Solid-phase extraction (SPE) has been widely applied as a pretreatment method.1–3 SPE is generally performed by using a cartridge into which a variety of particulate sorbents are packed; thus, the procedure of packing the particulate sorbent step is essential. This procedure of handling a particulate sorbent is sometimes difficult because the sorbents for SPE have small particle diameters and dry conditions, which lead to static clinging and scattering.4 Moreover, the particulate sorbent packed into the cartridge is often uneven and not flat, which causes channeling and/or voiding. Incomplete packing will produce poor repeatability and recovery upon any pretreatment.

To improve these issues, extraction disks with the sorbents immobilized in PTFE fibers or in glass fibers are now commercially available.5 Monolithic types of sorbents are another solution, which can be used for rods, pipette tips or 96-well plates.6–8 Other sintered disk types of sorbents, where there is a mixture of polyethylene powder and ion-exchange resin9 or chelating resin,4 have also been reported. These molding types of sorbents are effective for SPE because of their easy handling. However, the procedures for molding particulate sorbents are unique, and it is thus difficult to synthesize molding types of sorbents containing the desirable particulate sorbents for a specific purpose in house. For these reasons, the development of a simpler molding method is needed.

In this study, we proposed a simple method for molding a particulate sorbent by using commercially available adhesives. This is called the molding-type solid-phase extraction medium (M-SPEM) method. First, the molding abilities of three different types of commercially available adhesives [i.e., cyanoacrylate (3000KX, CEMEDINE Co., Ltd.), denaturing silicone (Super X Black, CEMEDINE Co., Ltd.), and epoxy resin/polyamidamine (E Set, Konishi Co., Ltd.)], were studied. In this study, our developed reversed-phase type of sorbent, which was poly(divinylbenzene (DVB)-co-trimethylolpropane trimethacrylate (TMPT)) (particle size: 90-150 μm),10 was used to evaluate the molding ability of each adhesive. The mixture of the particulate sorbent...
sorbent and each adhesive at a weight ratio of 1:1 (100 mg:100 mg, 50 wt% content of the particulate sorbent in an M-SPEM) was kneaded and inserted into a polypropylene mold, which had cylindrical column cavities (inner diameter of 8.8 mm). In the polypropylene mold, each kneaded sorbent was sandwiched by polyethylene frits. The mold with the kneaded sorbent was heated at 50°C for 14 h, and the molding ability of each adhesive was investigated. The denaturing silicone (Super X Black) and epoxy resin/polyamideamine (E Set) were found to mold the particulate sorbents (Fig. 1), whereas cyanoacrylate (3000KX) could not mold it. The differences in the molding ability may be because of the coefficient of viscosity. Cyanoacrylate (3000KX) has a low viscosity, and can easily permeate the pore of a particulate sorbent, which may cause difficulty of molding.

To determine the existence of consecutive through holes for permeation of the solution, two M-SPEMs (Super X Black or E Set) were put into a 3-mL empty cartridge (BondElut® Reservoir) for SPE, and methanol was loaded into each cartridge. We observed the successful permeability of methanol for both M-SPEMs. The specific surface areas (BET method) of the two M-SPEMs (50 wt% particulate sorbent content) are shown in Table 1. These two M-SPEMs had lower specific surface areas than the corresponding particulate sorbent, likely because the pores in the particulate sorbent were partially blocked by each adhesive.

Table 1 gives a comparison of the adsorption properties of the particulate sorbent and the M-SPEMs (Super X Black (X) and E Set (E)) for three hydrophilic compounds (caffeine, methyl p-hydroxybenzoate, and dimethyl phthalate). The adsorption property of each M-SPEM was evaluated by determining the recovery from each M-SPEM glued with two adhesives (“Particulate sorbent”, DVB/TMPT particulate sorbent without molding; “50%_X” and “85%_X”, 50% or 85% particulate sorbent content in M-SPEM molded by Super X Black; “50%_E and 85%_E”, 50% or 85% particulate sorbent content in M-SPEM molded by E Set.)

| Content of particulate sorbent, wt% | Specific surface area/m² g⁻¹ | Effective surface area, % |
|------------------------------------|-----------------------------|--------------------------|
| Particulate sorbent                 | 833.8                       | —                        |
| 50 Super X Black                   | 69.3                        | 17                       |
| E Set                              | 51.0                        | 12                       |
| 85 Super X Black                   | 57.6                        | 80                       |
| E Set                              | 465.4                       | 65                       |

Table 2

| Recovery, % (n = 4)               | Caffeine | Methyl p-hydroxybenzoate | Dimethyl phthalate |
|-----------------------------------|----------|-------------------------|-------------------|
| Passed                            | Eluted   | Passed                  | Eluted            |
| Particulate sorbent               | 0.0      | 101.3                   | 0.0              | 99.8              |
| [SD]                              | [2.1]    | [3.6]                   | [20.0]            |
| 50 wt%_X                          | 65.5     | 18.1                    | 61.3              |
| [SD]                              | [0.5]    | [0.5]                   | [0.5]             |
| 50 wt%_E                          | 67.2     | 10.4                    | 25.3              |
| [SD]                              | [5.2]    | [2.3]                   | [6.6]             |
| 85 wt%_X                          | 0.9      | 100.6                   | 98.5              |
| [SD]                              | [2.3]    | [2.8]                   | [2.8]             |
| 85 wt%_E                          | 1.0      | 103.3                   | 102.4             |
| [SD]                              | [5.4]    | [4.1]                   | [4.2]             |

Passed and Eluted ratios that passed through the M-SPEM at the sample loading process (Passed) and that eluted by methanol (Eluted). As expected from the specific surface areas shown in Table 1, the above-mentioned two M-SPEMs (50 wt% particulate sorbent content, 50 wt%_X and 50 wt%_E) had much lower extraction recoveries (Eluted shown in Table 2) compared with a particulate sorbent. Moreover, from the result that 100% was not obtained by adding the Passed ratio and Eluted ratio, complete elution from the M-SPEMs could not be achieved. Thus, complete elution of each compound was disturbed by the existence of pores with poor mass transfer in each M-SPEM.

To overcome this issue, the mixture ratio between the particulate sorbent and the adhesive was changed by decreasing each adhesive content. We could obtain M-SPEMs containing an 85 wt% particulate sorbent (particulate sorbent:adhesive = 100 mg:17 mg) by using Super X Black or E Set, respectively. The increase in the content of the particulate sorbent increased the specific surface area of each M-SPEM (Table 1). Compared with the specific surface area of the corresponding particulate sorbent, each M-SPEM containing 85 wt% particulate sorbent had specific surface areas of over 450 m² g⁻¹, which meant that over 65% surface areas of the particulate sorbent, itself (Table 1). Many monolithic adsorption media generally have specific surface areas of under 100 m² g⁻¹, which shows that our developed M-SPEMs have higher specific surface areas than general monolithic adsorption media. In this case, the M-SPEM using E Set had a relatively lower specific surface area than the M-SPEM using Super X Black, probably because the viscosity of E Set increased by the condensation reaction induced by the mixing of E Set’s two liquids (epoxy resin and polyamideamine), which led to block the pore entrance and between particulate sorbents. From this result, an appropriate range for the viscosity of the adhesives seems to exist in our developed method.

The increases of the particulate sorbent content also improve the SPE ability (Table 2). Each M-SPEM of 85 wt% particulate sorbent content drastically improved the desorption property, and obtained high recovery of each evaluated compound. From these results, the increase of the particulate sorbent content, namely, the decrease of the adhesive content, leads to the achievement of prompt mass transfer between the eluate and M-SPEM. Figure S1 shows the field emission scanning electron microscope (FE-SEM) images of the vertical section of 50 wt%_X and 85 wt%_X cut by a box cutter. While blockage at the surface of the particulate sorbent and the space between
the particulate sorbents by adhesive was observed in 50 wt% X, little blockage by adhesives was observed in 85 wt% X, which led to an increase of the specific surface area and to improved elution at the Eluted process.

The flow rates of each M-SPEM and particulate sorbent were as follows: 50 wt% X, 0.19 mL min⁻¹; 85 wt% X, 1.56 mL min⁻¹; 50 wt% E, 0.91 mL min⁻¹; 85 wt% E, 1.80 mL min⁻¹; particulate sorbent, 1.24 mL min⁻¹ (each flow rate was measured in the process of conditioning of water). From these results, each 85 wt% M-SPEM had a higher permeation ability than 50 wt% M-SPEM and a particulate sorbent, which indicated that the decrease in the absorption-desorption rate did not occur by molding the particulate sorbent.

In this study, we developed an M-SPEM using a commercially available adhesive. While the molding and permeation properties depend on the adhesive species, a proper adhesive can mold an M-SPEM containing an 85 wt% particulate sorbent. Moreover, our developed M-SPEMs have higher specific surface areas than general monolithic type media. The proposed method for molding sorbents can be applied for any particulate sorbents that have various separation modes with an improvement in handling, which is expected to not only be used for SPE, but also for an effective adsorptive removal of toxic substances.

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Supporting Information

Reagents, Instrumentation, Synthesis of smaller M-SPEM for measuring specific surface area, Evaluation of the adsorption property of M-SPEM by SPE, Fig. S1. This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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