{23,28,29} have been reported or
22 are commercially available. However, these adsorption media cannot fully demonstrate
23 the adsorption properties of the included particulate sorbent because the materials used to
24 fasten or bind the particulate sorbent have no or poor adsorption ability. Another problem
25 is that the content of the particulate sorbents in these adsorption media are never high.

For example, an adsorption medium having the particulate sorbent content of 50% sintered with polyethylene powder has been reported,²³ but no report has been found an adsorption medium having the particulate sorbent content of 50% or more. To improve the adsorption properties of these adsorption media, a new simple and easy binding techniques should be developed because the reported adsorption media are often prepared using unique techniques. Moreover, it is necessary to consider the increase of the particle sorbent content in the adsorption medium.

Conversely, nonparticulate-shaped sorbents, like solid-phase microextraction (SPME),³⁰ stir-bar sorptive extraction (SBSE),³¹ monolith,^{32–36} and stir-cake sorptive extraction (SCSE),³⁷ have been reported. SPME, SBSE, and SCSE prepared using polydimethylsiloxane or monolith have reduced solvent consumption and simplified the operation in the sample pretreatment process. However, these sorbents mostly have low specific surface areas, which is an important factor determining the adsorption property. For this reason, the improvement of these sorbents to have high specific surface areas is desirable.

We recently reported the molding-type solid-phase extraction medium (M-SPEM)^{38,39} as an adsorption medium, in which a particulate sorbent was bound using commercially available adhesives. The M-SPEM can be prepared simply by kneading a particulate sorbent and an adhesive and subsequently, heating the kneaded product. With the developed method, we prepared adsorption media containing 85 wt% of particulate sorbent, which has larger specific surface area than that of general monolith-type sorbents. In addition, some interactions, such as hydrophobic interactions, are expected to occur between the binding material (adhesive) and target analyte, if an appropriate binding material is chosen, which may improve the adsorption property of an M-SPEM. Considering these characteristics, M-SPEM can solve the problems of existing adsorption

media.

In this report, we investigated the preparation and evaluation of M-SPEM using 10 types of commercially available adhesives, including three types of adhesives reported previously.³⁸ The diameters of particulate sorbent contained in M-SPEM were also evaluated for improving the adsorption property. Each fabricated M-SPEM was evaluated for the specific surface area, liquid permeability, and adsorption properties toward nucleic acid-related compounds.

Experimental

Reagents

Divinylbenzene (DVB) and trimethylolpropane trimethacrylate (TMPT) were purchased from Sigma-Aldrich Japan. Toluene, 2,2'-azobis (isobutyronitrile) (AIBN), and methyl cellulose were obtained from FUJIFILM Wako Pure Chemicals. Uracil (Ura), uridine (U), adenosine (A), caffeine (Caf), and dimethyl phthalate (DMP), which were used as analytes to examine the adsorption recoveries in SPE, were obtained from Tokyo Chemical Industries. Adenine (Ade), theophylline (The), and methyl *p*-hydroxybenzoate (methylparaben, MP), which were also used as analytes, were obtained from FUJIFILM Wako Pure Chemicals. For SPE and HPLC, methanol (HPLC grade) was obtained from KANTO CHEMICAL. The names and product numbers of the adhesives are summarized in Table 1. Adhesives of Nos. 1–3 and 10 were obtained from CEMEDINE, and Nos. 4–9 were purchased from Konishi. As summarized in Table 1, the abbreviations used to denote the adhesives are as follows: Si-B, Si-C, and Si-S for denaturing silicone-based adhesives (Nos. 1–3); Epoxy-AA, Epoxy-A, and Epoxy-T for two-component adhesives

comprising epoxy resin and hardening reagent (Nos. 4–6); SBR and PVC for polymer-based solvent-type adhesives (Nos. 7 and 8); Urethane for urethane-based adhesive (No. 9); Instant for instantaneous adhesive (No. 10).

Instrumentation

The HPLC system consisted of an AS-4050 autosampler, PU-2085 pump, DG-2080-53 degasser, CO-2065 Plus column oven, UV-2070 detector, and LC-Net II /ADC interface box (JASCO). An InertSustain AQ-C18 (3 or 5 μm , 150 mm $\times$ 2.1 mm I.D.; GL Sciences) was used for the separation of each evaluated compound on HPLC. The separation conditions were as follows: flow rate: 0.2 mL min⁻¹; mobile phase: 5% methanol (for the evaluation of Ura, U, Ade, InertSustain AQ-C18 (3 μm)), a 15% methanol (for the evaluation of A, The, InertSustain AQ-C18 (5 μm)), or a 50% methanol (for the evaluation of Caf, MP, DMP, InertSustain AQ-C18 (5 μm)); column temperature: 40°C; injection volume: 10 μL . The specific surface areas of particulate sorbent and M-SPEM were measured using the TriStar II surface area and porosity analyzer (Micromeritics).

The effective surface area ratio was defined as the residual ratio of the specific surface area of the particulate sorbent in M-SPEM corrected by the content of particulate sorbent:

$$\text{Effective surface area ratio(\%)} = \frac{S_{\text{M-SPEM}}}{S_{\text{p}} \times W_{\text{p}}} \times 100$$

, where $S_{\text{M-SPEM}}$ and S_{p} are the specific surface areas of M-SPEM and particulate sorbent, and W_{p} is the content ratio of the particulate sorbent in M-SPEM. Surface images of M-SPEM were observed using a field-emission scanning electron microscope (FE-SEM, JSM-6335F (JEOL)).

Preparation of particulate sorbent

The particulate sorbent was synthesized using the suspension copolymerization of DVB and TMPT (4/1 (mol/mol)).¹⁶ Toluene (inert diluent for pore generation) was added to the monomer mixture in the weight ratio of 1:2 (monomer mixture:toluene). AIBN (1 wt% for a total volume of monomers and inert diluent solution) was added to the above organic mixture. The organic mixture was added to a 0.2% (w/v) methyl cellulose aqueous solution, and the mixture was suspended by stirring at 500 rpm. After the dispersion, the suspended mixture was heated at 78°C with stirring at 250 rpm for 6 h to perform the copolymerization of DVB and TMPT. The copolymerized sorbent was washed with excess water, ethanol, and ethyl acetate in that order. After drying the washed sorbent, the sorbent was classified to 53–90, and 90–150 µm using standard sieves.

Preparation of M-SPEM

The particulate sorbent was bound as follows. A particulate sorbent (100 mg) was mixed and kneaded with each adhesive (17, 50, and 100 mg). The kneaded sorbent was inserted into a polypropylene mold, which has six-hole cylindrical cavities with an inner diameter of 8.8 mm (Fig. 1). In the polypropylene mold, each kneaded product was sandwiched between polyethylene frits. The polypropylene mold containing the kneaded sorbents was heated at 50°C for 14 h, and then, six pieces of M-SPEM were obtained by taking them out of the mold. Because the size of M-SPEM described above was too large to be inserted into the measurement cell of the surface and porosity analyzer, M-SPEM of 4.0 mm in diameter was also prepared using the same method.

SPE procedure in reversed phase

Each synthesized M-SPEM (diameter of 8.8 mm) was inserted into an SPE cartridge (inner diameter of 8.8 mm, BondElut[®] Reservoir, Agilent). The insertion and removal of the M-SPEM was easily performed only by pushing the rod without handling the particulate sorbent itself. One hundred milligram of particulate sorbent was also packed in another SPE cartridge for the comparative evaluation. In the conditioning process, methanol (3 mL) and water (50 mL) were passed into the cartridge. After the conditioning, a 1.5 mL aliquot of 100 mg L⁻¹ of each analyte dissolved in water was loaded into the SPE cartridge, and then the solution passed through the sorbent was collected as “Passed”. After that, each analyte adsorbed on the sorbent was eluted by 1.5 mL methanol, and the eluate was collected as “Eluted”. The obtained solutions, “Passed” and “Eluted”, were diluted 10 times with water and were subjected to HPLC to obtain the area under the peak of each analyte. The recovery of each analyte in SPE was calculated by comparing the peak areas of the chromatograms between the analyte in the “Passed” or “Eluted” and the solute in the initial sample solution (without the SPE procedure).

Results and Discussion

Effect of the adhesives on the M-SPEM preparation

The effects of each adhesive on the M-SPEM moldability, each liquid permeability, and adsorption property were investigated. Some pieces of M-SPEM containing 50 wt% of particulate sorbent (50%_M-SPEM) were prepared with 100 mg of adhesive and 100 mg of particulate sorbent (90–150 μ m in particle diameter). As shown with open circles in Table 1, Si-B, Epoxy-AA, Epoxy-A, and SBR (Nos. 1, 4, 5, and 7) were able to produce the corresponding M-SPEM with good liquid permeability. Contrarily, Si-S, Epoxy-T,

PVC, and Instant (Nos. 3, 6, 8, and 10) could not prepare any 50%_M-SPEM, which are indicated as crosses in Table 1. Among these adhesives, Si-S, Epoxy-T, and PVC but not Instant prepared the corresponding M-SPEM only when the particulate sorbent content was reduced to less than 50 wt% (the results are not shown in Table 1). Instant is a low-viscosity liquid adhesive (others are paste adhesives) and might easily permeate into the pores of the particulate sorbents; therefore, Instant did not stay on the surface of the particulate sorbent and did not effectively contribute to binding between the particulate sorbents. In fact, even though the content of particulate sorbent was reduced as low as 15 wt% (in other words, the content of Instant increased), Instant was not useful for preparing an M-SPEM. From these results, the viscosity of the adhesive is one of the important factors for the preparation of M-SPEM.

The main ingredient of Si-B, Si-C, and Si-S (Nos. 1–3) is denaturing silicone. However, the consistency in these adhesives was not confirmed in the preparation of M-SPEM. According to each adhesive's Safety Data Sheet, besides denaturing silicone, these adhesives contain inorganic filler and paraffin etc., and the blending ratios of ingredients differ. Among the three adhesives, the use of Si-B (denaturing silicone (60%–70%), inorganic filler (30%–40%), and paraffin (1%–10%)) and Si-C (denaturing silicone (80%–90%) and paraffin (1%–10%)) could prepare the M-SPEM, whereas the use of Si-S (denaturing silicone (20%–30%), inorganic filler (50%–60%), and paraffin (1%–5%)) could not prepare it. These results suggest that the ratio of denaturing silicone and inorganic filler affects moldability, and it was found that not only the main component but also the types and blending ratios of other components are important factors in affecting the molding of M-SPEM.

Next, to improve the adsorption property, the content of particulate sorbent in M-SPEM was increased. The weight of the adhesive was changed from 100 mg (50%_M-

1 SPEM) to 50 mg (67%_M-SPEM) or 17 mg (85%_M-SPEM) while keeping the weight
2 of the particulate sorbent at 100 mg. As summarized in Table 1, Si-B, Si-C, Epoxy-AA,
3 and Urethane (Nos. 1, 2, 4, and 9) can prepare 67%_ and 85%_M-SPEM. Figure 2 shows
4 the FE-SEM images of the cross sections of 50%_ and 85%_M-SPEM_Si-B and _Epoxy-
5 AA, and Fig. 3 shows the surface of the unmolded particulate sorbent and the molded
6 particulate sorbent in 50%_ and 85%_M-SPEM_Si-B. In the 50%_M-SPEM, the
7 adhesive filled the spaces between particulate sorbents (Fig. 2) and covered the surface
8 of the particulate sorbent (Fig. 3). In comparison, in the 85%_M-SPEM, spaces between
9 particulate sorbents were observed and the degree of particulate sorbent covered by
10 adhesive was decreased.

11 The liquid permeability of M-SPEM with deionized water was also investigated.
12 50%_M-SPEM_Si-C and _Urethane (Nos. 2 and 9) were impermeable, indicated as
13 triangles in Table 1. The FE-SEM images of the cross section of impermeable M-SPEM
14 (Fig. 4) showed that the spaces between the particulate sorbents were filled with the
15 adhesive, which may be difficult for water to permeate.

17 *Effects of the particulate sorbent content*

18 The adsorption properties of fabricated M-SPEM with different contents of the
19 particulate sorbent were evaluated using SPE under the reversed-phase condition.
20 85%_M-SPEM_Si-C and _Urethane (Nos. 2 and 9) collapsed after SPE evaluation, as
21 indicated with closed circles in Table 1. The recoveries of Caf, MP, and DMP using the
22 M-SPEM or the particulate sorbent are shown in Table 2. “Passed” indicates the ratio
23 of the analyte which was not trapped by solid-phase, and “Eluted” indicates the ratio of
24 the analyte eluted from the solid-phase by the eluent. The particulate sorbent trapped the
25 three analytes, and the three analytes were completely eluted from the solid phase. On the

contrary, the almost all total value of Passed and Eluted in 50%_M-SPEM was less than 80%, which meant the analytes remained in the M-SPEM after the SPE procedure. However, an increase in the particulate sorbent content improved the total value of Passed and Eluted. In particular, the adsorption properties of 85%_M-SPEM_Si-B and _Epoxy-AA for Caf, MP, and DMP were almost similar to those obtained using the particulate sorbent. Furthermore, the reproducibility of the recovery using each M-SPEM was also similar to that using the particulate sorbent.

Effects of the particle size of the particulate sorbent

The difference in particle size of particulate sorbent was presumed to affect the M-SPEM's properties. The particle diameter of the particulate sorbent in M-SPEM in the previous sections was 90–150 μm , whereas the average particle diameter of the general solid-phase extractant is 30–70 μm .⁴⁰ Therefore, 85%_M-SPEM_Si-B and _Epoxy-AA (Nos. 1 and 4) containing the particulate sorbent with its diameter of 53–90 μm (M-SPEM/53–90 μm) were also fabricated, and the adsorption properties and pore properties of M-SPEM were evaluated.

The adsorption recoveries of the analytes using the particulate sorbent and M-SPEM with different particle diameters are listed in Table 3. Regardless of the particle size, 85%_M-SPEM completely trapped and eluted the analytes ranging from A to DMP except The. However, in the analytes ranging from Ura to Ade, there were the differences in the adsorption properties in 85%_M-SPEM_Si-B on varying the particle diameter. The adsorption properties of the particulate sorbent and 85%_M-SPEM_Epoxy-AA were comparable, and neither of them was significantly affected by the difference in particle diameter. However, the adsorption property of 85%_M-SPEM_Si-B was affected by changing the particle diameter of the particulate sorbent. In general, the adsorption

property improves with decreasing particle diameter of particulate sorbent. However, the recoveries of Ura, U, and Ade with the M-SPEM_{_Si-B} decreased as the particle diameter of the particulate sorbent decreased.

Because the adsorption property can also depend on the specific surface area of the particulate sorbent and the contact efficiency with the sample solution, the particle diameter, specific surface area, and flow rate of the prepared M-SPEM were then evaluated. The obtained results are listed in Table 4. The respective specific surface areas and the effective surface area ratios were 571.6 m² g⁻¹ and 80% for 85%_{_M-SPEM/90–150 μm_Si-B}, and 465.4 m² g⁻¹ and 65% for 85%_{_M-SPEM/90–150 μm_Epoxy-AA}. However, the specific surface area and effective surface area ratio for 85 %_{_M-SPEM/53–90 μm} decreased by about 10% compared with those of 85%_{_M-SPEM/90–150 μm}. In the comparison of flow rate in Table 4, 85%_{_M-SPEM/53–90 μm} had a higher flow rate than that of particulate sorbent, and 85%_{_M-SPEM/90–150 μm} had almost the same flow rate as that of particulate sorbent. Thus, 85%_{_M-SPEM/90–150 μm} showed the highest similarity to the particulate sorbent in adsorption properties, pore properties, and liquid permeability.

The adsorption property and the specific surface area of 85%_{_M-SPEM} were affected by the particle size, whereas these characteristics of the particulate sorbent were almost constant regardless of the particle diameter. Therefore, the weight, width, and height of each 85%_{_M-SPEM} with different particle diameters were measured (Table 4). As the particle diameter of particulate sorbent in M-SPEM became smaller, the weight and height of M-SPEM decreased, whereas the width of M-SPEM remained constant. In particular, the weight reduction of M-SPEM indicated a decrease in the particulate sorbent content, which caused a decrease in the specific surface area and the adsorption property of M-SPEM. As the particle diameter became smaller, the operation of kneading became

more difficult because the adsorption of the particulate sorbent by scattering and static electricity occurred easily. This difficulty in the operation of kneading probably decreased the content of particulate sorbent in M-SPEM, which leads to a decrease in the adsorption property in 85%_M-SPEM_Si-B/53–90 μm . On the other hand, in 85%_M-SPEM_Epoxy-AA, the same adsorption property in changing the particle diameter may be derived from the effective expression of adsorption property of Epoxy-AA, whereas the content of particulate sorbent in M-SPEM decreased.

Conclusions

In this study, we proposed a binding technique of the particulate sorbent for improving the handling of the particulate sorbent. The M-SPEM containing 85 wt% particulate reversed-phase-type sorbent had a specific surface area of about $500 \text{ m}^2 \text{ g}^{-1}$, which was comparable to the specific surface area of the particulate sorbent. Our developed M-SPEM had a sufficient adsorption property as a solid-phase extractant. Moreover, the M-SPEM can be easily changed to various shapes. Therefore, the M-SPEM is expected to be applied to fabricate the miniaturized SPE. Our developed method will be an important technique for spreading the use of the particulate sorbent.

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Table 1 Product names, abbreviations, and ingredients of each adhesive, as well as the molding ability and liquid permeability of M-SPEM

No.	Product name	Product No.	Abbreviation	Ingredients of adhesive		Molding ability and liquid permeability ^a		
				Main ingredient	Additive or harding agent	Content of particulate sorbent in M-SPEM		
						50%	67%	85%
1	Super X Black	AX-035	Si-B	denaturing silicone	inorganic fillers, paraffin	○	○	○
2	Super X Clear	AX-041	Si-C	denaturing silicone	paraffin	△	○	●
3	POS Seal Multi	SL-619	Si-S	denaturing silicone	inorganic fillers, acrylic resin	×	×	×
4	E Set	#16023	Epoxy-AA	epoxy resin	polyamideamine	○	○	○
5	MOS8	#04975	Epoxy-A	epoxy resin	tertiary amine, denaturing silicone	○	×	×
6	Quick Set 30	#16223	Epoxy-T	epoxy resin	polythiol, tertiary amine	×	×	×
7	GP Clear	#14372	SBR	styrene-butadiene rubber	cyclohexane	○	×	×
8	Vinyl Adhesive	#11023	PVC	vinyl chloride	acetone, butyl acetate	×	×	×
9	Ultra Multi-Purpose SU	#05139	Urethane	silylated urethane resin	undisclosed	△	○	●
10	3000KX	CA-061	Instant	ethyl 2-cyanoacrylate	acrylic resin	×	×	×

a. ○, moldable and permeable; △, moldable but impermeable; ×, not moldable; ●, moldable and permeable but collapse after SPE.

Table 2 Recoveries of caffeine (Caf), methylparaben (MP), and dimethyl phthalate (DMP) in SPE obtained using particulate sorbent and M-SPEM with different particulate sorbent content

Sorbent		Recovery, % [SD] (<i>n</i> =4)					
		Caf		MP		DMP	
		Passed	Eluted	Passed	Eluted	Passed	Eluted
Particulate sorbent ^a		0.0 [—]	101.3 [2.1]	0.0 [—]	101.7 [3.6]	0.0 [—]	99.8 [2.0]
M-SPEM_Si-B	50% ^a	65.5 [1.9]	18.1 [0.5]	12.5 [2.4]	64.7 [3.3]	15.4 [3.8]	61.3 [4.5]
	67%	22.3 [4.5]	73.9 [4.6]	1.0 [0.2]	98.6 [1.2]	0.0 [—]	98.1 [1.2]
	85% ^a	0.9 [0.5]	100.6 [2.3]	0.1 [0.1]	100.5 [2.8]	0.0 [—]	98.5 [6.6]
M-SPEM_Si-C	67%	22.9 [3.4]	57.8 [3.8]	0.7 [1.3]	79.6 [2.0]	0.7 [1.4]	78.2 [2.6]
M-SPEM_Epoxy-AA	50% ^a	67.2 [11.0]	10.4 [5.2]	20.7 [13.9]	32.7 [2.3]	47.9 [17.9]	25.3 [1.9]
	67%	22.0 [6.1]	65.8 [4.4]	0.0 [—]	58.4 [3.8]	3.6 [2.6]	80.4 [4.2]
	85% ^a	1.0 [0.8]	103.3 [5.4]	0.0 [0.1]	102.2 [4.1]	0.0 [—]	102.4 [4.2]
M-SPEM_Epoxy-A	50%	30.6 [6.0]	64.6 [8.5]	0.1 [0.1]	35.8 [8.9]	0.0 [—]	99.8 [4.6]
M-SPEM_SBR	50%	37.6 [14.6]	29.7 [9.5]	30.1 [14.5]	37.5 [9.5]	22.6 [14.3]	40.8 [9.7]
M-SPEM_Urethane	67%	37.7 [2.6]	50.6 [5.2]	3.4 [1.8]	88.7 [6.5]	4.2 [3.7]	84.6 [7.6]

a. The same data as reference 38).

Table 3 Recoveries of uracil (Ura), uridine (U), adenine (Ade), adenosine (A), theophylline (The), caffeine (Caf), methylparaben (MP), and dimethyl phthalate (DMP) in SPE obtained using particulate sorbent and M-SPEM with two different particle diameters

Sorbent	Particle diameter / μm	Recovery, % [SD] ($n=4$)															
		Ura		U		Ade		A		The		Caf		MP		DMP	
		Passed	Eluted	Passed	Eluted	Passed	Eluted	Passed	Eluted	Passed	Eluted	Passed	Eluted	Passed	Eluted	Passed	Eluted
Particulate sorbent	53–90	44.9 [2.7]	48.5 [3.1]	11.0 [2.8]	92.8 [3.4]	0.0 [—]	109.8 [1.0]	0.0 [0.1]	108.3 [0.7]	0.0 [—]	106.5 [0.4]	0.0 [—]	106.4 [4.0]	0.1 [—]	105.6 [4.1]	0.0 [—]	104.1 [4.8]
	90–150	29.8 [0.5]	66.8 [4.1]	7.5 [0.3]	97.2 [5.2]	0.1 [0.1]	109.8 [5.7]	0.0 [0.1]	106.7 [2.2]	0.0 [—]	106.5 [2.4]	0.0 ^a [—]	101.3 ^a [2.1]	0.0 ^a [—]	101.7 ^a [3.6]	0.0 ^a [—]	99.8 ^a [2.0]
85%_M-SPEM _Si-B	53–90	52.2 [3.4]	36.3 [4.6]	39.9 [5.8]	50.7 [8.8]	8.9 [6.4]	91.6 [11.4]	4.3 [3.6]	95.0 [1.7]	5.1 [4.4]	93.6 [2.4]	0.0 [0.1]	103.4 [2.0]	0.1 [—]	102.0 [0.9]	0.0 [—]	101.3 [0.4]
	90–150	30.0 [4.1]	63.3 [7.3]	13.9 [2.8]	84.6 [6.2]	1.6 [0.8]	102.2 [2.6]	3.6 [2.7]	100.2 [8.7]	3.0 [3.4]	91.7 [5.7]	0.9 ^a [0.5]	100.6 ^a [2.3]	0.1 ^a [0.1]	100.5 ^a [2.8]	0.0 ^a [—]	98.5 ^a [6.6]
85%_M-SPEM _Epoxy-AA	53–90	27.7 [6.3]	67.9 [5.5]	11.2 [4.3]	90.5 [4.1]	1.7 [1.0]	104.7 [2.2]	0.1 [0.1]	106.2 [7.8]	0.0 [—]	95.8 [4.1]	3.1 [1.9]	99.8 [1.9]	0.1 [—]	101.4 [1.9]	0.5 [0.4]	100.7 [2.1]
	90–150	23.2 [6.3]	72.0 [8.7]	12.1 [5.3]	86.7 [8.2]	1.9 [1.1]	102.2 [3.9]	1.9 [1.4]	102.8 [3.4]	0.0 [—]	86.1 [6.0]	1.0 ^a [0.8]	103.3 ^a [5.4]	0.0 ^a [0.1]	102.2 ^a [4.1]	0.0 ^a [—]	102.4 ^a [4.2]

The order of the analytes from left to right is the elution order of analytes in the separation of reversed-phase chromatography.

a. The same data as reference 38).

Table 4 The estimated pore properties, flow rate, weight, and size of the particulate sorbent and the M-SPEM with two different particle diameters

Sorbent	Particle diameter / μm	Specific surface area / $\text{m}^2 \text{g}^{-1}$	Effective surface area ratio ^a / %	Flow rate ^b / mL min^{-1}	Weight ^c / mg	Width ^c / mm	Height ^c / mm
Particulate sorbent	53–90	852.5	—	0.51	—	—	—
	90–150	833.8 ^d	—	1.33	—	—	—
85%_M-SPEM _Si-B	53–90	500.0	69	0.94	87	8.8	4.2
	90–150	571.6 ^d	80 ^d	1.28	97	8.8	4.9
85%_M-SPEM _Epoxy-AA	53–90	382.4	53	1.02	89	8.8	4.3
	90–150	465.4 ^d	65 ^d	1.48	108	8.8	5.5

a. Defined in Experimental section.

b. $n = 12$.

c. $n = 8$.

d. The same data as reference 38).

Figure Captions

Fig. 1 Six-hole cylindrical mold for preparing M-SPEM (left side), a typical molded M-SPEM (center), and M-SPEM in a SPE cartridge (right side).

Fig. 2 FE-SEM images of the cross section of M-SPEM with 50 % and 85 % particulate sorbent contents. The images of 50%_ and 85%_M-SPEM_Si-B (the left side) are the same as reference 38).

Fig. 3 FE-SEM images of the surface of particulate sorbent, and 50%_ and 85%_M-SPEM_Si-B.

Fig. 4 FE-SEM images of the cross section of 50%_M-SPEM_Si-C and _Urethane.

Fig. 1 Six-hole cylindrical mold for preparing M-SPEM (left side), a typical molded M-SPEM (center), and M-SPEM in a SPE cartridge (right side).

Fig. 2 FE-SEM images of the cross section of M-SPeM with 50 % and 85 % particulate sorbent contents.

The images of 50%_ and 85%_M-SPeM_Si-B (the left side) are the same as reference 38).

Fig. 3 FE-SEM images of the surface of particulate sorbent, and 50%_ and 85%_M-SPeM_Si-B.

Fig. 4 FE-SEM images of the cross section of 50%_M-SPEM_Si-C and _Urethane.

Graphical Index